



Wydział Chemii
Uniwersytet im. Adama Mickiewicza w Poznaniu

Rozprawa doktorska

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Badanie kierunków potencjalnego
zastosowania cieczy jonowych w procesach
wytwarzania i modyfikacji kompozytów
epoksydowych oraz ocena ich właściwości



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**Zakład Chemii i Technologii Związków Krzemu, Wydział Chemii UAM
Poznań 2024**

Podziękowania

/ Prof. dr hab. Inż. Hieronim Maciejewski

Dziękuję prof. dr hab. inż. Hieronimowi Maciejewskiemu za to, że zawsze był dla mnie wzorem nie tylko jako Naukowiec, ale także jako Lider. Pana wiedza, profesjonalizm i doskonała organizacja pracy, a także podejście do nauki i konsekwencja w działaniu, zainspirowały mnie do stawania się lepszym badaczem.

/ Dr hab. Inż. Marcin Śmiglak

Dziękuję dr hab. inż. Marcinowi Śmiglakowi za to, że nawet w swoim unikalnym stylu pracy, potrafił inspirować mnie do osiągnięcia więcej, niż kiedykolwiek uważałem za możliwe. Doceniam każdą szansę, którą mi dałeś, oraz wszystkie te niezapomniane, czasem szalone dyskusje naukowe – nawet te, które odbywały się o 4 nad ranem lub na drugim końcu świata! Pana gotowość do dzielenia się wiedzą i poświęcania czasu, nawet w najmniej spodziewanych momentach, była dla mnie bezcenna. Dziękuję za to, że był Pan nie tylko moim promotorem, ale także mentorem, który pokazał mi, że czasem największe osiągnięcia rodzą się z odrobiny chaosu i nieprzewidywalności.

/ Dr Andrea Szpecht

Dziękuję dr Andrei Szpecht za wszystkie niezliczone godziny spędzone razem – zarówno na naukowych i nienaukowych dyskusjach w biurze, jak i na długich dniach w laboratorium. Choć dziś trudno mi przypomnieć sobie, po co nam było tyle chemikaliów (a pewnie niektóre wciąż są gdzieś schowane), jedno jest pewne – każdy z tych szalonych pomysłów nosi w sobie cząstkę Twojej energii. Z całego serca dziękuję, że towarzyszyłaś mi w tej podróży i nieustannie wierzyłaś w sukces, nawet gdy ja miałem wątpliwości. Twoje uwagi zawsze trafiały w punkt – nawet jeśli czasem sprawiały, że czułem się jakbym musiał zacząć od nowa.

/ Mgr inż. Bartosz Labuhn

Serdeczne podziękowania kieruję do mgr. inż. Bartosza Labuhna, który był nieocenionym wsparciem w przygotowaniu wizualnym tej pracy. Dziękuję za to, że byłeś mistrzem bolesnej, ale zawsze konstruktywnej krytyki – Twoje uwagi, choć czasem trudne do przyjęcia, pomogły mi stworzyć pracę, z której dzisiaj jestem naprawdę dumny. Twoja cierpliwość w znoszeniu moich nadgorliwych pytań i umiejętność uspokajania moich czasem fantastycznych pomysłów dotyczących wizualizacji wyników były dla mnie nieocenione.

/ Dr Adrian Zając

Dziękuję dr Adrianowi Zającowi za to, że zawsze wiedział, kiedy udawać zainteresowanie moimi opowieściami o kompozytach i kiedy zmieniać temat na coś bardziej interesującego.

/ Współpracownicy

Serdeczne podziękowania dla wszystkich współpracowników z Poznańskiego Parku Naukowo-Technologicznego, zarówno z zespołów naukowych, jak i nienaukowych. Dziękuję za wsparcie techniczne, nieocenioną motywację oraz tworzenie przyjaznej atmosfery. Wasze nieustanne pytania „Kiedy w końcu skończysz?” były dla mnie prawdziwym źródłem motywacji i napędzały mnie do osiągnięcia mety.

/ Rodzina

Dziękuję mojej rodzinie za cierpliwość i wyrozumiałość w najtrudniejszych momentach – obiecuję, że już nigdy nie zanudzę Was na temat cieczy jonowych i kompozytów! Wasza cierpliwość i wsparcie, szczególnie w chwilach, gdy potrzebowałem ciszy i skupienia, były dla mnie nieocenione. Dziękuję, że po latach przestaliście pytać „A po co ci ten doktorat?” i za to, że wspieraliście mnie, nawet gdy nie zawsze było jasne, czym właściwie się zajmuję, a Wasze spojrzenia sugerowały, że macie wrażenie, iż właśnie wpadliście do świata science fiction.

/ Przyjaciele

Dziękuję moim przyjaciołom, którzy potrafili mnie oderwać od książek i przypomnieć, że czasami trzeba odetchnąć – wasze wsparcie było bezcenne. Dzięki, moi drodzy przyjaciele, za to, że zawsze mieliście czas na opowieści na temat moich „wielkich odkryć”, które w praktyce okazywały się czasami równie rewolucyjne, co robienie kawy w mikrofali. Wasza cierpliwość i gotowość do wysłuchania moich naukowych perypetii były niezastąpione – szczególnie gdy próbowałem Was przekonać, że „ciecze jonowe” są naprawdę fascynujące.

/ Czester

Dziękuję również mojemu psu Czesterowi za towarzystwo podczas pisania – i za przypomnianie mi, że nawet w środku najtrudniejszego rozdziału, czas na przerwę i zabawę jest zawsze!

Badania zawarte w pracy były finansowane w ramach:



NARODOWE CENTRUM NAUKI

- / Projektu „Wielofunkcyjne układy kompozytowe na bazie żywic epoksydowych z cieczami jonowymi, jako inicjatorami procesu sieciowania”.
(SONATA BIS, 2017/26/E/ST8/01059)
- / Projektu „ILFLAME - Synergistyczne oddziaływanie fosforu, krzemu i azotu w zmniejszaniu palności kompozytów epoksydowych przy użyciu cieczy jonowych i materiałów SILP, z dodatkową aktywnością jako czynniki utwardzające”.
(PRELUDIUM, 2023/49/N/ST11/04057)



Narodowe Centrum Badań i Rozwoju

- / Projektu „Innowacyjne, wielofunkcjonalne układy kompozytowe z przeznaczeniem na elementy konstrukcyjne autonomicznych platform bezzałogowych – MULTIKOMP”.
(Projekty badawcze na rzecz obronności i bezpieczeństwa, DOB-1P/02/19/2016)



- / Projektu „Inkubator Innowacyjności 4.0” przyznanego dla Fundacji Uniwersytetu im. Adama Mickiewicza w Poznaniu.
(Program Operacyjny Inteligentny Rozwój 2014-2020, MNiSW/2020/349/DIR)



- / Projektu „Inicjatywa Doskonałości – Uczelnia Badawcza (ID-UB)” przyznanego dla Uniwersytetu im. Adama Mickiewicza w Poznaniu.
(Zadanie 13 - Wsparcie umiędzynarodowienia badań naukowych prowadzonych w Szkole Doktorskiej UAM, 080/13/UAM/0040)

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/_WYKAZ SKRÓTÓW

- / [(EtOH)NH₃][NO₃] – azotan etanoloamoniowy
- / [DCA] – anion dicyjanoamidowy
- / [EMIM] [BF₄] – tetrafluoroboran 1-etylo-3-metyloimidazoliowy
- / [EMIM] [DCA] – dicyjanoamid 1-etylo-3-metyloimidazoliowy
- / [EtNH₃][NO₃] – azotan etyloamoniowy
- / [NTf₂] – anion bis(trifluorometanosulfonylo)imidkowy
- / [OTf] – anion trifluorometanosulfonowy
- / AgDCA – dicyjanoamid srebra
- / APB – Autonomiczne Platformy Bezzałogowe
- / CAGR – roczny skumulowany wskaźnik wzrostu, ang. *Compound Annual Growth Rate*
- / CO₂ – dwutlenek węgla, ang. *carbon dioxide*
- / DABCO – 1,4-diazabicyklo[2.2.2]oktan
- / DCM – dichlorometan
- / DMA – dynamiczna analiza mechaniczna, ang. *Dynamic Mechanical Analysis*
- / DMSO – dimetylosulfotlenek
- / DSSC – ogniwo słoneczne uczulane barwnikiem, ang. *Dye-Sensitized Solar Cell*
- / EtOAc – octan etylu
- / HB – klasa palności, ang. *Horizontal Burning*
- / HDT – temperatura ugięcia pod obciążeniem, ang. *Heat Deflection Temperature*
- / ILs – ciecze jonowe, ang. *Ionic Liquids*
- / IR – promieniowanie podczerwone, ang. *Infrared*
- / LCA – analiza cyklu życia, ang. *Life Cycle Analysis*
- / LiNTf₂ – bis(trifluorometanosulfonylo)imidek litu
- / LOI – graniczny indeks tlenowy, ang. *Limiting Oxygen Index*
- / MDG – Milenijne Cele Rozwoju, ang. *Millennium Development Goals*
- / MeOH – metanol

///_WYKAZ SKRÓTÓW

- / MLC – kalorymetria stożkowa utraty masy, ang. *Mass Loss Cone test* lub *Mass Loss Calorimetry*
- / MULTIKOMP – akronim projektu “Innowacyjne, wielofunkcyjne układy kompozytowe z przeznaczeniem na elementy konstrukcyjne autonomicznych platform bezzałogowych
- / ONZ – Organizacja Narodów Zjednoczonych
- / PANI – polianilina
- / pHHR – szczyt szybkości wydzielania ciepła, ang. *peak of heat release rate*
- / phr – części na sto części żywicy, ang. *parts per hundred resin*
- / PILs – protonowane ciecze jonowe, ang. *Protic Ionic Liquids*
- / PVD – fizyczne osadzanie z fazy gazowej, ang. *Physical Vapour Deposition*
- / RT – temperatura pokojowa, ang. *Room Temperature*
- / SDG – Cele Zrównoważonego Rozwoju, ang. *Sustainable Development Goals*
- / SEM – skaningowa mikroskopia elektronowa, ang. *Scanning Electron Microscopy*
- / SILP – materiały typu SILP, ang. *Supported Ionic Liquid Phase*
- / T_{5%} – temperatura odpowiadająca 5% utraty masy próbki
- / T_{50%} – temperatura odpowiadająca 50% utraty masy próbki
- / T_{endset} – temperatura końca polimeryzacji
- / T_g – temperatura zeszklenia
- / T_{max} – szczyt temperaturowy
- / T_{onset} – temperatura początku polimeryzacji
- / UL-94 – test poziomego spalania
- / UV – promieniowanie ultrafioletowe, ang. *Ultraviolet Radiation*

/_STRESZCZENIE W JĘZYKU POLSKIM

Niniejsza rozprawa doktorska koncentruje się na syntezie, charakterystyce oraz zastosowaniu cieczy jonowych i ich mieszanin jako wielofunkcyjnych modyfikatorów i utwardzaczy dla żywic epoksydowych oraz kompozytów wzmocnionych włóknami. Praca składa się z dwóch głównych części: teoretycznej analizy oraz przewodnika po cyklu siedmiu publikacji naukowych, które szczegółowo opisują badania nad nowymi formułacjami cieczy jonowych oraz ich wpływem na właściwości badanych materiałów kompozytowych.

W części teoretycznej przedstawiono szczegółowy przegląd literatury dotyczącej historii cieczy jonowych, poczynając od syntezy pierwszych związków przez Paula Waldena, aż po współczesne badania nad ich właściwościami i zastosowaniami. Omówiono klasyfikację cieczy jonowych oraz ich unikalne właściwości fizykochemiczne, takie jak niska prężność par, niepalność, szerokie okno elektrochemiczne, wysoka stabilność termiczna oraz przewodnictwo elektryczne. Szczególną uwagę poświęcono właściwościom cieczy jonowych w połączeniu z żywicami epoksydowymi.

W części stanowiącej przewodnik po cyklu publikacji skupiono się na przytoczeniu najważniejszych wyników otrzymanych podczas badań, dzieląc je na trzy rozdziały: (i) syntezę cieczy jonowych, (ii) proces polimeryzacji żywicy epoksydowej oraz (iii) właściwości struktur kompozytowych. Pierwsza praca [A1] była poświęcona cieczom jonowym na bazie bicyklicznej aminy, 1,4-diazabicyklo[2.2.2]oktanu, oraz badaniom nad możliwościami zastosowania otrzymanych, nowych związków z żywicami epoksydowymi, z naciskiem na inicjowanie procesu utwardzania i poprawę właściwości utwardzonej żywicy. Druga publikacja [A2] przedstawiała syntezę nowych cieczy jonowych na bazie heksametylenotetraminy, które zostały użyte do opracowania systemów utwardzających z glikolem etylenowym, wykazując wysoką aktywność tych cieczy w procesach sieciowania. Trzecia praca [A3] opisywała syntezę i przygotowanie formułacji modyfikujących opartych na cieczach jonowych, będących pochodnymi aniliny, oraz ich wpływ na właściwości żywic epoksydowych, podkreślając efektywność omawianych cieczy jonowych w procesach utwardzania, jak również właściwości mechaniczne kompozytów wzmocnianych włóknami. Czwarta publikacja [A4] z cyklu dotyczyła opracowania nowych systemów modyfikujących, wykorzystujących ciecze

jonowe do zmiany właściwości żywic epoksydowych i kompozytów. Przeprowadzono testy termiczne, mechaniczne i odporności ogniowej, wykazując, że prawidłowo zaprojektowane ciecze jonowe mogą pełnić wiele funkcji w materiale kompozytowym. W piątym artykule [A5] badano mieszaniny cieczy jonowych z anionem dicyjanoamidowym jako środki utwardzające i modyfikujące kompozyty epoksydowe wzmacniane włóknem lnianym, co znacząco wpłynęło na właściwości termiczne i mechaniczne tych kompozytów. Szósta publikacja cyklu [A6] wprowadziła materiały SILP jako nośniki wypełnienia krzemionkowego i utwardzacze dla kompozytów epoksydowych wzmocnionych włóknem węglowym i lnianym, poprawiając parametry użytkowe materiałów. Siódmy artykuł cyklu [A7] skupił się na zastosowaniu celulozy rozpuszczonej w cieczach jonowych jako wypełniacza generowanego *in situ* w biokompozytach epoksydowych, co badano pod kątem wpływu na proces utwardzania oraz właściwości mechaniczne końcowych materiałów.

Badania wykazały, że ciecze jonowe są wszechstronnymi i efektywnymi modyfikatorami żywic epoksydowych oraz kompozytów. Ich zastosowanie umożliwia kontrolowane procesy sieciowania, poprawę właściwości mechanicznych, termicznych oraz polepszenie odporności ogniowej. Wyniki te otwierają nowe możliwości w dziedzinie materiałów kompozytowych, umożliwiając lepsze zrozumienie działania cieczy jonowych oraz dostarczając wiedzę o doborze optymalnych struktur tych związków pod kątem pożądanych cech zarówno procesu sieciowania, jak i właściwości końcowych kompozytów.

/_STRESZCZENIE W JĘZYKU ANGIELSKIM

This doctoral dissertation focuses on the synthesis, characterization, and application of ionic liquids and their mixtures as multifunctional modifiers and hardeners for epoxy resins and fiber-reinforced composites. The work consists of two main parts: a theoretical analysis and a guide to a series of seven scientific publications that detail the research on new formulations of ionic liquids and their impact on the properties of composite materials.

In the theoretical part, a detailed literature review is presented, covering the history of ionic liquids from the synthesis of the first compounds by Paul Walden to contemporary research on their properties and applications. The classification of ionic liquids and their unique physicochemical properties, such as low vapor pressure, non-flammability, wide electrochemical window, high thermal stability, and electrical conductivity, are discussed. A section of the chapter is also dedicated to the properties of ionic liquids in combination with epoxy resins.

The guide to the series of publications focuses on presenting the most important results obtained during the research, divided into three chapters: (i) synthesis of ionic liquids, (ii) epoxy resin curing process, and (iii) properties of composite structures. The first paper [A1] was dedicated to ionic liquids based on bicyclic amine, 1,4-diazabicyclo[2.2.2]octane, and the exploration of the application possibilities of the obtained new compounds with epoxy resins, emphasizing the initiation of the curing process and the improvement of the cured resin properties. The second publication [A2] presented the synthesis of new ionic liquids based on hexamethylenetetramine, which were used to develop curing systems with ethylene glycol, demonstrating high activity of these liquids in curing processes. The third paper [A3] described the synthesis and preparation of modifying formulations based on ionic liquids derived from aniline and their impact on the properties of epoxy resins, highlighting the effectiveness of ionic liquids in curing processes as well as the mechanical properties of fiber-reinforced composites. The fourth publication [A4] in the series concerned the development of new modifying systems using ionic liquids to alter the properties of epoxy resins and composites. Thermal, mechanical, and fire resistance tests were conducted, presenting that properly designed ionic liquids can perform multiple functions in composite

material. In the fifth article [A5], mixtures of ionic liquids with a dicyanamide anion were investigated as curing and modifying agents for flax fiber-reinforced epoxy composites, significantly affecting the thermal and mechanical properties of these composites. The sixth publication [A6] introduced SILP materials as carriers for silica fillers and hardeners for carbon fiber- and flax fiber-reinforced epoxy composites, improving the performance parameters of the materials. The seventh article [A7] focused on the use of cellulose dissolved in ionic liquids as an *in situ* generated filler in epoxy biocomposites, studied in terms of its impact on the curing process and the mechanical properties of the final materials.

The research demonstrated that ionic liquids are versatile and effective modifiers for epoxy resins and composites. Their application enables controlled curing processes, improved mechanical and thermal properties, and enhanced fire resistance. These results open new possibilities in the field of composite materials, allowing for a better understanding of the action of ionic liquids and providing knowledge on the selection of optimal structures of these compounds for the desired characteristics of both the curing process and the final properties of the composites.

Poniższa część pracy to ankieta dorobku naukowego oraz wykaz opublikowanych prac naukowych, a także informacje o osiągnięciach naukowych, współpracy naukowej oraz popularyzacji nauki.

WYKAZ PUBLIKACJI STANOWIĄCYCH OSIĄGNIĘCIA NAUKOWE

Wykaz publikacji stanowiących osiągnięcie naukowe, o którym mowa w art. 13 ust. 2 ustawy o stopniach naukowych i tytule naukowym oraz o stopniach i tytule w zakresie sztuki, w rozprawie doktorskiej pt. „Badanie kierunków potencjalnego zastosowania cieczy jonowych w procesach wytwarzania i modyfikacji kompozytów epoksydowych oraz ocena ich właściwości”.

Na końcu niniejszej pracy załączono oświadczenia współautorów niżej wymienionych prac wraz z informacją o zakresie ich zaangażowania w powstanie poszczególnych artykułów.

Wykaz publikacji:

- / **[A1] Zielinski, D.,** Szpecht, A., Hinc, P., Maciejewski, H. & Smiglak, M. Mono N-Alkylated DABCO-Based Ionic Liquids and Their Application as Latent Curing Agents for Epoxy Resins. *ACS Appl. Polym. Mater.* 3, 5481–5493 (2021). [IF = 4,855, MNiSW = 20]
- / **[A2] Zielinski, D.,** Szpecht, A., Hinc, P. & Smiglak, M. Synthesis and Behavior of Hexamethylenetetramine-Based Ionic Liquids as an Active Ingredient in Latent Curing Formulations with Ethylene Glycol for DGEBA. *Molecules* 28, 892 (2023). [IF = 4,2, MNiSW = 140]
- / **[A3] Zielinski, D.,** Szpecht, A., Nadobna, P., Palacz, M. & Smiglak, M. Behavior, synthesis, and effectiveness of an activity of anilinium-based Ionic Liquids (AnILs) as a hardeners and modifiers for epoxy-coatings of flax biocomposites. *Progress in Organic Coatings* 189, 108353 (2024). [IF = 6,5, MNiSW = 100]

- / [A4] Zielinski, D. et al. Multifunctional Modifying Systems Based on Ionic Liquids for Epoxy Resin Systems and Composites. *Applied Sciences* 13, 10661 (2023). [IF = 2,5, MNiSW = 100]
- / [A5] Zielinski, D., Szpecht, A. & Smiglak, M. Dicyanamide ionic liquid mixtures for curing and modifying flax-fiber reinforced epoxy resin composites. *Journal of Molecular Liquids* 408, 125340 (2024). [IF = 5,3, MNiSW = 100]
- / [A6] Zielinski, D. et al. Supported Ionic Liquid-Phase Materials (SILP) as a Multifunctional Group of Highly Stable Modifiers and Hardeners for Carbon and Flax Epoxy Composites. *ChemPlusChem* 89, e202400193 (2024). [IF = 3, MNiSW = 100]
- / [A7] Zielinski, D., Szpecht, A., Maciejewski, H. & Smiglak, M. Cellulose dissolved in ionic liquids as in situ generated filler in epoxy biocomposites with simultaneous curing initiated by ionic liquids. *Cellulose* 31, 6747-6760(2024). [IF = 4,9, MNiSW = 100]

WYKAZ POZOSTAŁYCH PUBLIKACJI

Monografie

- / Kośla K., Zielińska D., Chmal-Fudali E., Wrzesień A., Wańczyk A., Zielinski D., Śmiglak M., Innovative, Multi-Functional Composite Systems For The Construction Of Autonomous Unmanned Platforms - Introduction To Project Idea, Advanced Technologies And Materials In State Security, Łódź 2018, ISBN: 978-83-951668-0-8.

Publikacje naukowe

- / Zajac, A., Szpecht, A., Zielinski, D., Rola, K., Hoppe, J., Komorowska, K. & Smiglak, M. Synthesis and characterization of potentially polymerizable amine-derived ionic liquids bearing 4-vinylbenzyl group. *Journal of Molecular Liquids* 283, 427-439 (2019). [IF = 5,065, MNiSW = 100]
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Impact Factor

Sumaryczny **Impact Factor** dla publikacji wskazanych jako osiągnięcie, według listy *Journal Citation Reports* (JRC) na rok wydania publikacji wynosi **31,255**. Natomiast suma **punktów ministerialnych 660**. Sumaryczny **Impact Factor** dla wszystkich publikacji autora pracy, według JRC na rok wydania publikacji wynosi **63,781**. Z kolei suma **punktów ministerialnych 1280**.

Indeks Hirscha

Indeks Hirscha bez autocytowań wynosi 4.

UDZIAŁ W KONFERENCJACH

Wystąpienia ustne

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2. **Konferencja Nowa Perspektywa, Zielone Technologie**, Poznań, Polska, 29.06.2022, Hub B+R – inicjatywa w służbie współpracy badawczo-rozwojowej małych i średnich przedsiębiorstw z jednostkami naukowymi, **Zieliński, D.**
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PROJEKTY BADAWCZE

/ Kierownik projektu

„ILFLAME - Synergistyczne oddziaływanie fosforu, krzemu i azotu w zmniejszaniu palności kompozytów epoksydowych przy użyciu cieczy jonowych i materiałów SILP, z dodatkową aktywnością jako czynniki utwardzające”

Narodowe Centrum Nauki (NCN)

Konkurs **PRELUDIUM 22** (2023/49/N/ST11/04057)

/ Kierownik projektu

„Modyfikacja wodnych tuszy fotograficznych w celu zwiększenia ich odporności na promieniowanie UV oraz powietrze, a także zmiana parametrów fizykochemicznych”

„**Inkubator Innowacyjności 4.0**”. Priorytet IV, Działanie 4.4. Programu Operacyjnego Inteligentny Rozwój 2014-2020 (MNiSW/2020/349/DIR)

/ Kierownik projektu

„Zmodyfikowane systemy żywiczne wykorzystywane w wytwarzaniu biokompozytów lignocelulozowych w celu zmniejszenia emisji wolnego formaldehydu z końcowego wyrobu”

„**Inkubator Innowacyjności 4.0**”. Priorytet IV, Działanie 4.4. Programu Operacyjnego Inteligentny Rozwój 2014-2020 (MNiSW/2020/349/DIR)

/ **Wykonawca**

„Wielofunkcyjne układy kompozytowe na bazie żywic epoksydowych z cieczami jonowymi jako inicjatorami procesu sieciowania”

Narodowe Centrum Nauki (NCN)

Konkurs **SONATA BIS 7** (2017/26/E/ST8/01059)

/ **Wykonawca**

„Innowacyjne, wielofunkcjonalne układy kompozytowe z przeznaczeniem na elementy konstrukcyjne autonomicznych platform bezzałogowych – MULTIKOMP”

Narodowe Centrum Badań i Rozwoju

Program na rzecz OBRONNOŚCI i BEZPIECZEŃSTWA PAŃSTWA, pt.: „Przyszłościowe technologie dla obronności – Konkurs Młodych Naukowców” (1P/02/19/2016)

/ **Wykonawca**

„Nowe żywice i cząsteczki epoksydowe wytworzone na bazie surowców naturalnych lub porecyklingowych”

„**Inkubator Innowacyjności 4.0**”. Priorytet IV, Działanie 4.4. Programu Operacyjnego Inteligentny Rozwój 2014-2020 (MNiSW/2020/349/DIR)

WIZYTY ZAGRANICZNE

/ **Wizyta studyjna**

Organizowana przez Polską Agencję Rozwoju Przedsiębiorczości (PARP) oraz Innovation Norway, przy wsparciu finansowym w ramach programu Travel Grants, wizyta studyjna dla klastrów i instytucji otoczenia biznesu oferujących innowacyjne rozwiązania z zakresu zielonych i błękitnych technologii.

Kraj: Norwegia

Miasto: Haugesund, Trondheim, Bergen i Stavanger

Instytucja: Siedziby Innovation Norway w Trondheim i Bergen, Targi Floating Wind Days 2023 w Haugesund oraz Innoasis by Nordic Edge w Stavanger

Daty: 22.05.2023 – 25.05.2023 roku

/ **Staż**

Krótkoterminowy staż badawczy, finansowany ze środków „Inicjatywa Doskonałości – Uczelnia Badawcza (ID-UB)”, Uniwersytet im. Adama Mickiewicza w Poznaniu (nr wniosku: 080/13/UAM/0040)

Kraj: Węgry

Miasto: Budapeszt

Instytucja: Polimertechika Tanszéken, Gépészmérnöki Kar, Budapesti Műszaki és Gazdaságtudományi Egyetem

(Department of Polymer Engineering, Faculty of Mechanical Engineering, Budapest University of Technology and Economics)

Daty: 6.05.2023 – 19.05.2023 roku

/ **Staż**

Staż badawczy, finansowany w ramach programu Erasmus+, Uniwersytet im. Adama Mickiewicza w Poznaniu (nr umowy: IN/129/16)

Kraj: Czechy

Miasto: Praga

Instytucja: Katedra analytické chemie, Přírodovědecká fakulta, Univerzita Karlova (Department of Analytical Chemistry, Faculty of Science, Charles University)

Daty: 1.10.2016 – 31.01.2017 roku

/ **Staż**

Staż finansowany w ramach projektu „Poczuj chemię do chemii– zwiększenie liczby absolwentów kierunku CHEMIA na Uniwersytecie im. A. Mickiewicza w Poznaniu”

Kraj: Polska

Miasto: Lublin

Instytucja: Centrum Metal Odczynniki Chemiczne- Midas Investment Sp. z o.o.

Daty: 22.07.2013 – 9.08.2013 roku

INNA DZIAŁALNOŚĆ NAUKOWA I NAGRODY

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- / [2019] Wraz z zespołem PPNT zdobycie wyróżnienia w XXII edycji konkursu „Polski Produkt Przyszłości” dla technologii ILAGRO.
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- / [2023 – 2025] „Kto pyta nie błądzi – nauka dostarczy odpowiedzi” – współtwórca i realizator projektu popularyzatorskiego dofinansowanego ze środków budżetu państwa, przyznanego przez Ministra Nauki i Szkolnictwa Wyższego w ramach Programu Społeczna odpowiedzialność nauki II. Dofinansowanie z MNiSW: 404 800,00 zł. Całkowita wartość projektu: 452 350,00 zł.

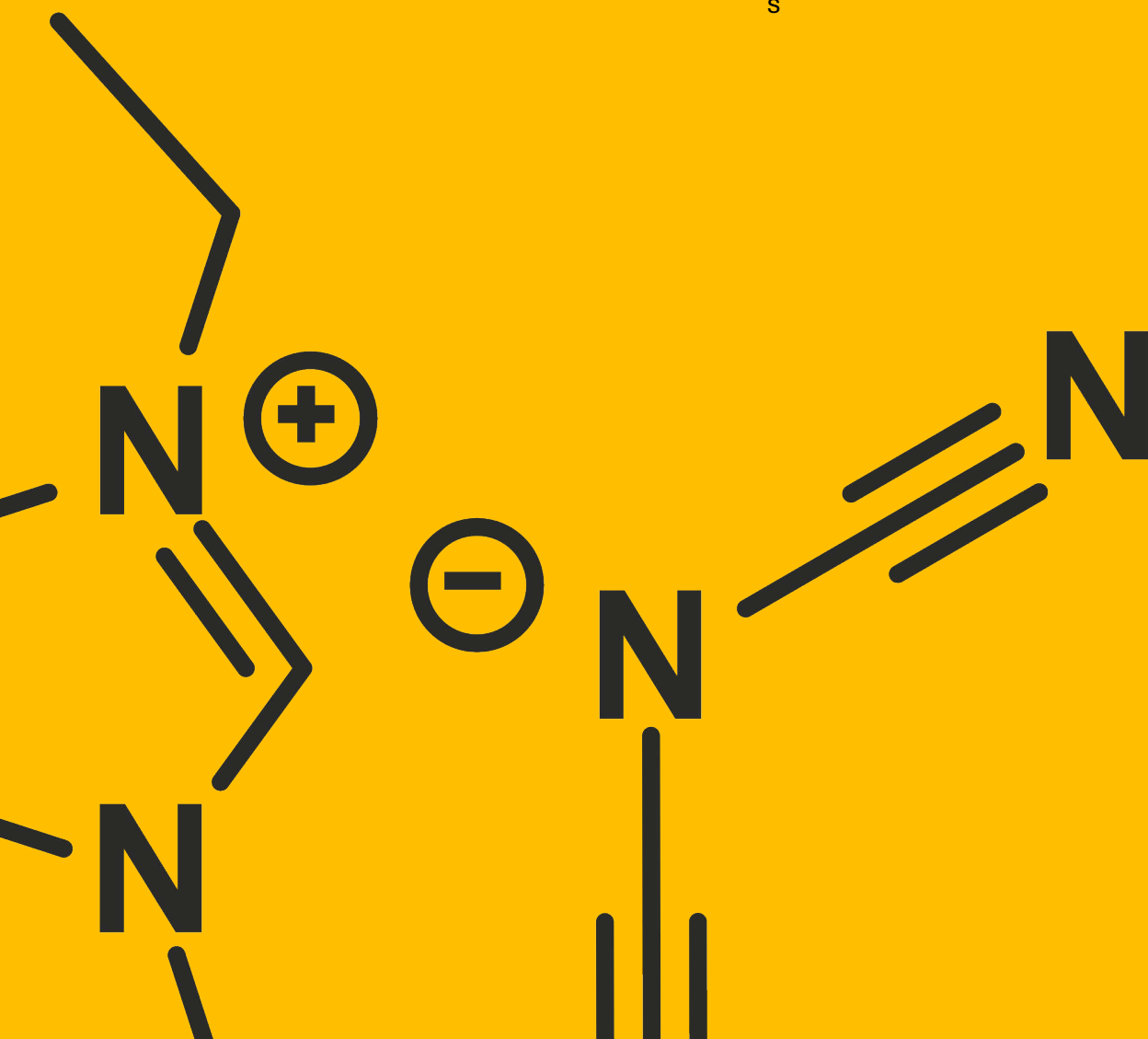
Inna działania popularyzatorskie

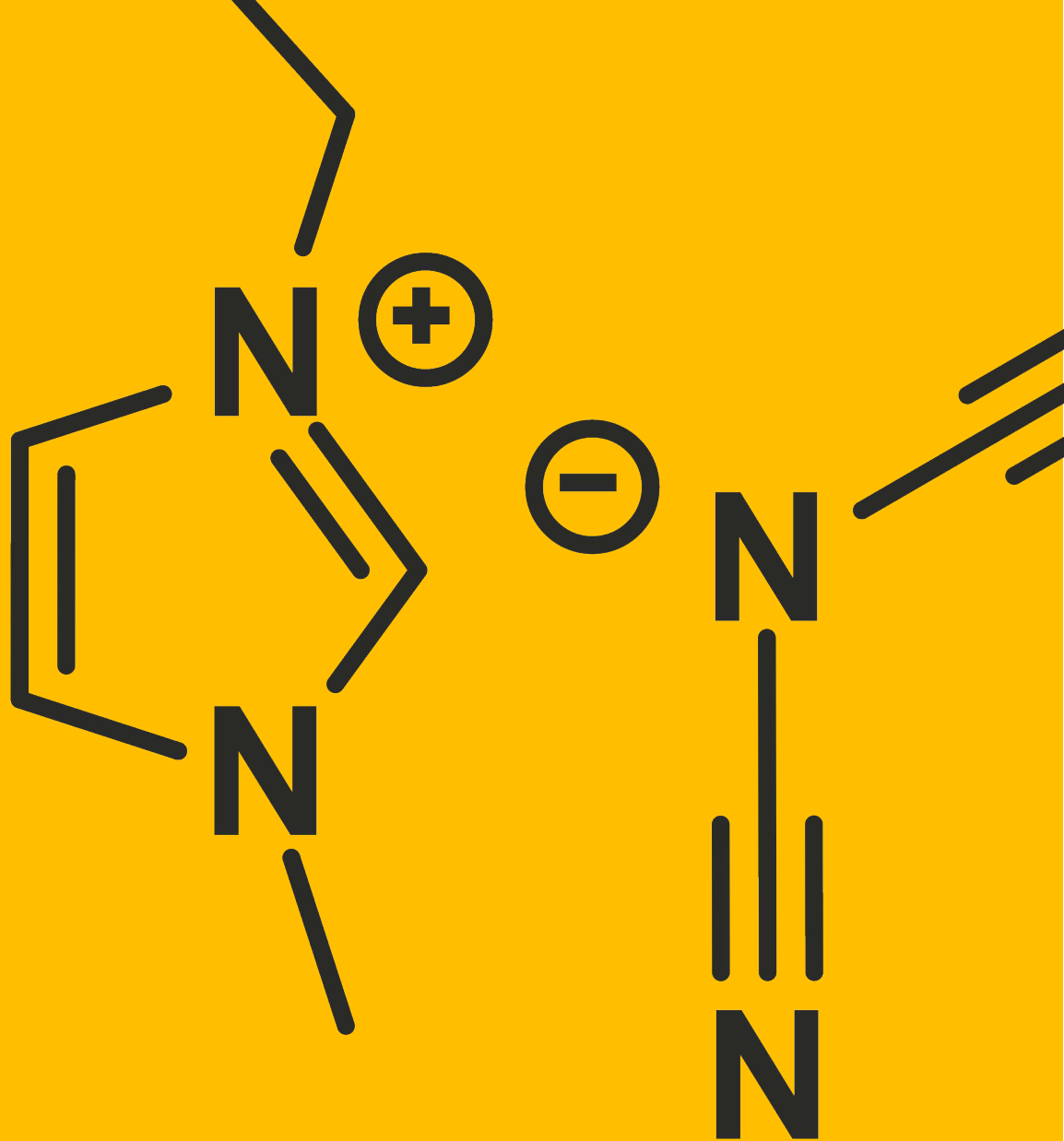
- / Wywiady i wypowiedzi popularnonaukowe w radiach: radiu Poznań, radiu Emaus, Muzo.fm, RMF FM, Radiu Afera oraz telewizyjne wystąpienia w Telewizji WTK.

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WPRO- WADZE- NIE/

Książki oraz artykuły naukowe poświęcone historii cieczy jonowych (ILs, ang. *Ionic Liquids*) praktycznie jednogłośnie uznają Paula Waldena za naukowca, od którego rozpoczęły się badania nad tymi związkami [1–5]. Użycie terminu "prawie jednogłośnie" nie jest przypadkowe – istnieją bowiem pewne wyjątki wśród badaczy, którzy wskazują na inne, wcześniejsze prace lub odkrycia w tej dziedzinie. Warto zauważyć, że choć większość literatury przypisuje Waldenowi pionierską rolę, niektórzy naukowcy podkreślają znaczenie innych badań, takich jak obserwacje

podczas reakcji Friedla-Craftsa w drugiej połowie XIX wieku, w czasie której zaobserwowano powstawanie odrębnej ciekłej fazy po dodaniu do reakcji zawierającej chlorek amylu, niewielkich ilości bezwodnego chlorku glinu. Prawie wiek później okazało się, że obserwacje z reakcji przeprowadzonej w 1877 roku to nic innego jak moment tworzenia cieczy jonowej, a czerwony olej to alkiłowany pierścień aromatyczny stanowiący kation i anion chloroglinianowy [6]. Z kolei w 1888 roku, Siegmund Gabriel oraz James Weiner zaprezentowali pracę, w której opisano azotan etanoloamoniowy, dla którego raportowano temperaturę topnienia wynoszącą 52 - 55°C, co jednocześnie czyni ten związek pierwszą odkrytą solą organiczną o temperaturze topnienia poniżej 100°C [7–10].

Mimo tych różnych historycznych perspektyw, to właśnie synteza azotanu etyloamoniowego przez Waldena w 1914 roku jest powszechnie wspominana za punkt wyjścia dla współczesnych badań nad cieczami jonowymi, które trwają już od ponad 100 lat. Co więcej, zarówno azotan etanoloamoniowy odkryty przez Gabriela i Weinerja jak i azotan etyloamoniowy Waldena, dzisiaj należą do tej samej klasy cieczy jonowych, czyli reprezentują protonowane ciecze jonowe (PILs, ang. *Protic Ionic Liquids*).

1.1. „CIECZE JONOWE”

W 1961 roku Harry Bloom po raz pierwszy wykorzystał termin „*ionic liquids*” podczas swojego wykładu poświęconego stopionym solom (ang. *molten salts*). Tak właśnie określenie „*ciecze jonowe*” padło pierwszy raz w dyskusji o związkach składających się głównie z jonów. Dzisiaj ciecze jonowe są definiowane jako organiczne sole, które pozostają w stanie ciekłym w temperaturze poniżej 100°C, choć temperatura topnienia nie jest jedynym kryterium klasyfikującym te związki. Ponadto, składają się w całości z jonów [11]. ILs charakteryzuje posiadanie unikalnych właściwości fizykochemicznych, takich jak: (i) niska prężność par, (ii) niepalność, (iii) szerokie okno elektrochemiczne, (iv) wysoka stabilność termiczna oraz (v) przewodnictwo elektryczne [11]. Ciecze jonowe mogą być dostosowywane przez zmianę składu jonowego, w tym rodzaju kationów (np. imidazoliowe, pirydyniowe czy fosfoniowe) i anionów oraz grup funkcyjnych czy długości łańcuchów alkilowych, co pozwala na precyzyjne dostosowanie ich właściwości do konkretnych zastosowań. Dzięki tym właściwościom, ILs są często określane jako „*designer solvents*” (projektowalne rozpuszczalniki, tłumaczenie własne) [11–13]. Zwykle są to sole organiczne lub organiczno-nieorganiczne [7], a właściwości fizykochemiczne ILs wynikają z obecności dużych, niesymetrycznych jonów, które tworzą struktury o niskiej symetrii, różniące się od tradycyjnych soli, takich jak np. chlorek sodu. Tak jak wspomniano, struktura i ostateczne właściwości cieczy jonowej mogą być optymalnie i precyzyjnie dostosowywane przez odpowiedni dobór kombinacji kationów i anionów oraz funkcjonalizację ich struktur, a dzięki temu są przedmiotem intensywnych badań, oferując potencjał do szerokiego zastosowania w wielu dziedzinach przemysłu i różnych technologiach, pełniąc rozmaite funkcje [3, 11–14].

1.2. KLASYFIKACJA

Ciecze jonowe mogą być klasyfikowane pod różnymi względami. Z uwagi na rodzaj kationu, można spotkać imidazoliowe ILs, pirydyniowe ILs, amoniowe ILs czy np. fosfoniowe ILs. Z kolei na podstawie ogólnych właściwości wyróżnić można hydrofilowe czy hydrofobowe ILs. Za najbardziej precyzyjny podział można jednak uznać klasyfikację strukturalno-funkcjonalną, którą przedstawiono w Tabeli 1. Warto zaznaczyć, że jedna ciecz jonowa może mieć cechy klasyfikujące ją do kilku grup [15, 16].

Tabela 1. Klasyfikacja strukturalno-funkcjonalna cieczy jonowych (opracowanie na podstawie [7, 14–19]).

Nazwa angielska	Nazwa polska	Cecha
<i>Task Specific Ionic Liquids</i>	Ciecze jonowe do dedykowanych zastosowań	ILs zaprojektowane do jak najlepszego działania w konkretnych zastosowaniach.

Nazwa angielska	Nazwa polska	Cecha
<i>Chiral Ionic Liquids</i>	Chiralne ciecze jonowe	ILs zawierające centra chiralne w kationach, anionach lub obu.
<i>Switchable Polarity Solvent Ionic Liquids</i>	Ciecze jonowe o zmiennej polarności	ILs, które mogą zmieniać swoją polarność w zależności od zastosowanego aktywatora.
<i>Bio-Ionic Liquids</i>	Biociecze jonowe	ILs pochodzące ze związków naturalnych, takich jak cukry, aminokwasy, cholina czy kwasy organiczne.
<i>Poly-Ionic Liquids</i>	Polimeryczne ciecze jonowe	Polimery, które zawierają jednostki monomeryczne ILs.
<i>Polymerizable Ionic Liquids</i>	Polimeryzowalne ciecze jonowe	ILs zawierające polimeryzujące grupy w strukturach kationu lub anionu.
<i>Energetic Ionic Liquids</i>	Energetyczne ciecze jonowe	ILs o wysokiej gęstości energetycznej.
<i>Neutral Ionic Liquids</i>	Neutralne ciecze jonowe	ILs z bardzo słabymi interakcjami elektrostatycznymi między kationami i anionami.
<i>Protic Ionic Liquids</i>	Protonowane ciecze jonowe	ILs zawierające protyczną grupę kwasową
<i>Metallic Ionic Liquids</i>	Metaliczne ciecze jonowe	ILs zawierające jony metali, które nadają im właściwości kwasowości Brønsteda lub Lewisa.
<i>Magnetic Ionic Liquids</i>	Magnetyczne ciecze jonowe	ILs, które wykazują właściwości magnetyczne dzięki obecności jonów metali przejściowych w ich strukturze.
<i>Basic Ionic Liquids</i>	Zasadowe ciecze jonowe	ILs działające jako zasady.
<i>Surface Active Ionic Liquids</i>	Ciecze jonowe powierzchniowo czynne	ILs zawierające grupy nadające im właściwości surfaktantów.

1.3. ZASTOSOWANIA CIECZY JONOWYCH

Do chwili obecnej wydano ponad 125 000* publikacji naukowych i złożono ponad 40 000† wniosków patentowych związanych z cieczami jonowymi. Ta dziedzina przeszła przez typowy cykl zachwyty, który obejmował początkowe przeszacowanie możliwości, fazę rozczarowania, a obecnie znajduje się na ścieżce ku dalszemu rozwojowi i dojrzewaniu. Choć ciecze jonowe jeszcze nie zdobyły zastosowań na ogromną skalę, istnieje wiele oznak wskazujących, że ciecze jonowe mają potencjał do komercyjnego sukcesu w przyszłości [20].

Duże zainteresowanie naukowców tą grupą związków przyniosło liczne doniesienia o ich zastosowaniach. ILs mają znaczący wpływ na technologie energetyczne: jako elektrolity w bateriach (litowo-jonowych, litowo-tlenowych, aluminiumowych, redoksowych) poprawiają stabilność termiczną i bezpieczeństwo, w superkondensatorach umożliwiają magazynowanie energii przy wysokiej mocy i długiej żywotności, a w ogniwach paliwowych, szczególnie w membranach wymiany protonów, zwiększają przewodnictwo i stabilność termiczną [11]. W technologii ogniw słonecznych ILs stosowane są jako elektrolity np. w DSSC (ang. *dye-sensitized solar cell*), zapewniając wysoką przewodność i stabilność elektrochemiczną [21–23]. Jako środki smarne ILs mogą być używane samodzielnie lub jako dodatki do tradycyjnych smarów, poprawiając właściwości smarne i zmniejszając tarcie oraz zużycie [24]. Natomiast jako inhibitory korozji chronią metale przed utlenianiem i korozją, co jest kluczowe w przemyśle petrochemicznym i morskim [25]. Dzięki możliwości wprowadzenia do ich struktury długich łańcuchów alkilowych, ciecze jonowe działają jako surfaktanty w detergentach, farbach i kosmetykach [11]. Ponadto, są również katalizatorami w reakcjach organicznych (alkilacja [26–29], acylacja [30,31], polimeryzacja [32,33]), zastępując tradycyjne, mniej ekologiczne katalizatory, oraz jako środowisko reakcyjne i stabilizatory w syntezie chemicznej [34,35]. Dzięki stabilizowaniu enzymów, ILs są wykorzystywane w reakcjach enzymatycznych, umożliwiając przetwarzanie trudno rozpuszczalnych substratów [11,36]. Ich zdolność rozpuszczania biomasy (ligniny, celulozy) jest użyteczna w procesach jej dalszego przetwórstwa [37–39]. Ciecze jonowe użyte do opracowania sensorów mogą wspierać wykrywanie gazów dzięki wysokiej przewodności jonowej i niskiej prężności par, są używane w czujnikach chemicznych i biosensorach do wykrywania związków chemicznych i biologicznych, a także w czujnikach wilgotności [40]. W procesach oczyszczania wody, ILs usuwają metale ciężkie, fenole i inne zanieczyszczenia, a ich zdolność do selektywnego usuwania CO₂ z gazów przemysłowych ma kluczowe znaczenie dla redukcji emisji gazów cieplarnianych [11]. Mogą selektywnie wydzielać i przetwarzać radionuklidy z odpadów nuklearnych, poprawiając bezpieczeństwo i efektywność zarządzania odpadami radioaktywnymi [41,42].

* Według bazy Web of Science [dostęp: 26 sierpnia 2024 roku]

† Według bazy patentów Espacenet [dostęp 26 sierpnia 2024 roku]

1.4. SYNTEZA CIECZY JONOWYCH

Z uwagi na fakt, że ciecze jonowe charakteryzują się dużą elastycznością struktur i liczbą kombinacji kationów i anionów, ciężko wskazać jedną, standardową metodę ich syntezy, a ich jakość opiera się wyłącznie na wewnętrznym doświadczeniu każdej grupy badawczej. Co więcej, każda metoda syntezy ma zarówno wady, jak i zalety, a wybór odpowiedniej metody do otrzymania pożądanego związku powinien być uzależniony od planowanego zastosowania, uwzględniając, czy IL ma być ultraczysta, czy synteza powinna być tania, czy też szybka [43].

Synteza ILs jest procesem, który można przeprowadzać za pomocą różnych metod konwencjonalnych i niekonwencjonalnych. Konwencjonalne techniki obejmują dwa główne etapy: tworzenie poświadanych kationów oraz wymianę anionów. Proces tworzenia kationów może zachodzić poprzez reakcję Menshutkina aminy czy też fosfiny z halogenkiem alkilowym lub protonowanie wolnym kwasem, podczas gdy reakcje wymiany anionów mogą przebiegać przez reakcję halogenków z kwasami Lewisa lub reakcję metatezy. W reakcji metatezy, typowo stosowane są sole srebra, sodu lub potasu, zawierające poświadany anion [16].

Metody niekonwencjonalne, takie jak techniki mikrofalowe i ultradźwiękowe, zyskują na popularności dzięki swojej ekonomiczności i braku konieczności stosowania rozpuszczalników. Technika mikrofalowa jest ceniona za szybkość, selektywność i przyjazność dla środowiska, umożliwiając osiągnięcie wyższych szybkości reakcji dzięki efektowi przegrzewania. Jej wadą jest ograniczenie tylko do małej skali syntezy. Natomiast metoda ultradźwiękowa, od dawna stosowana w syntezie różnych związków, pozwala na szybkie, efektywne przyspieszenie reakcji i konwersję reagentów bez potrzeby używania rozpuszczalników, ale jest to zadanie niezwykle trudne i wymagające [15,16].

1.5. ZASTOSOWANIE CIECZY JONOWYCH W OBSZARZE ŻYWIC EPOKSYDOWYCH

W 2003 roku, na łamach czasopisma *Polimery*, naukowcy z Zachodniopomorskiego Uniwersytetu Technologicznego opublikowali przełomową pracę dotyczącą zastosowania cieczy jonowych w żywicach epoksydowych. Profesorowie Kowalczyk i Spychaj wykazali, że tetrafluoroboran 1-butylo-3-metyloimidazoliowy może efektywnie służyć jako inicjator sieciowania dla komercyjnej żywicy epoksydowej. Dodatkowo, stwierdzono, że kompozycja tej żywicy z cieczą jonową zachowuje stałą lepkość przez okres do sześciu miesięcy podczas przechowywania w temperaturze pokojowej. Mimo, że autorzy nie przeprowadzili szczegółowych analiz mechanizmu utwardzania, a badaniom poddano jedynie jedną ciecz jonową, ich artykuł stanowi pierwsze w literaturze doniesienie o wykorzystaniu IL jako inicjatora sieciowania żywicy epoksydowej [44]. Po 6 latach, w czasopiśmie *Macromolecules* ukazała się kolejna praca poświęcona tej aplikacji cieczy jonowych. Rahmathullah i współautorzy, omówili zastosowanie dicyjanamidu 1-etylo-3-metyloimidazoliowego jako termicznie latentnego czynnika utwardzającego żywice epoksydowe. Wykazali, że IL może skutecznie inicjować

polimeryzację epoksydów, oferując doskonałą mieszalność i długoterminową stabilność w temperaturze pokojowej. Przy stężeniu około 3,3% wagowych, konwersja grup epoksydowych nie zachodziła przez godzinę w temperaturze 80°C, ale wzrost temperatury do 165°C zakończył reakcję w ciągu 20 minut. Przy pomocy analizy spektroskopowej w bliskiej podczerwieni, po raz pierwszy zbadano mechanizm utwardzania, który polegać miał na reakcjach między grupami epoksydowymi a dicyjanamidem, co prowadzi do powstania stabilnej sieci polimerowej. Wzrost stężenia IL obniża temperaturę zeszklenia (T_g) i moduł sprężystości, co wynika ze zmniejszenia gęstości sieciowania polimeru. Próbki utwardzane cieczą jonową wykazują stabilność termiczną porównywalną do próbek utwardzanych aminami [45]. ILs skutecznie działając sieciująco tylko w podwyższonej temperaturze, nazywane są często utajonymi lub latentnymi inicjatorami utwardzania. Pozostają względnie nieaktywne w temperaturze pokojowej, umożliwiając przechowywanie gotowej mieszanki żywicznej przez dłuższy czas, w porównaniu z klasycznymi utwardzaczami, które rozpoczynają reakcję w niedługim czasie po zmieszaniu z żywicą. W ciągu ostatnich lat zaobserwowano znaczny wzrost zainteresowania naukowego w dziedzinie cieczy jonowych oraz żywic epoksydowych, a to zainteresowanie utrzymuje się do dziś. Ponad dwadzieścia lat po pierwszych doniesieniach, nasza wiedza na temat mechanizmów działania cieczy jonowych znacząco się pogłębiła. Dodatkowo, zidentyfikowano liczne nowe obszary zastosowań żywic epoksydowych, w tym w kompozytach epoksydowych, wykraczające poza samo inicjowanie procesu sieciowania [3]. Jednym z kluczowych zastosowań cieczy jonowych pozostała ich rola jako inicjatorów sieciowania żywic epoksydowych [3,46–49]. Tradycyjne metody sieciowania epoksydów, takie jak użycie amin, bezwodników kwasowych czy izocyjanianów, osiągnęły swoje technologiczne limity w zakresie projektowania procesu sieciowania, w tym sterowania temperaturą tego procesu jak również są ograniczane przez nowe regulacje prawne i środowiskowe. ILs oferują nowatorskie podejście do tego procesu. Działają one jako nowe inicjatory lub funkcjonalne bloki budulcowe, co prowadzi do powstania sieci epoksydowych o ulepszonych właściwościach fizycznych [3,50].

1.5.1. Imidazoliowe ciecze jonowe

Reakcja między prepolimerem epoksydowym a imidazolem (i jego pochodnymi) jest dobrze udokumentowana. Początkowo, imidazol działa jako nukleofil, co prowadzi do tworzenia adduktów epoksydowo-imidazolowych, które są pierwszym etapem procesu utwardzania. Następnie, nadmiar epoksydu powoduje powstawanie centrów wzrostu, po czym rozpoczyna się propagacja polimeru przez dodanie nowej cząsteczki epoksydu. Proces kończy się przez *N*-dealkilację lub eliminację β podstawionej grupy *N* z rosnącego polimeru. W trakcie tego procesu mogą także powstawać etery lub ketony oraz regenerować się addukty 1:1 lub imidazol [3,51–53]. Dzięki tak obszernej wiedzy na temat działania imidazolu, mechanizm działania imidazoliowych ILs należy do najlepiej poznanych. Imidazoliowe ILs działają jako inicjatory polimeryzacji anionowej poprzez

kilka mechanizmów: (i) ścieżka karbenowa, (ii) ścieżka imidazoliowa, w wyniku degradacji IL do produktów dealiklowanych, (iii) wpływ anionu towarzyszącego ze względu na jego nukleofilowość lub zasadowość [54–56]. W pierwszej ścieżce dochodzi do formowania karbenów, które są bardzo reaktywnymi pośrednikami. Karbeny atakują pierścień epoksydowy, co prowadzi do otwarcia pierścienia i inicjacji polimeryzacji anionowej. Ścieżka imidazoliowa, polega na dealkilacji kationu IL do imidazolu. Imidazol działa jako nukleofil, który atakuje epoksyd, inicjując otwarcie pierścienia epoksydowego i dalszą propagację polimeru [3,54].

1.5.2. Fosfoniowe ciecze jonowe

Fosfoniowe ciecze jonowe działają jako katalityczne środki sieciujące epoksydy poprzez nieco inny mechanizm niż imidazoliowe ILs. Po pierwsze, głównym czynnikiem inicjującym jest anion, np. dicyjanoamidowy [57], fosfinianowy lub fosforanowy [58], który działa jako nukleofil, atakując pierścień epoksydowy i inicjując jego otwarcie. Powoduje to rozpoczęcie polimeryzacji anionowej, gdzie to właśnie anion katalizuje reakcję, prowadząc do tworzenia sieci polimerowej. Po drugie, podczas polimeryzacji mogą powstawać wiązania jonowe między kationami fosfoniowymi, które straciły swoje aniony, a nierozprężonymi grupami alkoholowymi powstałymi podczas otwarcia pierścienia epoksydowego. Te wiązania jonowe stabilizują sieć polimerową i wpływają na jej właściwości mechaniczne [3,59]. Trzeci potencjalny szlak działania fosfoniowych ILs polega na ich roli jako współutwardzaczy w reakcji, co wpływa na kinetykę i temperaturę sieciowania. Takie zjawisko badano w układzie żywicy epoksydowej z klasycznym aminowym utwardzaczem (Jeffamine®D2000), do którego dodano bis(2,4,4-trimetylo-pentylo)fosfinian triheksylo(tetradecylo)fosfoniowy. Zaobserwowano, że obecność IL wpłynęła na zwiększenie konwersji grup epoksydowych oraz drugorzędowych grup aminowych obecnych w utwardzaczu, obniżając konwersję pierwszorzędowych grup aminowych. Wykazano, że IL może działać jako inicjator polimeryzacji anionowej, promując reakcję eteryfikacji w konkurencji z reakcją epoksydu z aminą, a w utwardzonej żywicy potwierdzono obecność nieprzereagowanych grup aminowych, zarówno pierwszorzędowych jak i drugorzędowych. W zależności od rodzaju anionu, fosfoniowe ILs mogą przyspieszać reakcję polimeryzacji poprzez aktywację grup epoksydowych, prowadząc do szybszego utwardzania i modyfikacji właściwości końcowych materiału [57,58].

1.5.3. Inne właściwości

Ze względu na różnorodność struktur kationów i anionów cieczy jonowych, można wprowadzić do materiału żywicznego takie ciecze jonowe, które będą zdolne do pełnienia różnych funkcji [3,50,59]. Należy jednak pamiętać, że nieodpowiedni dobór struktur cieczy jonowych może prowadzić do pogorszenia niektórych właściwości materiału, przy jednoczesnym polepszeniu innych. Na przykład, niektóre wysoce stabilne ciecze jonowe

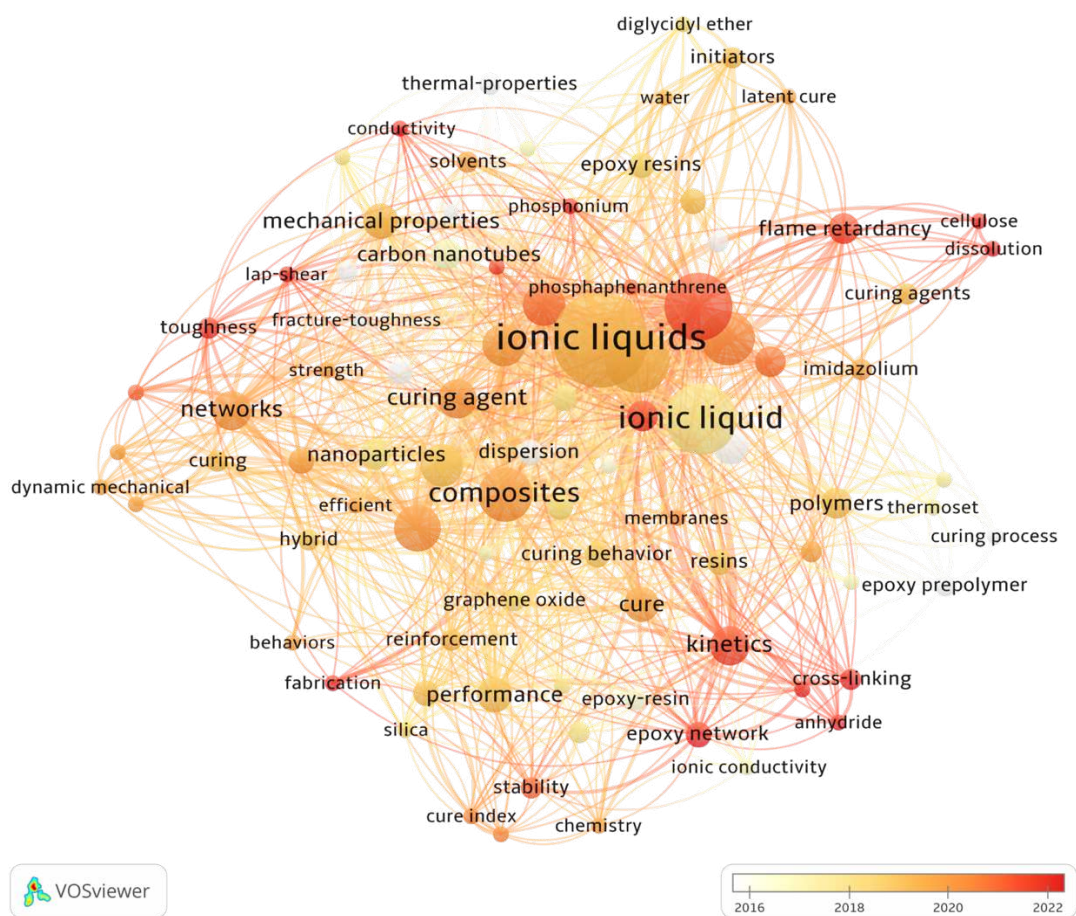
mogą nie być w stanie efektywnie inicjować polimeryzacji ze względu na konieczność dostarczenia bardzo wysokiej temperatury do układu [3]. Wiadomo również, że nie wszystkie ciecze jonowe są kompatybilne i mieszalne z żywicami [60]. Jednakże, ciecze jonowe mają zdolność do poprawy właściwości mechanicznych i termicznych sieci epoksydowych. Modyfikowane cieczami jonowymi sieci epoksydowe charakteryzują się zwiększoną wytrzymałością na rozciąganie, lepszą stabilnością termiczną oraz zwiększoną odpornością na działanie ognia [3,50,59]. Wynika to z unikalnych interakcji pomiędzy cieczami jonowymi a matrycą epoksydową, które prowadzą do powstania bardziej zwartych i jednorodnych struktur polimerowych. Dodatkowo, ciecze jonowe mogą działać jako plastyfikatory, poprawiając elastyczność materiałów epoksydowych i zmniejszając ich kruchość, co jest szczególnie istotne w aplikacjach wymagających wysokiej wytrzymałości mechanicznej [3]. Znane są również zastosowania cieczy jonowych jako stabilizatorów czy dyspersantów dla wypełnień w matrycy epoksydowej [61]. Co więcej, odpowiednio dobrane ciecze jonowe mogą wpływać na parametry elektrochemiczne żywicy epoksydowej, na przykład w stałych elektrolitach [62,63].

1.6. ANALIZA BIBLIOGRAFICZNA

Do przeprowadzenia analizy bibliograficznej wykorzystano narzędzie badawcze jakim jest *VOSviewer*. Posłużyło ono do analizy współwystępowania słów kluczowych w publikacjach, co pozwoliło na zobrazowanie specyficznych domen badawczych. Mapa wzajemnych powiązań (Rysunek 1) została stworzona na podstawie 210 artykułów naukowych zawierających słowa kluczowe "*ionic liquid*", "*curing*" oraz "*epoxy*". Dla tej mapy, *VOSviewer* zidentyfikował 302 słowa kluczowe, a po ustawieniu progu współwystępowania na poziomie 2, do wizualizacji wybrano 89 słów kluczowych podzielonych na 8 klastrów.

Wizualizacja ukazuje sieć wzajemnych powiązań słów kluczowych w ramach 8 klastrów. Intensywność ciemnych odcieni żółci oraz czerwieni sugeruje, że największe zagęszczenie tych słów występuje po roku 2018, czyli 15 lat po pierwszych doniesieniach literaturowych o zastosowaniu cieczy jonowej z żywicą epoksydową. Na podstawie intensywności kolorów można określić średni rok, w którym dane słowo kluczowe najczęściej się pojawiało w doniesieniach literaturowych. W okolicach roku 2013, główna uwaga badaczy była skierowana na kinetykę procesu sieciowania, stabilność mieszanek żywicy z cieczami jonowymi oraz morfologię tych układów. Wcześniej, około roku 2010, popularność zyskało słowo kluczowe „*crosslinking*”, co pokrywa się z istotną pracą opublikowaną przez Rahmathullaha i współautorów w roku 2009. Rok 2014 był okresem intensywnych badań nad nanokompozytami i nanorurkami w połączeniu z cieczami jonowymi i żywicami epoksydowymi. Z kolei w latach 2016-2020 badania skoncentrowały się na właściwościach elektrochemicznych, takich jak przewodnictwo elektryczne i stałych elektrolitach na bazie ILs i żywic epoksydowych. Wizualizacja pokazuje, że lata 2018-2022 charakteryzują się największym skupieniem wokół badań nad właściwościami

uniepalamiającymi cieczy jonowych względem żywic epoksydowych oraz kompozytów epoksydowych.



Rysunek 1. Wizualizacja sieci współwystępowania słów kluczowych opracowana przy użyciu oprogramowania VOSviewer.

Podział słów kluczowych na aż 8 klastrów może wskazywać na wysoki stopień specjalizacji poszczególnych domen badawczych. Współwystępowanie tych słów nie tylko podkreśla różnorodność tematów badawczych, ale także pomaga zidentyfikować multidyscyplinarny charakter oraz kierunki dalszego rozwoju w danej dziedzinie. Uzupełnieniem wizualizacji jest Tabela 2, w której przedstawiono 15 pierwszych słów kluczowych według rankingu VOSviewer.

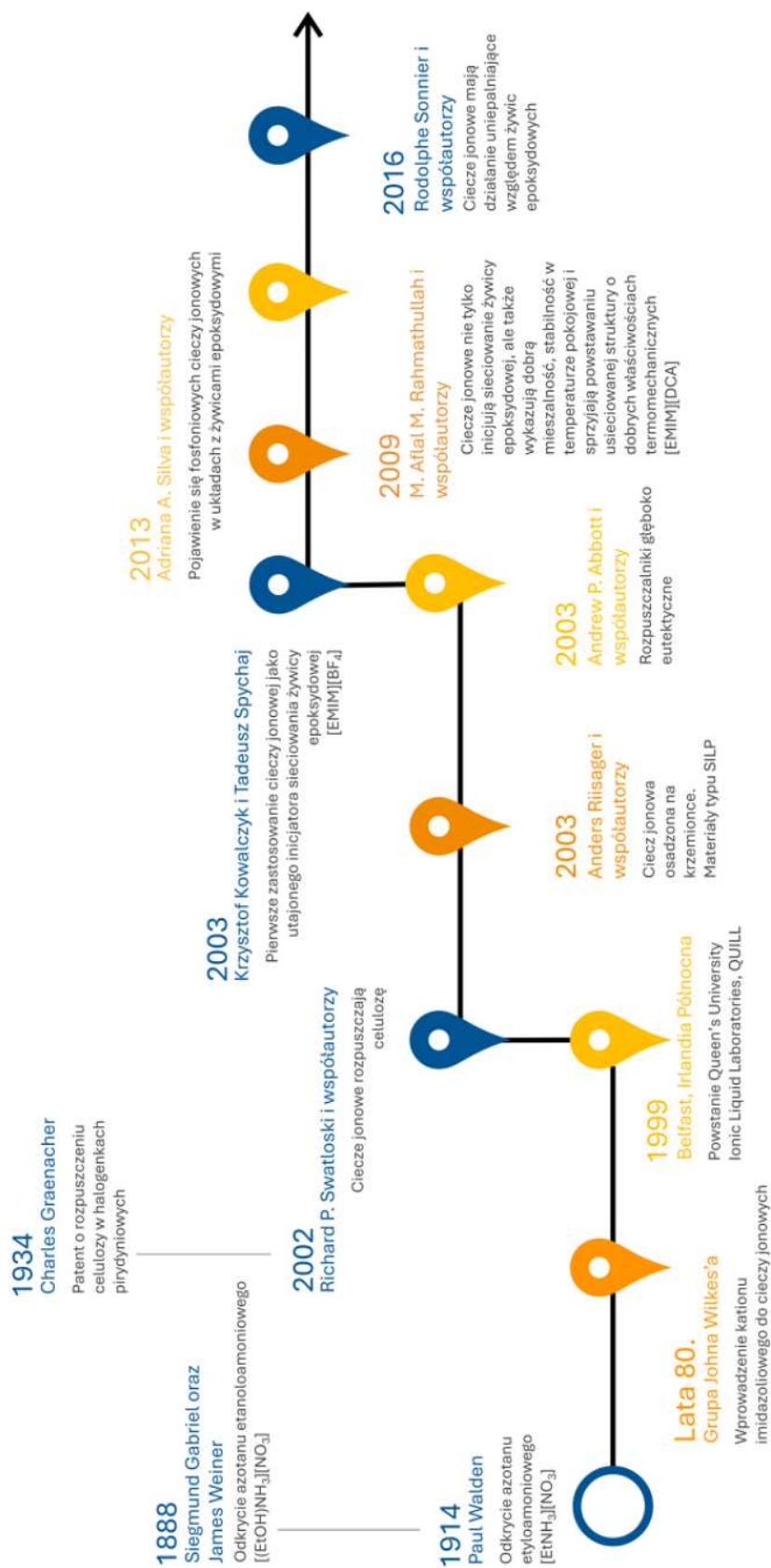
Każde przedstawione słowo kluczowe zostało zdefiniowane poprzez siłę połączenia (ang. *Link*), czyli wartość liczbową określającą połączenie lub relację między dwoma słowami kluczowymi na mapie. Im wyższa wartość, tym silniejsze jest połączenie, co może wskazywać na częstsze współwystępowanie tych słów kluczowych w publikacjach naukowych. Całkowita siła wszystkich połączeń (ang. *Total link strength*) w badaniu słów kluczowych, odnosi się do całkowitej siły wszystkich połączeń danego słowa kluczowego z innymi słowami kluczowymi. Oznacza to sumę wartości sił połączeń danego słowa kluczowego ze wszystkimi innymi słowami kluczowymi [64]. Dalej

przedstawiono liczbę wystąpień słów kluczowych w artykułach naukowych z badanego zbioru oraz średni rok występowania. Tabela pokazuje, że słowa kluczowe „*Ionic Liquids*” oraz „*polymerization*”, jak również „*ionic liquid*” i „*composites*”, mając największą siłę połączeń często pojawiają się razem w publikacjach naukowych, co może sugerować, że są one silnie powiązane tematycznie lub są częścią tej samej dziedziny badań. Ich wysoka całkowita siła połączeń oznacza, że każde z nich jest powiązane z wieloma innymi słowami kluczowymi i te powiązania są silne. Może to sugerować, że te słowa kluczowe odgrywają centralną rolę w literaturze naukowej dotyczącej badanej dziedziny.

Tabela 2. Lista 15 słów kluczowych uszeregowanych według rankingu istotności na podstawie analizy bazy publikacji w programie VOSviewer.

Słowo kluczowe	Tłumaczenie	Siła połączenia	Całkowita siła wszystkich połączeń	Liczba wystąpień słowa	Średni rok wystąpień
<i>ionic liquids</i>	ciecze jonowe	66	159	24	2020
<i>polymerization</i>	polimeryzacja	56	108	15	2021
<i>ionic liquid</i>	ciecz jonowa	55	100	16	2018
<i>composites</i>	kompozyty	55	108	15	2021
<i>epoxy resin</i>	żywice epoksydowe	50	96	14	2019
<i>behavior</i>	sposób działania	49	79	11	2021
<i>epoxy</i>	epoksyd	44	69	9	2020
<i>temperature</i>	temperatura	47	68	8	2019
<i>resin</i>	żywica	43	67	8	2021
<i>kinetics</i>	kinetyka	38	60	7	2021
<i>network</i>	sieć	35	56	7	2020
<i>mechanical properties</i>	właściwości mechaniczne	36	55	6	2020
<i>curing agent</i>	środek utwardzający	35	54	7	2020
<i>performance</i>	działanie	39	51	6	2019
<i>mechanism</i>	mechanizm	33	50	8	2020

Podsumowaniem analizy bibliograficznej jest przygotowane na podstawie przytoczonych wcześniej rozdziałów w monografiach oraz artykułów naukowych, kalendarium osiągnięć w dziedzinie cieczy jonowych, od ich wynalezienia przez przełomowe doniesienia literaturowe, aż po teraźniejszość. Kalendarium przedstawiono na Rysunku 2. W miejscach, gdzie istnieją rozbieżności w zależności od doniesień literaturowych, wprowadzono kilka dat dotyczących danego osiągnięcia.



Rysunek 2. Kalendarium osiągnięć w dziedzinie cieczy jonowych.

1.7. CIECZE JONOWE W KONTEKŚCIE CELÓW ZRÓWNOWAŻONEGO ROZWOJU

Konwencjonalne rozwiązania w dziedzinie kompozytów epoksydowych cechują się licznymi zagrożeniami środowiskowymi związanymi z produkcją komponentów: żywic epoksydowych czy utwardzaczy oraz modyfikatorów. Są to produkty pochodne ropy naftowej otrzymywane na bardzo dużą skalę w procesach generujących tony niebezpiecznych produktów ubocznych i odpadów. Poświęcono wiele prac badawczych podkreślaniu potrzeby rozwoju technologii kompozytowych w kierunku bardziej zrównoważonego rozwoju [65] i nowych, pochodzących ze źródeł naturalnych lub biodegradowalnych komponentów. W ślad za nimi idą szeregi prac poświęconych nowoczesnym biożywicom epoksydowym czy nowoczesnym katalizatorom ich polimeryzacji [66–70], np. bazującym na strukturach protoporfirynowych [71] czy aminokwasach [72,73]. Nieuniknione było również zainicjowanie prac związanych z cieczami jonowymi jako wielofunkcyjnymi komponentami dedykowanymi do żywic epoksydowych, ale czy mają one szansę stać się komercyjnym rozwiązaniem? Do roku 2024 roku złożono ponad 40 000 wniosków patentowych dotyczących cieczy jonowych, co stanowi optymistyczny sygnał wskazujący na wzrastające zainteresowanie komercyjne tą domeną badawczą. Jest to szczególnie znaczące w kontekście kluczowych prognozowanych wskaźników rynkowych, omówionych w kolejnych częściach tego rozdziału. Już dziś znane są komercyjne i pilotażowe technologie wykorzystujące ciecze jonowe. W obszarze rozpuszczalników warto wskazać chociażby na dimeryzację olefin (Difasol process, Axens) czy chlorowanie (BASF). Z kolei katalizatory na bazie ILs używane są w reakcjach alkilowania opracowanych przez Chevron/Honeywell UOP (technologia ISOALKY™). Natomiast 3M oraz BASF wdrożyli technologię dodatków antystatycznych na bazie cieczy jonowych do polimerów [20].

W 2015 roku Organizacja Narodów Zjednoczonych (ONZ) przyjęła rezolucję zwaną Agenda 2030, która obejmuje 17 Celów Zrównoważonego Rozwoju (ang. *Sustainable Development Goals, SDGs*, Rysunek 3). Zawarte w dokumencie cele stanowią ambitny i uniwersalny plan działania, mający na celu eliminację ubóstwa, ochronę środowiska oraz zapewnienie pokoju i dobrobytu dla wszystkich ludzi na świecie do 2030 roku. Z uwagi na ich wzajemne powiązania, realizacja tych celów wymaga szeroko zakrojonej współpracy międzynarodowej, zaangażowania społeczności lokalnych oraz wdrażania innowacyjnych rozwiązań w różnych dziedzinach. Osiągnięcie SDGs jest kluczowe dla zrównoważonego rozwoju globalnej społeczności i wymaga integracji działań na poziomie politycznym, społecznym i gospodarczym. Prace nad Agendą 2030 rozpoczęto w 2012 roku, w trakcie Konferencji Narodów Zjednoczonych organizowanej w Rio de Janeiro, a opracowywane cele miały zastąpić i zarazem rozszerzyć Milenijne Cele Rozwoju (ang. *Millennium Development Goals, MDGs*), obowiązujące do 2015 roku.



Rysunek 3. Globalne cele zrównoważonego rozwoju. [źródło: <https://www.un.org.pl>]

Z perspektywy 2024 roku, odniesienie prowadzonych badań naukowych do SDGs przynosi liczne korzyści, zarówno dla samych naukowców, jak i dla społeczeństwa. Po pierwsze, analiza własnych badań w świetle SDGs pozwala dostrzec w nich bezpośredni wpływ na poprawę jakości życia ludzi oraz ochronę środowiska. Włączając aspekty zrównoważonego rozwoju, naukowcy mogą przyczyniać się do rozwiązywania globalnych problemów, takich jak zmiany klimatyczne, ubóstwo, brak dostępu do czystej wody i edukacji. Co więcej, wiele instytucji finansujących, w tym rządy, organizacje międzynarodowe i fundacje prywatne, preferuje wspieranie projektów badawczych, które wspierają cele zrównoważonego rozwoju. Projekty zgodne z SDGs mogą łatwiej uzyskać finansowanie i wsparcie, a same SDGs zachęcają do podejścia interdyscyplinarnego, co sprzyja współpracy między różnymi dziedzinami nauki. Takie działanie umożliwia bardziej kompleksowe i innowacyjne rozwiązania problemów, które często są wieloaspektowe i wymagają współdziałania specjalistów z różnych obszarów. Po drugie, zwiększenie znaczenia i widoczności badań. Projekty badawcze powiązane z SDGs są często bardziej doceniane, zarówno w środowisku akademickim, jak i poza nim. Przyciągają uwagę mediów, decydentów oraz opinii publicznej, co zwiększa ich wpływ i znaczenie. Cele Zrównoważonego Rozwoju nadają badaniom długoterminowy kontekst i cel, umożliwiając wywieranie trwałego, pozytywnego wpływu na przyszłe pokolenia. Włączenie SDGs do badań naukowych pozwala również na myślenie globalne i działanie lokalne, co sprzyja lepszemu zrozumieniu i rozwiązaniu problemów dotyczących społeczności na całym świecie. Dodatkowo, taka integracja podkreśla etyczny wymiar pracy naukowej, promując zasady zrównoważonego rozwoju, takie jak odpowiedzialne zarządzanie zasobami, sprawiedliwość społeczną i ochrona środowiska.

W ramach uzupełnienia badań przedstawionych w pracy, przeanalizowano wszystkie 17 Celów Zrównoważonego Rozwoju oraz zadania przypisane każdemu z nich,

identyfikując jednocześnie te z nich, w realizacji których badania te mogą okazać się użyteczne. W wyniku tej analizy, wybrano 6 SDGs, w których badania nad zastosowaniem cieczy jonowych jako inicjatorów sieciowania żywic epoksydowych oraz ich wpływem na właściwości kompozytów wzmacnianych włóknami się wpisują.

Cel 8: Wzrost gospodarczy i godna praca

Zastąpienie powszechnie stosowanych w produkcji materiałów kompozytowych, utwardzaczy na bazie amin czy bezwodników kwasowych, a także dodatków funkcyjnych, którymi są w dużej mierze związki organiczne, przez ciecze jonowe, może w znaczący sposób wpłynąć na bezpieczeństwo pracy w zakładach przemysłowych. Zadanie 8.8 („Chronić prawa pracownicze oraz promować bezpieczne środowisko pracy dla wszystkich, w tym dla pracowników, w tym pracowników - migrantów, w szczególności dla kobiet migrantek i osób mających niepewne zatrudnienie”). Ciecze jonowe mają bardzo niską prężność par, co oznacza, że w normalnych warunkach praktycznie nie parują. Dzięki temu ryzyko wdychania szkodliwych oparów przez pracowników jest znacznie mniejsze w porównaniu z lotnymi związkami organicznymi. Również ze względu na tą niską lotność i ich właściwości chemiczne, ciecze jonowe są zwykle niepalne lub mają znacznie wyższą temperaturę zapłonu w porównaniu do wielu rozpuszczalników organicznych. To zmniejsza ryzyko pożarów i eksplozji w miejscach pracy. Ponadto, są często chemicznie stabilne oraz mogą być używane w szerokim zakresie temperatur i warunków, co zmniejsza ryzyko niekontrolowanych reakcji chemicznych.



Cel 9: Innowacyjność, przemysł i infrastruktura

Zastosowanie cieczy jonowych w wytwarzaniu materiałów kompozytowych, w szczególności ich zdolność do pełnienia więcej niż jednej funkcji w kompozycie, np. (i) inicjowanie sieciowania żywicy epoksydowej, (ii) uniepalnienie czy (iii) modyfikacji właściwości mechanicznych/reologicznych może prowadzić do opracowania nowych, bardziej wydajnych i zrównoważonych kompozytów, które znajdą szerokie zastosowanie w przemyśle motoryzacyjnym, lotniczym i budowlanym. Innowacje w materiałach kompozytowych, wynikające z zastosowania cieczy jonowych, mogą znacząco podnieść wydajność oraz ekologiczność procesów produkcyjnych, co jest zgodne z ideą zrównoważonych technologii. Zastosowanie cieczy jonowych jako inicjatorów sieciowania żywic epoksydowych ma potencjał do zwiększenia efektywności oraz zmniejszenia ekologicznego śladu produkcji, w szczególności poprzez eliminację konieczności wytwarzania i stosowania organicznych utwardzaczy czy modyfikatorów.



Cel 12: Odpowiedzialna konsumpcja i produkcja

Opisywane w pracy badania mogą przyczynić się do zmniejszenia ilości odpadów i toksycznych emisji dzięki zastosowaniu cieczy jonowych, które mimo wszystko są bardziej ekologiczne niż tradycyjne rozpuszczalniki czy związki organiczne wykorzystywane przy produkcji klasycznych inicjatorów sieciowania czy dodatków funkcyjnych dedykowanych żywicom epoksydowym. Optymalizacja procesów sieciowania żywic epoksydowych z użyciem cieczy jonowych może prowadzić do bardziej zrównoważonej produkcji materiałów kompozytowych, co wpisuje się w ramy odpowiedzialnej konsumpcji i produkcji. Zmniejszenie odpadów i emisji jest kluczowym elementem tego celu i ma bezpośrednie znaczenie dla ochrony środowiska.



Cel 13: Działania w dziedzinie klimatu

W analizie Celów Zrównoważonego Rozwoju dostrzeżono, że poprawa efektywności energetycznej procesów sieciowania oraz redukcja emisji związanych z produkcją klasycznych komponentów do żywic epoksydowych, mogą przyczynić się do ograniczenia globalnego śladu węglowego. Badania nad bardziej efektywnymi i mniej energochłonnymi metodami produkcji wspierają działania w dziedzinie klimatu, co jest kluczowe w walce ze zmianami klimatycznymi. Co więcej, nieustannie prowadzone są badania nad optymalizacją metod wytwarzania cieczy jonowych, które to z każdym rokiem stają się coraz bardziej przyjazne środowisku. W przypadku klasycznych komponentów analogiczne działania nie są realizowane z taką samą intensywnością.



Cel 15: Życie na lądzie

Pomimo trwających badań nad toksycznością cieczy jonowych oraz poszukiwaniu balansu między zachowaniem ich właściwości, a strukturą możliwie jak najbardziej składającą się ze związków naturalnych, można z pewną dozą niepewności uznać, że stosowanie cieczy jonowych, które będą mniej toksyczne i bardziej biodegradowalne, może zmniejszyć negatywny wpływ na ekosystemy lądowe i wodne. Omawiane badania mogą więc wspierać ochronę bioróżnorodności oraz zapobiegać degradacji środowiska naturalnego, co jest zgodne z celem ochrony życia na lądzie.



Cel 17: Partnerstwa na rzecz celów

Badania nad cieczami jonowymi jako inicjatorami sieciowania oraz modyfikatorami żywic epoksydowych mogą promować współpracę między instytucjami naukowymi a przemysłem, wspierając rozwój zrównoważonych technologii i praktyk. Tego rodzaju partnerstwa są niezbędne dla realizacji celów zrównoważonego rozwoju, gdyż łączą wiedzę i zasoby różnych sektorów, co prowadzi do bardziej efektywnych i innowacyjnych rozwiązań.



1.8. SZANSE KOMERCJALIZACJI WYNIKÓW BADAŃ

Jednoznaczne określenie wielkości rynku cieczy jonowych to wyzwania dla wielu agencji zajmujących się przygotowywaniem raportów rynkowych. Każda z globalnie rozpoznawalnych agencji dostarcza innych informacji o prognozach wzrostu wielkości rynku, jego wartości i wielkości rocznego skumulowanego wskaźnika wzrostu (CAGR, ang. *Compound Annual Growth Rate*). Global Market Insights oszacował wartość rynku ILs w roku 2023 na 2,38 mld dolarów. Jednocześnie podając wartość CAGR (w prognozie na lata 2024 – 2032) na poziomie 13,5%, prowadząc do osiągnięcia wartości rynku w 2032 roku na poziomie 7,76 mld dolarów. Domenę katalizy wskazano jako kluczową w rozwoju branży ILs, a wśród pięciu największych przedsiębiorstw mający wpływ na rynek wymienia: (i) BASF SE, (ii) Tokyo Chemical Industry, (iii) Solvionic, (iv) IoLiTec GmbH oraz (v) Scionix. Do kluczowych gospodarek należą gospodarka amerykańska oraz niemiecka, mające w 2023 roku rynek cieczy jonowych o wielkości odpowiednio 882 mln dolarów i 768 mln dolarów [74].

Nieco wyprzedzając szczegółowe omówienie wyników badań w cyklu publikacji, przeanalizowano ogólne szanse komercjalizacji takich technologii, powstałych na bazie prac naukowych [A1] – [A7]. Wydaje się, że kluczowym czynnikiem będzie zwiększenie dostępności cieczy jonowych na rynku, szczególnie w skali wielkotonażowej. Branża kompozytowa zużywa duże ilości komponentów i z reguły są to substancje tanie, zatem oprócz dostępności ILs, kluczowym będzie także optymalizacja kosztów syntezy i wprowadzenie dostępności produktów o czystości technicznej. Dzisiejsze obszary aplikacji ILs wymagają wysokiej czystości, szczególnie zastosowania związane z elektrochemią, jednakże z punktu widzenia branży kompozytowej, wysoka czystość nie jest niezbędna do utrzymania założonych parametrów materiałów. W literaturze znane są doniesienia o skalowaniu syntezy cieczy jonowych [75–77], więc można założyć, że w najbliższych latach problemy z dostępnością zostaną zaspokojone. Z kolei ceny cieczy jonowych, zgodnie z zasadami rynkowymi, powinny obniżyć się wraz ze wzrostem popytu i podaży, co koreluje z wcześniejszym stwierdzeniem dotyczącym dostępności. Jak zatem można przekonać przemysł do nowych rozwiązań? Zasadnym wydaje się wykorzystanie czynnika zrównoważonego rozwoju i bezpieczeństwa jakie niosą ciecze jonowe. Nowe rozwiązania technologiczne przechodzą ocenę na podstawie analizy cyklu życia (LCA,

ang. *Life Cycle Analysis*), która jest szczegółowym badaniem danej technologii, produktu lub surowca i wszystkich elementów z nią/nim związanych. Jednakże w życiu codziennym, ciekawą alternatywą wydaje się wykorzystanie narzędzi komputerowych do rutynowej oceny procesów np. syntezy pod kątem ich zrównoważenia. Coraz większą popularnością cieszą się rozwiązania dostarczane przez liczne firmy, a jednym z nich jest np. GREEN MOTION™ opracowane przez firmę Mane, lidera w branży produkcji substancji zapachowych i smakowych. Niektóre publikacje już teraz wykorzystują to oprogramowanie do oceny raportowanych, nowych związków chemicznych i procesów ich otrzymywania pod kątem zrównoważonego rozwoju [78,79], również cieczy jonowych [75].



Rysunek 4. Ocena syntezy cieczy jonowej - dicyjanoamidu 1-etylo-3-metyloimidazoliowego, dokonana przy użyciu narzędzia GREEN MOTION™.

Jako przykład, że ciecze jonowe mogą wykorzystywać fakt zrównoważonego rozwoju jako swoją przewagę nad klasycznymi komponentami w branży kompozytów, wykonano analizę procesu syntezy jednej z najlepiej poznanych cieczy jonowych, działających jako inicjator sieciowania żywicy epoksydowej – dicyjanoamid 1-etylo-3-metyloimidazoliowy. W tym celu wykorzystano narzędzie GREEN MOTION™, a wynik oceny przedstawiono na Rysunku 4. Kryterium analizowanym było spełnienie 12 zasad zielonej chemii, a proces syntezy ewaluowano w skali 100 kg, zakładając czystość na poziomie 85% i wykorzystując metodę syntezy cieczy jonowych z anionem [DCA] z użyciem żywic jonowymiennych, która obecnie rozwijana i optymalizowana jest w Poznańskim Parku Naukowo-Technologicznym.

Podczas analizy wzięto pod uwagę, między innymi, wpływ produktów na środowisko, zdrowie i bezpieczeństwo, szczegółowo ewaluując:

- / surowce;
- / rozpuszczalniki;
- / zagrożenia i toksyczność reagentów;
- / wydajność i selektywność reakcji;

- / efektywność procesu;
- / zagrożenia i toksyczność produktu końcowego;
- / odpady.

Każdy z tych aspektów jest oceniany według określonych kryteriów, które są zestawiane w ogólny wynik od 0 do 100 punktów. Im wyższy wynik, tym bardziej "zielony" jest dany proces lub produkt. Wynik powyżej 50 punktów jest uznawany za "zielony" i sugeruje, że proces spełnia wyższe standardy zrównoważonego rozwoju. Uzyskano wynik 52, który jest powyżej minimalnego progu. Analiza wykazała, że choć niektóre aspekty, takie jak pochodzenie surowców petrochemicznych, obniżają ogólną ocenę, to proces jest oceniany jako zrównoważony dzięki wysokiemu wynikowi w kategoriach odpadów i procesu.

Podsumowując tę część pracy, wyniki badań opisywane w cyklu publikacji mają szansę komercjalizacji, jednak potrzeba czasu niezbędnego do zapewnienia odpowiedniej dostępności komponentów w postaci cieczy jonowych i osiągnięcia akceptowanego w branży materiałów kompozytowych pułapu cenowego. Równolegle należy wykorzystywać przewagę ILs w postaci osiągania celów zrównoważonego rozwoju i monitorować zmieniające się regulacje prawne, które w wielu nowych technologiach okazują się bodźcem do wdrożenia, wymuszając na przemyśle pewne zmiany i działania na rzecz środowiska.

CEL PRACY



Celem niniejszej pracy doktorskiej było opracowanie, synteza oraz charakterystyka cieczy jonowych jako utwardzaczy, wielofunkcyjnych modyfikatorów i nośników wypełnienia dla żywic epoksydowych oraz kompozytów wzmocnionych włóknami. Praca ta dążyła do zrozumienia i zoptymalizowania wpływu cieczy jonowych na proces sieciowania żywic epoksydowych oraz właściwości mechaniczne i termiczne żywic oraz kompozytów. Badania miały na celu rozwinięcie nowatorskich systemów modyfikujących czy sposób wprowadzania do kompozytów wypełnienia, które będą mogły znaleźć zastosowanie w przemyśle,

zwiększając efektywność i funkcjonalność materiałów kompozytowych. Sformułowano również cele szczegółowe:

- / synteza cieczy jonowych, stanowiących pochodne różnych amin, w tym: 1,4-diazabicyklo[2.2.2]oktanu, urotropiny oraz aniliny oraz charakterystyka ich właściwości;
- / zbadanie cieczy jonowych oraz ich mieszanin jako środków sieciujących w rozwoju zaawansowanych systemów żywic epoksydowych i kompozytów;
- / zbadanie cieczy jonowych oraz ich mieszanin jako modyfikatorów w układach żywic epoksydowych oraz struktur kompozytowych w celu stworzenia wysokowydajnych, trwałych i wszechstronnych kompozytów odpowiednich do szerokiego zakresu zastosowań przemysłowych;
- / zbadanie cieczy jonowych oraz ich mieszanin jako nośników wypełnienia w układach żywic epoksydowych i kompozytów oraz identyfikacja optymalnych obszarów zastosowania w dziedzinie materiałów kompozytowych, w których ciecze jonowe stanowić mogą konkurencję lub posiadać przewagę nad rozwiązaniami konwencjonalnymi;

- / zbadanie wpływu cieczy jonowych oraz ich mieszanin na właściwości mechaniczne struktur kompozytowych.

Uzupełnieniem celu pracy były postawione hipotezy badawcze, na które odpowiedź miała przynieść niniejsza praca. Sformułowano poniższe hipotezy.

- / Ciecze jonowe skutecznie pełnią rolę modyfikatorów żywic epoksydowych, poprawiając ich właściwości mechaniczne i termiczne bez konieczności stosowania dodatkowych substancji modyfikujących;
- / Nowo zsyntetyzowane ciecze jonowe na bazie trzech różnych amin: (i) 1,4-diazabicyklo[2.2.2]oktanu (DABCO), (ii) urotropiny oraz (iii) pochodnych aniliny jako struktur wyjściowych w projektowaniu kationów mogą być skutecznymi inicjatorami utwardzania żywic epoksydowych, umożliwiając kontrolowane procesy sieciowania i tworzenie stabilnych układów kompozytowych. Aniony takie jak: (i) dicyjanoamid [DCA], (ii) trifluorometanosulfonian [OTf] oraz (iii) bis(trifluorometanosulfonylo)imidek [NTf₂], również mają istotny wpływ na proces sieciowania żywicy epoksydowej, poprzez czynny udział w powstawaniu sieci polimerowej;
- / Zastosowanie cieczy jonowych osadzonych na krzemionce jako modyfikatorów i utwardzaczy kompozytów epoksydowych wzmocnionych włóknem węglowym i lnianym, zwiększy ich wytrzymałość mechaniczną. Ponadto, jest to skuteczny sposób wprowadzania do układu kompozytowego wypełnienia krzemionkowego, które poprzez obecność inicjatora utwardzania na swojej powierzchni, inicjuje polimeryzację matrycy epoksydowej, możliwie jak najbliżej powierzchni wypełniacza, uniemożliwiając powstawanie defektów w strukturze utwardzonego polimeru;
- / Mieszanki cieczy jonowych z anionem dicyjanoamidowym będą miały istotny wpływ na właściwości termiczne i mechaniczne kompozytów epoksydowych wzmocnionych włóknem lnianym, zwiększając ich potencjał aplikacyjny w specjalistycznych warunkach, w których niektóre cechy materiału są pożądane. Mieszanki cieczy jonowych mają charakter addytywny względem nadawania właściwości kompozytom;
- / Celuloza rozpuszczona w cieczach jonowych jako wypełniacz generowany *in situ*, wpływa na proces utwardzania żywic epoksydowych oraz na właściwości mechaniczne końcowych materiałów kompozytowych, oferując ekologiczną alternatywę dla tradycyjnych wypełniaczy i nowatorski sposób jego wprowadzania do układu żywicznego – płynne wypełnienie;
- / Ciecze jonowe mogą być projektowane jako wielofunkcyjne modyfikatory, które mogą jednocześnie wpływać na kilka kluczowych parametrów materiałowych, takich jak wytrzymałość, stabilność termiczna oraz

odporność ogniowa, co otworzy nowe możliwości zastosowania tych materiałów w różnych gałęziach przemysłu. Odpowiednio dobrane ciecze jonowe mogą w różny sposób modyfikować właściwości struktur polimerowych, w szczególności wpływając na stopień usieciowania, wartość temperatur zeszklenia czy temperatury procesu sieciowania.

Poprzez weryfikację powyższych hipotez, niniejsza praca doktorska dąży do poszerzenia wiedzy na temat cieczy jonowych i ich zastosowań, a także do opracowania nowoczesnych materiałów kompozytowych o ulepszonych właściwościach, które stanowić mogą konkurencję dla komponentów konwencjonalnych, szeroko stosowanych w branży kompozytów.

WYNIKI BADAŃ



Niniejsza rozprawa doktorska poświęcona jest syntezie i charakterystyce cieczy jonowych bazujących na kationach pochodnych: (i) 1,4-diazabicyklo[2.2.2]oktanu, (ii) urotropiny, (iii) aniliny oraz (iv) imidazolu i przeciwjonach w formie przede wszystkim, ale nie tylko, anionu: (i) dicyjanoamidowego, (ii) trifluorometanosulfonowego oraz (iii) bis(trifluorometanosulfonylo)imidkowego. W pracy wskazano także wielofunkcjonalne zastosowanie cieczy jonowych, zarówno w formie czystych cieczy jonowych, jak również ich mieszanin, w obszarze żywic

epoksydowych i kompozytów epoksydowych wzmacnianych włóknami. Wszystkie opisywane w kolejnych podrozdziałach wyniki badań zostały szeroko przedstawione w cyklu siedmiu publikacji naukowych przedstawionych poniżej.

3.1. CYKL PUBLIKACJI

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- [A3] Zielinski, D., Szpecht, A., Nadobna, P., Palacz, M. & Smiglak, M. Behavior, synthesis, and effectiveness of an activity of anilinium-based Ionic Liquids (AnILs) as a hardeners and modifiers for epoxy-coatings of flax biocomposites. *Progress in Organic Coatings* **189**, 108353 (2024).
- [A4] Zielinski, D. et al. Multifunctional Modifying Systems Based on Ionic Liquids for Epoxy Resin Systems and Composites. *Applied Sciences* **13**, 10661 (2023).

- [A5] Zielinski, D., Szpecht, A. & Smiglak, M. Dicyanamide ionic liquid mixtures for curing and modifying flax-fiber reinforced epoxy resin composites. *Journal of Molecular Liquids* **408**, 125340 (2024).
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- [A7] Zielinski, D., Szpecht, A., Maciejewski, H. & Smiglak, M. Cellulose dissolved in ionic liquids as in situ generated filler in epoxy biocomposites with simultaneous curing initiated by ionic liquids. *Cellulose* **31**, 6747–6760 (2024).

3.2. PROJEKT „MULTIKOMP”

Projekt „Innowacyjne, wielofunkcjonalne układy kompozytowe z przeznaczeniem na elementy konstrukcyjne autonomicznych platform bezzałogowych – MULTIKOMP”, był realizowany w latach 2016 – 2021 przez konsorcjum, w skład którego wchodziły cztery instytucje:

- / Instytut Technologii Bezpieczeństwa „Moratex” w Łodzi (ITB „Moratex”);
- / Śląskie Centrum Naukowo-Technologiczne Przemysłu Lotniczego Sp. z o.o. w Czechowicach-Dziedzicach (obecnie WB Centrum Kompozytów sp. z o. o.);
- / Fundacja Uniwersytetu im. Adama Mickiewicza w Poznaniu;
- / oraz Akademia Sztuk Pięknych im. Władysława Strzemińskiego w Łodzi.

Celem projektu „MULTIKOMP” było opracowanie nowatorskich rozwiązań kompozytowych w zakresie zaawansowanych, wielofunkcyjnych materiałów przeznaczonych do wytwarzania kompozytowych konstrukcji powietrznych, lądowych i morskich autonomicznych platform bezzałogowych (APB). Wdrożenie opracowanych rozwiązań materiałowych ma potencjalny wpływ na rozwój zdolności operacyjnych Sił Zbrojnych RP oraz służb odpowiedzialnych za zapewnienie bezpieczeństwa publicznego. Co ważne, przeprowadzone w ramach projektu badania stanowiły fundament niniejszej rozprawy doktorskiej, będąc inspiracją do dalszych, pogłębionych zadań badawczych i nowych projektów.

Z wielu zaplanowanych w projekcie zadań autor pracy był bezpośrednio zaangażowany w dwa obszary. Opracowanie i skalowanie technologii: (i) żywicy z cieczami jonowymi oraz (ii) preimpregnatów włóknistych (prepregów) na bazie receptur żywic z cieczami jonowymi i bazujących na nich wielofunkcjonalnych układów kompozytowych będących elementami konstrukcyjnymi APBów.

3.2.1. Zadania związane z cieczami jonowymi w projekcie „MULTIKOMP”

Projekt koncentrował się na zastosowaniu cieczy jonowych jako inicjatorów sieciowania żywicy epoksydowej oraz optymalizacji tego procesu pod kątem wytwarzania preimpregnatów włóknistych (prepregów). Jednym z celów projektu było zapewnienie stabilności tych prepregów w temperaturze pokojowej, co stanowiłoby innowację

technologiczną w porównaniu do aktualnie produkowanych preimpregnatów, które wymagają przechowywania i transportu w warunkach chłodniczych (zwykle w temperaturze -19°C). Ponadto, planowano, że ta stabilność w temperaturze pokojowej będzie wydłużona względem stabilności w warunkach chłodniczych, dostępnych na rynku prepregów. Pierwotne założenia projektu przewidywały, że układy cieczy jonowych z żywicami epoksydowymi będą kompatybilne z różnymi rodzajami tkanin wzmacniających, w szczególności z włóknem węglowym oraz aramidowym, w szerokim zakresie ich splotu i gramatury. Jednak w toku badań okazało się, że mimo licznych prób kompatybilizacji, wytworzone układy żywiczne nie nadają się do stosowania z włóknem aramidowym. Problemy napotkane podczas badań obejmowały trudności w osiągnięciu wymaganych poziomów przesycenia żywicą tkaniny oraz jednorodności rozłożenia matrycy żywicznej na powierzchni włókniny aramidowej. Zadanie było o tyle utrudnione, że projekt nie zakładał wprowadzania substancji polepszających adhezję czy modyfikatorów reologii na tym etapie, kierując się celem osiągnięcia możliwie jak najprostszego składu surowcowego mieszanki żywicznej.

W pierwszym etapie określono warunki brzegowe dla cieczy jonowych oraz żywic epoksydowych. Na podstawie analizy literatury, opracowano typoszereg cieczy jonowych, sklasyfikowanych w ramach trzech grup: (i) cieczy jonowych alkilowanych, (ii) cieczy jonowych protonowanych oraz (iii) mieszanin eutektycznych oraz typoszereg żywic epoksydowych. Następnie rozpoczęto etap badań przesiewowych. Określono maksymalne, graniczne stężenie cieczy jonowych w kompozycji na poziomie 4 phr (części na sto części żywicy, ang. *parts per hundred resin*), temperaturę 120°C oraz czas utwardzania wynoszący 4 godziny. Badania w tym etapie miały na celu przede wszystkim wyeliminowanie tych ILs z typoszeregu, które nie inicjowały utwardzania żywicy w założonych warunkach, co doprowadziło do redukcji pierwotnego typoszeregu z 44 pozycji do 15 cieczy jonowych/mieszanin, które zakwalifikowano do drugiego etapu badań przesiewowych. Kontynuując, prowadzono eksperymenty nie tylko pod kątem utwardzania, ale również pod względem między innymi: (i) mieszalności i kompatybilności z żywicami epoksydowymi, (ii) lepkości, (iii) optymalizacji stężenia w stosunku do żywicy epoksydowej oraz (iv) tendencji do samoutwardzania w temperaturze pokojowej. Badania przesiewowe obejmowały wytworzenie łącznie 510 kompozycji cieczy jonowych i mieszanin z żywicami epoksydowymi, w tym 220 kompozycji w pierwszym etapie oraz 290 kompozycji w drugim etapie, a rezultatem było wytypowanie dwóch najlepszych cieczy jonowych.

Walidacja uzyskanych wyników wprowadziła projekt w fazę optymalizacji i modyfikacji, która miała na celu przede wszystkim poprawę właściwości prepregów, a w konsekwencji także struktur kompozytowych. Wychwycone problemy na różnych etapach przetwórstwa mieszanki żywicznej, pozwoliły określić kierunek modyfikacji w postaci doboru substancji pomocniczych, wspierających proces utwardzania w spełnieniu warunków brzegowych. Ostatecznie wytypowany układ żywiczny scharakteryzowano przy użyciu technik analizy termicznej oraz przeprowadzono analizę

podstawowych właściwości mechanicznych utwardzonej mieszanki modyfikowanej, w tym badania wytrzymałości przy statycznym rozciąganiu oraz wytrzymałości przy zginaniu. Analizy te uzupełnione zostały poprzez badania wytrzymałości mechanicznej dla wytworzonych struktur kompozytowych, wzmacnianych włóknem węglowym.

3.2.2. Efekty projektu

Projekt „MULTIKOMP” osiągnął znaczące rezultaty w zakresie technologii kompozytów stosowanych w konstrukcjach powietrznych, lądowych i morskich autonomicznych platform bezzałogowych. Opracowano usystematyzowane podejście projektowe przy wykorzystaniu metodologii *Design Thinking* do projektowania nowych układów kompozytowych dla APB. Metodologia ta pozwala na lepszą implementację innowacji oraz integrację użytkowników końcowych w proces projektowy. Z uwagi na specyfikę tego projektu oraz objęcie wyników poufnością, nie zostały one przytoczone w przewodniku na rzecz ogólnego zarysu i zakresu. Z tego samego powodu, wyniki prac badawczych w projekcie „MULTIKOMP” nie mogły być swobodnie publikowane w artykułach naukowych. Projekt był inauguracją i wskazaniem przyszłych kierunków badań, których wyniki będą omawiane w niniejszej pracy.

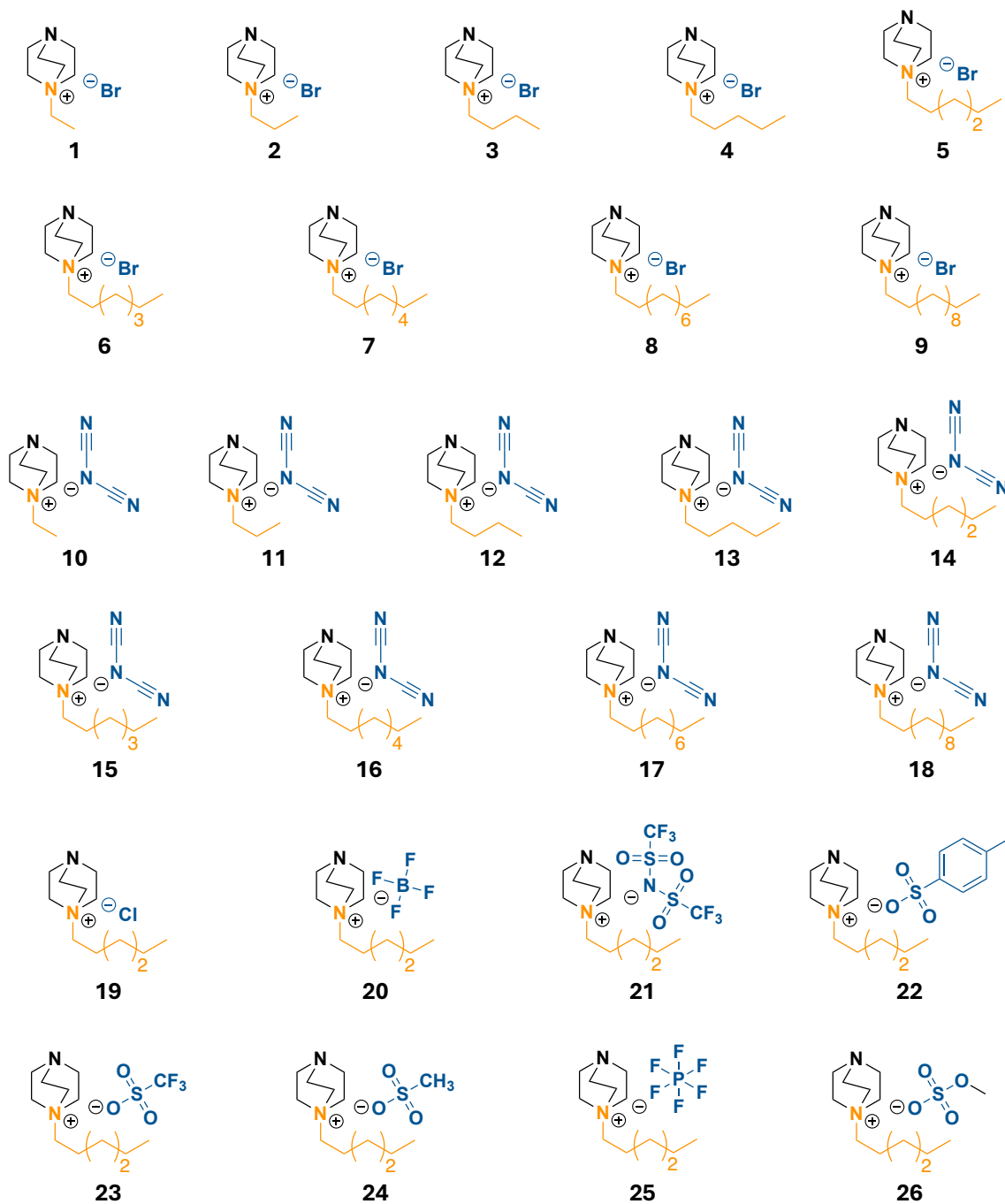
SYNTEZA CIECZY JONOWYCH

Jednym z ważnych elementów badań zaprezentowanych w pracach [A1], [A2], [A3], [A4] oraz [A5] była synteza cieczy jonowych. W ramach tych badań przeanalizowano ich właściwości jako inicjatorów i modyfikatorów żywicy epoksydowej, zarówno w formie czystych cieczy jonowych, jak i w postaci mieszanin. Ponadto, szczegółowo zbadano ich właściwości termiczne. Większość otrzymanych związków chemicznych, przedstawionych w tych pracach jest nowa, a ich pełna charakterystyka ma istotne znaczenie dla dostarczenia cennej wiedzy

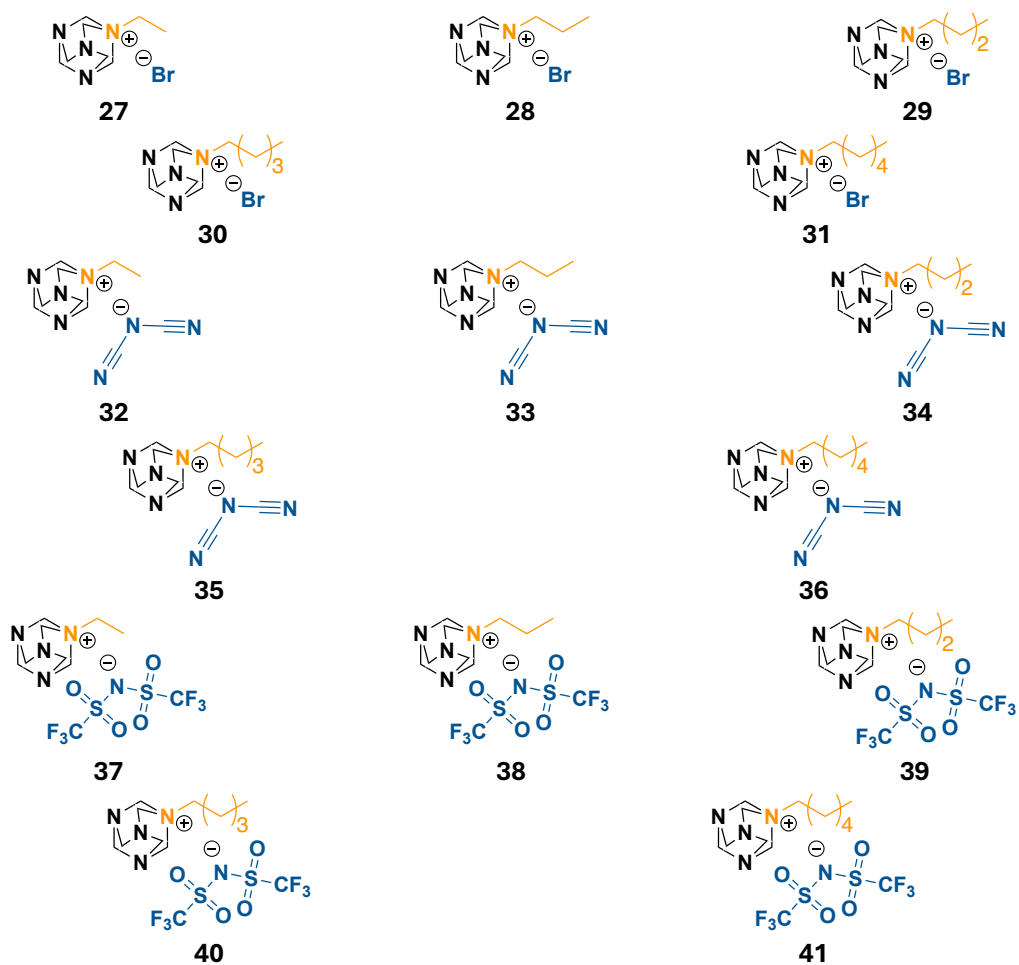
innym naukowcom. Dla wszystkich związków określono podstawowe parametry jakościowe, takie jak czystość oraz zawartość wody. Szczegółowa metodologia tych badań jakościowych oraz wyniki otrzymane dla poszczególnych substancji zostały przedstawione w odpowiednich pracach, składających się na tę rozprawę. W kolejnych podrozdziałach zostanie ogólnie omówiony proces syntezy, tworzenia mieszanin cieczy jonowych oraz ich właściwości termiczne, którego szczegóły zawarte są w cyklu prac naukowych wchodzących w skład rozprawy.

4.1. STRUKTURY OTRZYMANYCH ZWIĄZKÓW CHEMICZNYCH

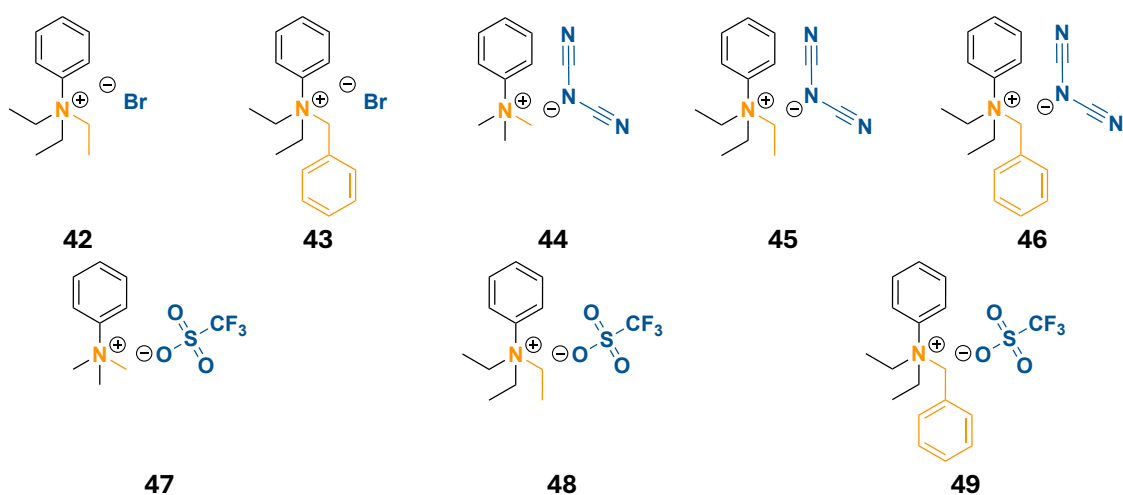
Na Rysunkach 5 – 8 przedstawiono wszystkie struktury związków chemicznych, które zostały otrzymane na drodze syntezy w pracach [A1], [A2], [A3], [A4] oraz [A5], wraz z przypisanymi im numerami, co ułatwi dalszą interpretację wyników. Ponadto, na końcu niniejszej pracy ponownie zamieszczono wykaz struktur, aby w każdej chwili możliwe było odwołanie się do dokładnej struktury omawianej w akapicie.



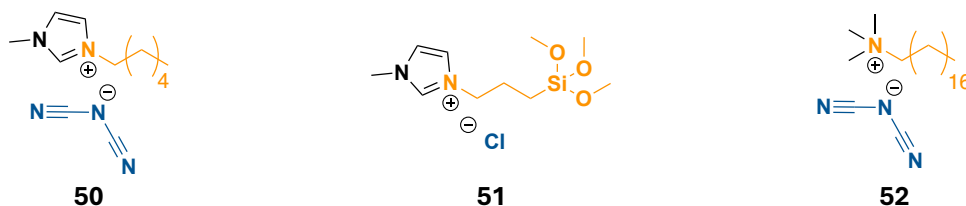
Rysunek 5. Struktury związków chemicznych, pochodnych DABCO otrzymanych na drodze syntezy w pracy [A1].



Rysunek 6. Struktury związków chemicznych, pochodnych urotropiny otrzymanych na drodze syntezy w pracy [A2].



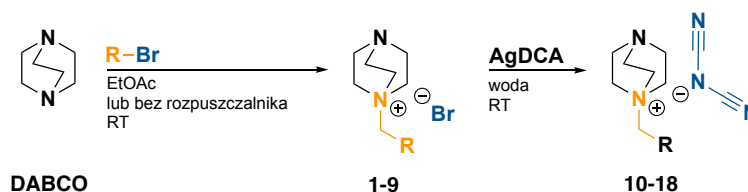
Rysunek 7. Struktury związków chemicznych, pochodnych aniliny otrzymanych na drodze syntezy chemicznej w pracy [A3].



Rysunek 8. Struktury związków chemicznych otrzymanych na drodze syntezy w pracach [A4] i [A5].

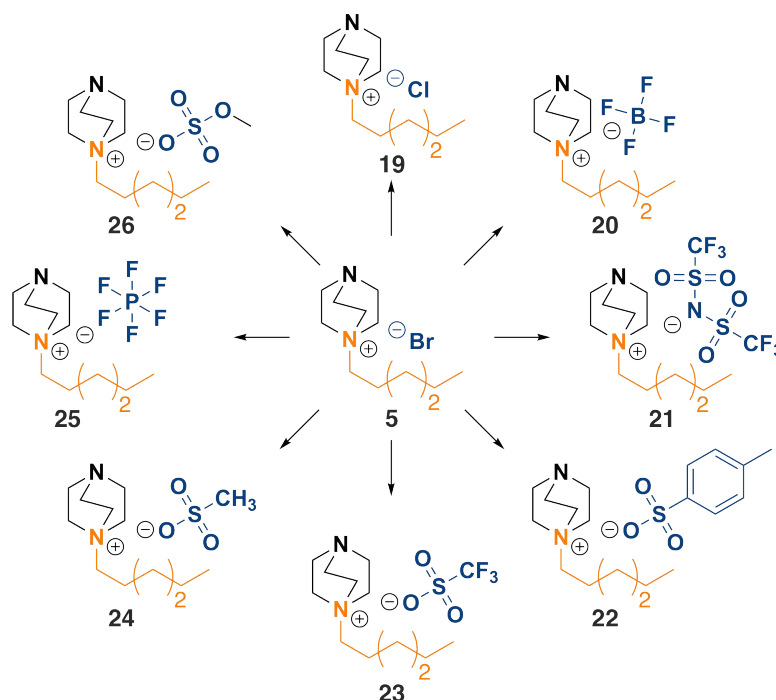
4.2. METODY SYNTEZY CIECZY JONOWYCH

Pierwsza grupa badanych cieczy jonowych to pochodne 1,4-diazabicyklo[2.2.2]oktanu. Ta bicykliczna amina, często wykorzystywana w syntezie organicznej, stanowi doskonałe źródło pozyskiwania cieczy jonowych. Dzięki swojej unikalnej strukturze, omawiany związek chemiczny podlega zarówno monoalkilowaniu, jak i dialkilowaniu [80–82]. Taka właściwość DABCO umożliwia syntezę cieczy jonowych, które w swojej strukturze zawierają dwa czwartorzędowe atomy azotu oraz dwa aniony. Kierunek reakcji substytucji nukleofilowej DABCO może być sterowany poprzez temperaturę oraz rozpuszczalnik, które odpowiednio dobrane pozwalają uzyskać pożądaną strukturę produktu. Dla przykładu, proces prowadzony w temperaturze pokojowej oraz octanie etylu, prowadzi do uzyskania produktu monopodstawionego [80]. Dzieje się tak, ponieważ produkt reakcji DABCO z wybranym halogenkiem, najczęściej bromkiem, wydziela się z układu reakcyjnego, przez co nie ulega drugiej substytucji. Z kolei aby uzyskać dipodstawioną pochodną, reakcję należy prowadzić w podwyższonej temperaturze oraz acetonitrylu, który skutecznie rozpuszcza monopodstawioną pochodną i umożliwia jej dalszą reakcję [80,83,84]. Co istotne, możliwe jest uzyskanie podstawienia DABCO różnymi grupami funkcyjnymi, poprzez połączenie procesu monosubstytucji, a następnie rozpuszczenie pochodnej w acetonitrylu i dalsza substytucja nukleofilowa, z użyciem innego czynnika alkilującego. Ponadto, umiejętne zaplanowanie syntezy prowadzi do uzyskania pochodnych, składających się z różnych przeciwjonów [80]. W pracy [A1] przeprowadzono syntezę monopodstawionych pochodnych DABCO poprzez reakcję tej aminy z odpowiednim bromkiem alkilowym. Portfolio związków zaplanowano w taki sposób, aby poszczególne pochodne różniły się długością łańcucha alkilowego, uwzględniając parzystą oraz nieparzystą liczbę atomów węgla w łańcuchu. Przedstawiona na Schemacie 1 reakcja, uwzględnia także drugi etap syntezy, czyli metatezę, prowadzącą do wymiany anionu bromkowego na anion dicyjanoamidowy. Reakcję metatezy przeprowadzono w sposób szeroko stosowany w literaturze, a wszystkie otrzymane związki scharakteryzowano spektroskopowo oraz określono ich czystość z wykorzystaniem chromatografii jonowej. Szczegółowe informacje dotyczące syntezy jak i charakterystyki otrzymanych substancji chemicznych są zawarte w pracy [A1].



Schemat 1. Schemat reakcji otrzymywania pochodnych DABCO w pracy [A1].

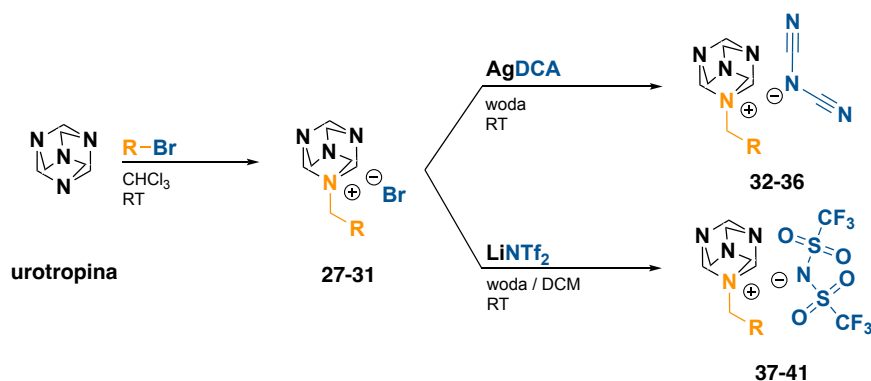
W toku prac badawczych, podczas badań przesiewowych, zaobserwowano dużą aktywność utwardzającą kationu DABCO, zawierającego łańcuch alkilowy składający się z sześciu atomów węgla. Uzupełniając badania, zdecydowano się otrzymać serię pochodnych, składających się z tego kationu oraz różnych przeciwjonów, które otrzymano zarówno na drodze metatezy z odpowiednim reagentami i warunkami, jak również przeprowadzając reakcję Menshutkina z użyciem 1-chloroheksanu, prowadzącą do otrzymania czwartorzędowej soli chlorkowej. Otrzymane związki przedstawiono na Rysunku 9. Celem tych badań było przede wszystkim określenie wpływu anionu na zdolność cieczy jonowej do inicjowania polimeryzacji żywicy epoksydowej, ale także lepsze poznanie grupy związków chemicznych na bazie DABCO. Tylko jedna z badanych pochodnych, zawierająca anion trifluorometanosulfonowy, wykazywała zdolność utwardzania żywicy epoksydowej w określonych w pracy warunkach brzegowych.



Rysunek 9. Struktury otrzymanych, dodatkowych pochodnych DABCO zawierających inne aniony w strukturze.

W roku 2015 Natalia V. Plechkova oraz Kenneth R. Seddon w jednej z prac, podczas opisywania urotropinowych cieczy jonowych, użyli zwrotu, że z uwagi na wysoką

predyspozycję tej aminy do tworzenia czwartorzędowych soli, w bardzo łagodnych warunkach, a przez to mnogość potencjalnych struktur, urotropina wydaje się być niedostatecznie zbadanym źródłem cieczy jonowych [85]. Ponadto, jest to substancja wyjątkowo łatwo dostępna i tania. Jej znaczenie w syntezie chemicznej to przede wszystkim otrzymywanie amin pierwszorzędowych poprzez reakcję Delépine’a, w której w początkowym etapie urotropina, ulegająca reakcji z czynnikiem alkilującym, prowadzi do powstania produktu pośredniego, czwartorzędowej soli, reagując dalej i prowadząc do powstania pierwszorzędowej aminy. Urotropina jest w tej reakcji donorem azotu, z którego w ostatnim etapie powstaje grupa aminowa w miejscu, w którym w czynniku alkilującym znajdował się atom halogenkowy [86]. Pierwszy etap reakcji Delépine’a przebiega w temperaturze pokojowej, zwykle w chloroformie, a czwartorzędowa sól wydziela się z mieszaniny wraz z postępem reakcji, w formie osadu, przez co izolacja tego produktu jest stosunkowo prosta. Właśnie ten I etap (Schemat 2) wykorzystano do otrzymania pochodnych urotropiny 27 – 41 opisanych w pracy [A2].

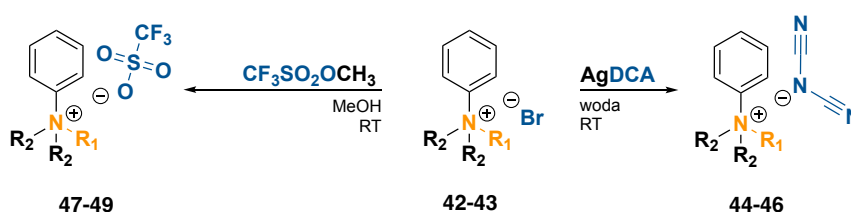


Schemat 2. Schemat otrzymywania pochodnych urotropiny opisywanych w pracy [A2].

Urotropina pozwala w łatwy sposób otrzymać bardzo zaawansowane struktury soli czwartorzędowych, jednakże związki te mają jedną zasadniczą właściwość. Czwartorzędowe sole urotropiny należą do związków o niskiej stabilności termicznej. Dzieje się tak prawdopodobnie dlatego, że zmiana jej uporządkowanego i symetrycznego układu wiązań poprzez wprowadzenie łańcucha alkilowego, powoduje destabilizację struktury. Ta właściwość sprawia, że czwartorzędowe sole halogenkowe urotropiny ulegają rozpadowi przeciętnie w przedziale około $120\text{--}160^\circ\text{C}$ [87] i jest to uzależnione od stopnia rozbudowania struktury. Niektóre, co bardziej rozbudowane ugrupowania, przesuwają temperaturę dekompozycji nawet w okolice 100°C , a najprostsze łańcuchy alkilowe, przyłączone do atomu azotu urotropiny zwykle rozpadają się poniżej 200°C [87–90]. Ta cecha urotropiny jest jeszcze bardziej uwidoczniła w przypadku jej soli, które są płynne w temperaturze pokojowej lub przeciwnie względem kationu pochodzi od silnego kwasu, który katalizuje jej rozpad. W praktyce, destabilizacja struktury objawia się stopniową zmianą koloru związku w stronę intensywnie czerwonego lub pomarańczowego, oraz wydzielaniem silnego, drażniącego zapachu amoniaku. Również w przypadku tej grupy związków dokonano charakterystyki spektroskopowej i analizy

czystości z użyciem chromatografii jonowej, a szczegółowe wyniki zestawione są w pracy [A2]. Z uwagi na niską stabilność otrzymanych związków, ich dalsze badania z żywicami epoksydowymi prowadzono w układach z glikolem etylenowym, który w literaturze opisywany jest jako związek zwiększający stabilność cieczy jonowych poprzez tworzenie układów pseudoeutektycznych [91].

Trzecią grupę otrzymanych cieczy jonowych, opisanych w pracy [A3], stanowią pochodne dimetyloaniliny oraz dietyloaniliny. Wybór tej grupy prekursorów był determinowany przez kilka czynników: (i) znane właściwości aniliny oraz jej pochodnych jako czynników utwardzających żywice różnego typu, w tym winylowe czy epoksydowe [92–94], (ii) zdolność pochodnych aniliny do tworzenia struktur polimerowych [95,96] oraz (iii) nieliczne doniesienia literaturowe dotyczące tego typu cieczy jonowych oraz ogólnie czwartorzędowych soli amoniowych zawierających grupę fenyłową. W pierwszym etapie syntezy otrzymano sole bromkowe pochodnych dimetylo- i dietyloaniliny, uzyskując trzy związki chemiczne zawierające w strukturze kationu kolejno: (i) trzy grupy metylowe oraz grupę fenyłową, (ii) trzy grupy etylowe oraz grupę fenyłową oraz (iii) dwie grupy metylowe, grupę fenyłową oraz grupę benzylową. Następnie, pochodne poddano reakcji metatezy w celu wymiany anionu bromkowego na anion dicyjanoamidowy oraz anion trifluorometanosulfonowy, wykorzystując znane w literaturze metody syntezy [97,98]. Drogę syntezy przedstawiono na Schemacie 3.



Schemat 3. Schemat otrzymywania pochodnych aniliny w pracy [A3].

Otrzymane pochodne 42 – 49 zostały scharakteryzowane metodami spektroskopowymi, a także określono ich czystość z użyciem chromatografii jonowej. Wyniki analiz otrzymane dla poszczególnych substancji zawarto w pracy [A3].

Przedstawiona w niniejszym podrozdziale metoda syntezy cieczy jonowych z anionem dicyjanoamidowym, wykorzystująca sole srebra, jest szeroko opisywana w literaturze. Jednakże z punktu widzenia opłacalności ekonomicznej może stanowić wyzwanie dla komercjalizacji wyników w proponowanym obszarze zastosowania. W opisywanych pracach wykorzystano ją między innymi z uwagi na selektywność, szybkość i możliwość otrzymania produktów o wysokiej czystości, ale jednocześnie rozpoczęto prace nad optymalizacją syntezy tej grupy związków. Obecnie na ukończeniu są badania własne nad wykorzystaniem żywic jonowymiennych do syntezy dicyjanoamidowych cieczy jonowych. Ta metoda charakteryzuje się wysoką wydajnością, jest tania oraz przyjazna środowisku i pozwala na otrzymanie ILs o czystości powyżej 90%, która w proponowanej aplikacji powinna być wystarczająca.

4.3. MIESZANINY CIECZY JONOWYCH

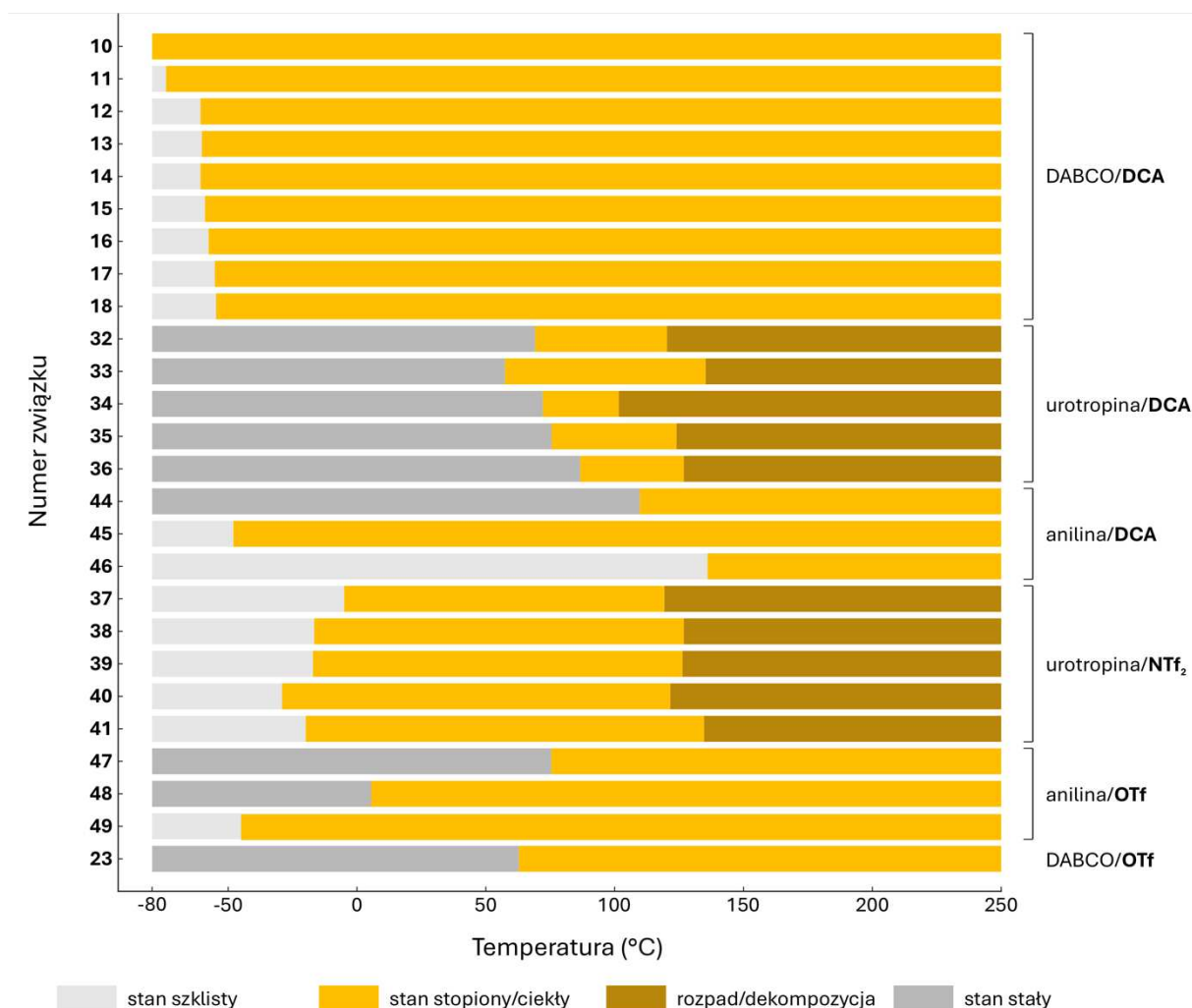
Prace [A4] oraz [A5] skupiały się już nie tylko na badaniu poszczególnych cieczy jonowych, ale także na opracowaniu mieszanin ILs, które będą poza inicjowaniem utwardzania żywicy epoksydowej, nadawać materiałom dodatkowych cech, wpływając na właściwości mechaniczne struktur kompozytowych. W ramach tych prac, część cieczy jonowych została otrzymana na drodze reakcji Menshutkina (związek 51) jak również dwuetapowo, gdzie po I Etapie otrzymywania soli halogenkowej, przeprowadzono metatezę, prowadzącą do ostatecznej struktury cieczy jonowej (związek 50 i 52). W celu otrzymania tych związków zastosowano analogiczne metody syntetyczne jak opisane powyżej, a szczegółowe dane dotyczące procesu syntezy jak i właściwości otrzymanych substancji zawarto w pracach [A4] oraz [A5].

Składy poszczególnych mieszanin zostaną przedstawione w kolejnych rozdziałach, a ich wytworzenie polegało na doborze optymalnych stosunków poszczególnych składników mieszaniny, uwzględniając pożądaną funkcję w kompozycie oraz zachowując optymalne właściwości inicjowania procesu utwardzania. Proces przygotowywania mieszanin prowadzono w podwyższonej temperaturze, a szczegółowy opis zawarto w odpowiednich pracach z cyklu publikacji.

4.4. WŁAŚCIWOŚCI TERMICZNE

Wszystkie otrzymane związki scharakteryzowano także pod kątem ich właściwości termicznych, wykorzystując w tym celu między innymi skaningową kalorymetrię różnicową. Wyniki otrzymane dla wybranych, najważniejszych w świetle badań opisywanych w niniejszej rozprawie związków chemicznych, przedstawiono na wykresie. Graficzne przedstawienie danych liczbowych zebranych w pracach [A1], [A2] oraz [A3] znajdujące się na Rysunku 10, pozwala przeanalizować jak w przypadku poszczególnych pochodnych dochodzi do przemian fazowych oraz w jakich zakresach temperatur występują one w stanie ciekłym lub szklistym. Warto zaznaczyć, że dla pochodnych urotropiny zaznaczono także wartości temperatur powyżej których ta grupa związków ulega dekompozycji. Największym zakresem fazy ciekłej charakteryzują się pochodne DABCO, dla których podczas badań DSC zidentyfikowano jedynie temperatury zeszklenia. Znaczna większość badanych związków zachowała stabilność termiczną w warunkach analizy, która była prowadzona od -80°C do 250°C.

Zebrane podczas analiz wyniki, pozwalają scharakteryzować otrzymane substancję poprzez określenie zakresów temperatury, w których występują one w danym stanie skupienia. Dla obszernej grupy związków badanej w ramach pracy [A1], których rdzeń kationu stanowi DABCO, zaobserwowano występowanie dużego zakresu temperatur fazy ciekłej oraz przejście fazowe w stan szklisty w niskich temperaturach. Taka właściwość sugeruje duże predyspozycje wykorzystania otrzymanych związków w różnych domenach aplikacyjnych, w których wymagane jest zachowanie stabilności termicznej oraz szeroki zakres występowania w stanie płynnym.



Rysunek 10. Zakres temperatur przemian termicznych dla wybranych, otrzymanych w cyklu publikacji, cieczy jonowych.

Ciecze jonowe, będące pochodnymi urotropiny, opisywane w pracy [A2], zawierające w swojej strukturze przeciwjon [DCA], wykazują bardzo niewielkie okno występowania w stanie ciekłym, po którym następuje dekompozycja związków, co jest zjawiskiem spodziewanym, w odniesieniu do obecnego stanu wiedzy i doniesień literaturowych. Co ciekawe, wymiana anionu [DCA] na anion [NTf₂] zwiększa zakres temperatur fazy ciekłej, zachowując zbliżoną wartość górnej granicy temperatury, po której następuje dekompozycja.

PROCES UTWAR- DZANIA ŻYWICY EPOKSY- DOWEJ/

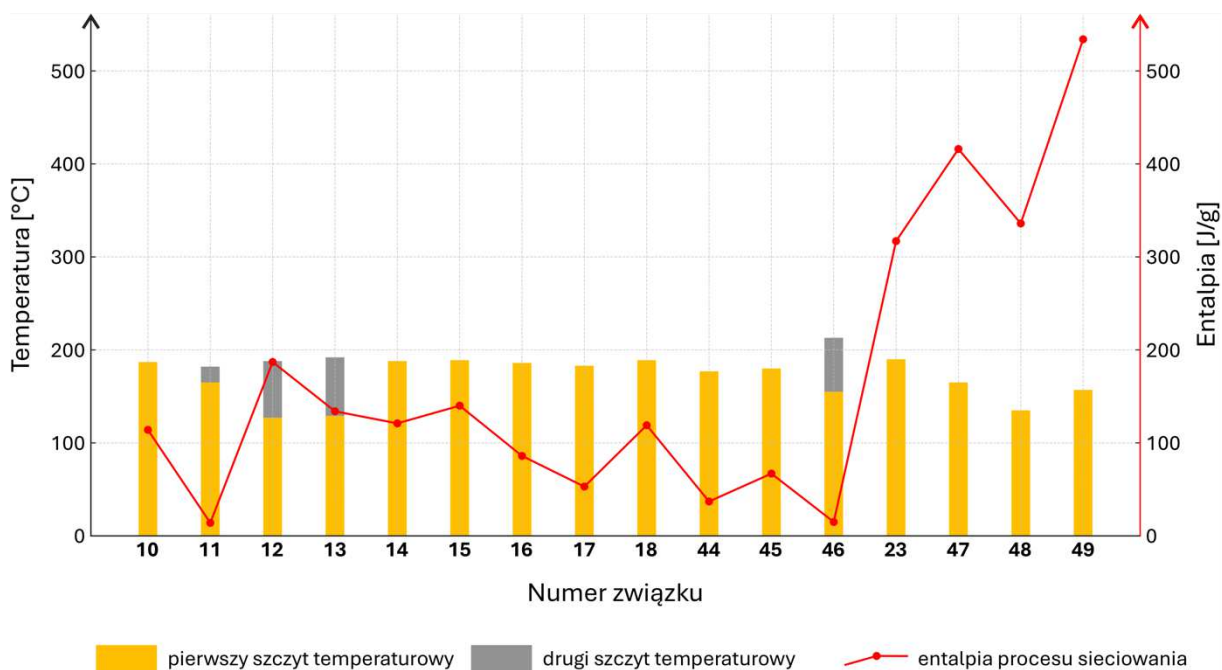
We wszystkich badaniach naukowych, przedstawionych w cyklu publikacji, analizowano proces utwardzania żywicy epoksydowej z zastosowaniem cieczy jonowych. Badania te przeprowadzono przy użyciu skaningowej kalorymetrii różnicowej, każdorazowo określając temperatury charakterystyczne dla procesu: (i) początku polimeryzacji, (ii) szczytu temperaturowego, oraz (iii) końca polimeryzacji. Szczyt temperatury procesu stanowi kluczowy moment, w którym reakcja utwardzania osiąga maksymalną intensywność, wyrażającą się najwyższą wartością temperatury oraz wydzielaną energią. Parametr ten ma istotne znaczenie z technologicznego punktu widzenia, gdyż przekroczenie tej granicznej temperatury, wynikające z nadmiernego dostarczenia ciepła, może prowadzić do niepożądanych efektów, takich jak przegrzanie mieszaniny żywicznej, niekontrolowana reakcja polimeryzacji, a nawet samozapłon. Z tego względu, precyzyjne monitorowanie temperatury jest niezbędne dla zapewnienia

bezpieczeństwa podczas pracy z żywicami epoksydowymi, zwłaszcza w kontekście zastosowania specjalistycznej infrastruktury, takiej jak autoklawy próżniowe. Uzupełnieniem charakterystyki temperaturowej procesu jest pomiar całkowitej entalpii, która stanowi miarę energii wydzielonej przez układ w trakcie sieciowania, wyrażoną w J/g. Ponadto, zastosowanie metody dwóch cykli temperaturowych umożliwiło wyznaczenie zakresu temperatury zeszklenia dla utwardzonej żywicy epoksydowej. W niniejszym

rozdziale skupiono się głównie na podstawowej charakterystyce procesu utwardzania, obejmującej temperaturę szczytu termicznego oraz entalpię, jednakże szczegółowe dane są dostępne w pracach [A1] – [A7].

5.1. CIECZE JONOWE

Badania opisane w publikacjach [A1] oraz [A3] koncentrowały się głównie na charakterystyce procesu sieciowania. Na Rysunku 11 przedstawiono wartości szczytu termicznego oraz entalpii procesu dla analizowanych substancji. Wartość drugiego pików termicznego, jeśli wystąpił w danej próbce, zaznaczono kolorem szarym. Dla większości cieczy jonowych, zawierających kationy o rdzeniu DABCO lub pochodnej aniliny oraz anion [DCA], obserwowano stabilne wartości szczytu temperaturowego na poziomie 180–200°C. Jednocześnie zauważono tendencję do obniżania się entalpii procesu sieciowania wraz ze wzrostem długości łańcucha alkilowego w kationie IL, lub w zależności od rodzaju rdzenia. W przypadku zamiany anionu na anion [OTf], zaobserwowano znaczący wzrost entalpii procesu oraz niższe wartości szczytu temperaturowego. Związki oznaczone numerami od 10 do 18 oraz 23, badano w układach z żywicą epoksydową EnviPOXY® 530 i ilości 4 phr, natomiast związki od 44 do 49, w układach z żywicą Epidian 53, w ilości 2 phr.



Rysunek 11. Wykres wartości szczytu temperaturowego oraz entalpii dla układów badanych w pracy [A1] oraz [A3].

Zależność właściwości sieciujących od temperatury rozpadu cieczy jonowej

Pierwsze badania prowadzone nad zastosowaniem ILs jako inicjatorów utwardzania żywicy epoksydowej zakładały bezpośrednią korelację pomiędzy

temperaturą rozpadu cieczy jonowej, a temperaturą utwardzania. Zakładano, że ciecz musi ulec rozpadowi, np. dealkilacji, aby powstały rodniki zdolne do wchodzenia w reakcję z żywicą epoksydową. Takie podejście miało otworzyć drogę do wyboru optymalnego inicjatora w postaci IL na podstawie danych, dotyczących stabilności temperaturowej cieczy jonowych.

W pracy [A3] charakterystykę otrzymanych związków uzupełniono o analizę termogravimetryczną (TGA), aby podczas ewaluacji wyników z procesu utwardzania, odnieść je do temperatury rozpadu cieczy jonowych. Zebrane w Tabeli 3 dane, dotyczące analizy TGA oraz temperatury początku polimeryzacji, ukazują jednak brak jednoznacznej korelacji między tymi wartościami. Analogiczne obserwacje można dostrzec także podczas odnoszenia wartości stabilności termicznej TGA np. dicyjanoamidu lub octanu 1-etylo-3-metyloimidazoliowego do parametrów procesów sieciowania żywicy epoksydowej przez te związki. Prawdopodobnie dzieje się tak, ze względu na różną stabilność ILs w zależności od matrycy, w której się znajdują, i tak czysta ciecz jonowa wykazująca dużą stabilność termiczną, może w układzie z żywicą epoksydową ulegać rozpadowi znacznie szybciej i w niższych wartościach temperatury.

Tabela 3. Wartości danych stabilności termicznej dla związków opisanych w pracy [A3] z odniesieniem do temperatury początku polimeryzacji epoksydowej inicjowanej przez tą grupę substancji.

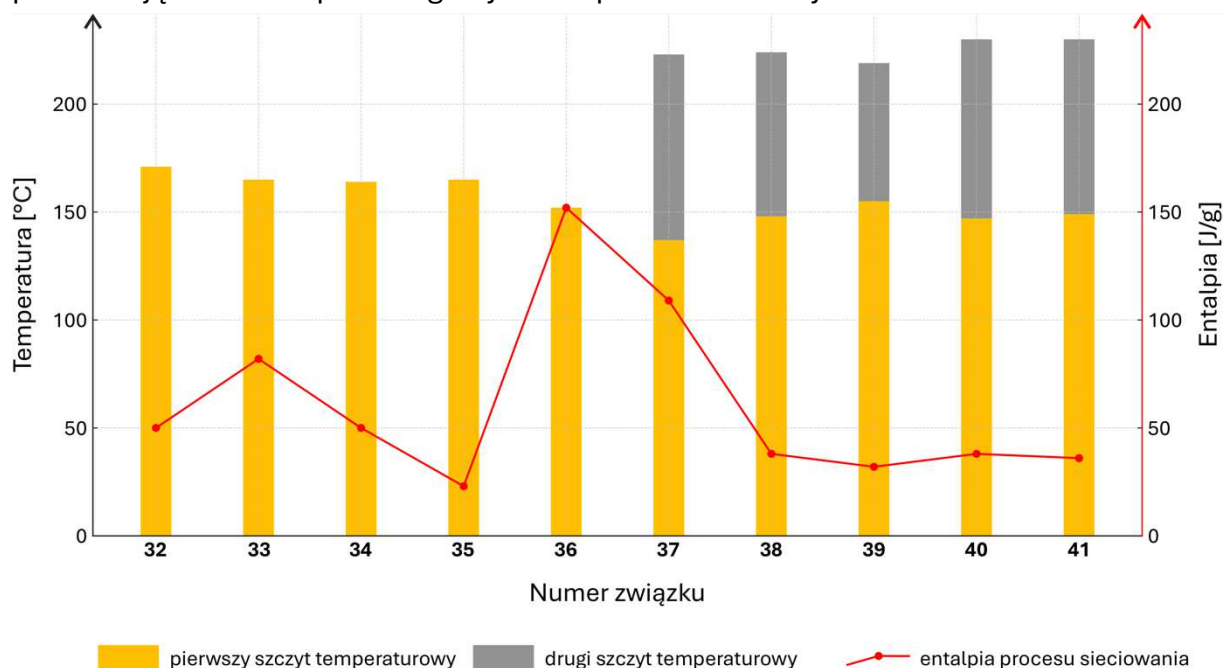
IL [numer związku]	$T_{5\%}^a$ [°C]	$T_{50\%}^b$ [°C]	T_{onset}^c [°C]
44	376	440	143
45	376	443	147
46	356	439	136
47	293	369	151
48	255	352	114
49	254	362	123

$^aT_{5\%}$ – temperatura odpowiadająca 5% utraty masy próbki, $^bT_{50\%}$ – temperatura odpowiadająca 50% utraty masy próbki, $^cT_{onset}$ – temperatura początku polimeryzacji.

5.2. CIECZE JONOWE STABILIZOWANE GLIKOLEM ETYLENOWYM

Związki oznaczone numerami od 32 do 41 badano w układach z modelową cząsteczką eteru diglicydylowego bisfenolu A, w ilości 4 phr. Graficzne przedstawienie wartości szczytu temperaturowego oraz entalpii procesu na Rysunku 12 wskazuje na zachodzenie dwóch szlaków polimeryzacji dla związków zawierających anion $[NTf_2]$, przy czym dla pierwszego szczytu obserwuje się stabilne wartości na poziomie 150 – 170°C. Należy w przypadku tej grupy związków wskazać na obniżenie wartości entalpii dla związków z anionem $[NTf_2]$ wraz ze wzrostem długości łańcucha alkilowego w kationie, powyżej dwóch atomów węgla. Co więcej, w odniesieniu do wcześniej omawianych związków, w pracy [A2] wykazano, że niska stabilność cieczy jonowych na bazie

urotropiny, może korzystnie wpływać na obniżenie parametrów utwardzania żywicy, przesuwając wartości poszczególnych temperatur ku niższym wartościom.



Rysunek 12. Wykres przedstawiający wartości szczytu termicznego oraz entalpii procesu utwardzania dla mieszanin badanych w pracy [A2].

5.3. MIESZANINY CIECZY JONOWYCH

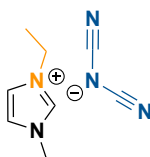
W badaniach opisanych w pracach [A4] oraz [A5] skupiono się na analizie mieszanin cieczy jonowych, od których oczekiwano pełnienia większej liczby funkcji w kompozycie niż jedynie inicjowanie procesu utwardzania. Zaprojektowane układy cieczy jonowych miały na celu poprawę właściwości mechanicznych kompozytów, jak to omówiono w pracach [A4] oraz [A5], oraz redukcję palności tych materiałów, co szczegółowo opisano w pracy [A4]. Realizacja tych celów była możliwa dzięki wprowadzeniu określonych cech do cieczy jonowych, takich jak:

- / długie łańcuchy alkilowe wpływające na właściwości mechaniczne struktur kompozytowych;
- / wprowadzenie fosfoniowych cieczy jonowych w połączeniu z długimi łańcuchami alkilowymi, wpływających na właściwości mechaniczne oraz obniżenie palności struktur kompozytowych;
- / wprowadzenie cieczy jonowych zawierających atom krzemu, jako wpływających na obniżenie palności struktur kompozytowych.

W pracy [A4] opracowano mieszaniny na bazie cieczy jonowej, dicyjanoamidu 1-etylo-3-metyloimidazoliowego, znanej z literatury jako związek o dobrze poznanych właściwościach sieciowania. W pierwszym etapie, ta IL została zastosowana do stworzenia układu żywica epoksydowa:ciecz jonowa, a następnie, do tego układu dodano mieszaniny cieczy jonowych o właściwościach modyfikujących, wprowadzając związki

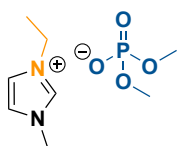
54–58, które, jak pokazano na Rysunku 13, mogą działać jako donory fosforu, oraz ciecz jonową 51, pełniącą rolę donora krzemu. Proporcje poszczególnych składników są przedstawione w Tabeli 4. Z kolei w pracy [A5] badano dwie mieszaniny, składające się z związków 14, 50 oraz 52. Punktem odniesienia dla analiz mieszanin w pracy [A4] była próbka zawierająca wyłącznie związek 53, natomiast w pracy [A5] analizowano próbki zawierające poszczególne ILs wchodzące w skład mieszanin.

Ciecz jonowa o właściwościach utwardzających

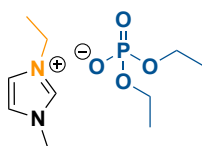


53

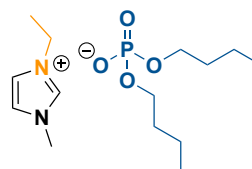
Imidazoliowe ciecze jonowe zawierające atomy fosforu w anionie



54

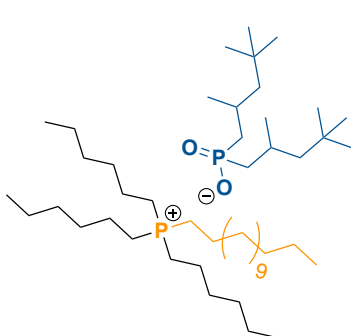


55

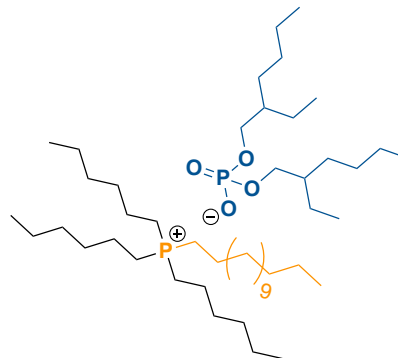


56

Fosfoniowe ciecze jonowe z długimi łańcuchami



57



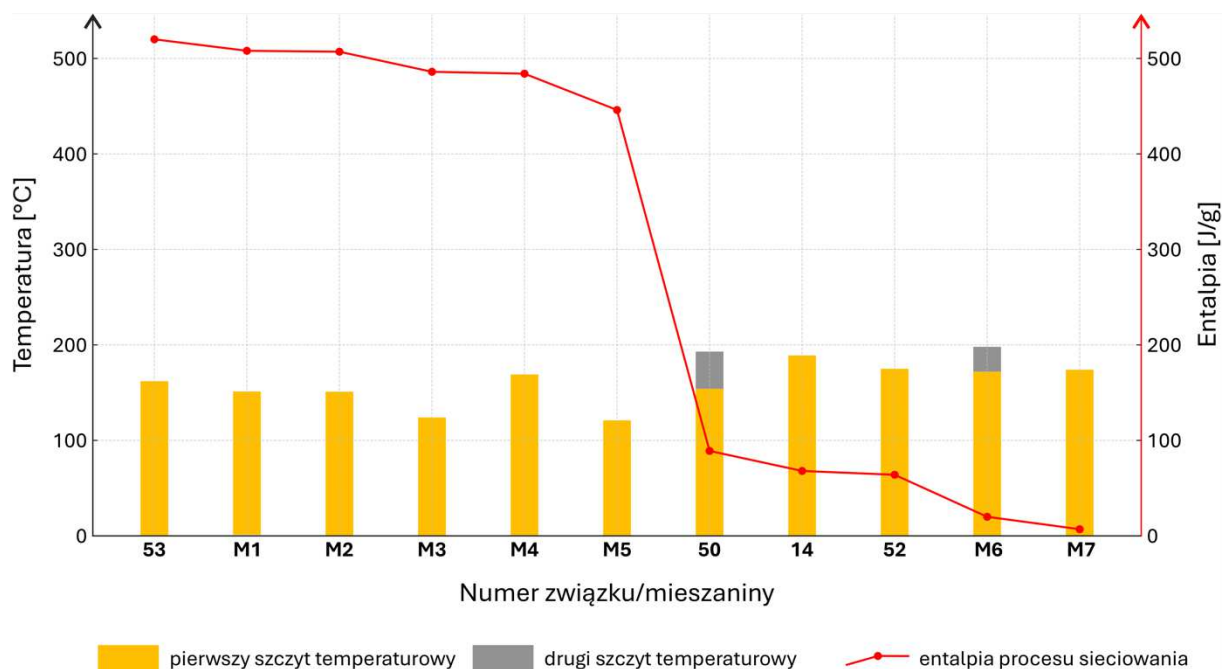
58

Rysunek 13. Struktury cieczy jonowych wykorzystanych do wytworzenia mieszanin badanych w pracy [A4].

Tabela 4. Skład molowy i jakościowy poszczególnych, badanych w pracach [A4] oraz [A5] mieszanin cieczy jonowych.

Mieszanina	Publikacja	Składniki	Stosunek molowy
		[numery związków]	[mol:mol]
M1	[A4]	54:51	1:1
M2		55:51	
M3		56:51	
M4		57:51	
M5		58:51	
M6	[A5]	50:14	2:1
M7		50:14:52	3:2:1

Tak jak wspomniano, proces inicjowania sieciowania badano przy użyciu techniki DSC, koncentrując się głównie na wpływie mieszanin modyfikujących na temperatury procesu oraz entalpię. W próbkach opisanych w pracy [A4] użyto żywicy epoksydowej EnviPOXY® 525, dodając 2 phr cieczy jonowej 53 oraz 11 phr mieszaniny modyfikującej. Natomiast w pracy [A5] zastosowano mieszaninę modyfikująco-utwardzającą w ilości 4 phr. Graficzne przedstawienie zależności szczytu termicznego oraz entalpii dla poszczególnych próbek zaprezentowano na Rysunku 14. Stwierdzono, że aby utrzymać odpowiednie parametry sieciowania żywicy, korzystniejsze jest wprowadzenie cieczy jonowej odpowiedzialnej za inicjowanie procesu w pierwszym etapie, a dopiero potem dodanie układu modyfikującego. Wyniki dla mieszanin M1-M5 wskazują na utrzymanie wysokiej wartości entalpii procesu utwardzania, podczas gdy dla mieszanin M6 i M7 wartość ta ulega obniżeniu. Należy jednak uwzględnić aktywność składników mieszanin M6 i M7 jako inicjatorów sieciowania, w porównaniu do związku 53, który jest jednym z najlepszych utwardzaczy na bazie cieczy jonowych znanych w literaturze. Badania ilustrują ciekawy przykład wpływu użytej żywicy epoksydowej na właściwości cieczy jonowej jako inicjatora sieciowania. Związek 14, zastosowany w pracy [A1] z żywicą epoksydową EnviPOXY® 530 w ilości 4 phr, wykazywał szczyt termiczny na poziomie 188°C oraz analogicznie w pracy [A5] z żywicą LH 289 w tej samej ilości, osiągnął 189°C, jednocześnie notując spadek wartości entalpii procesu z 121 J/g w pracy [A1] do 68 J/g w pracy [A5].



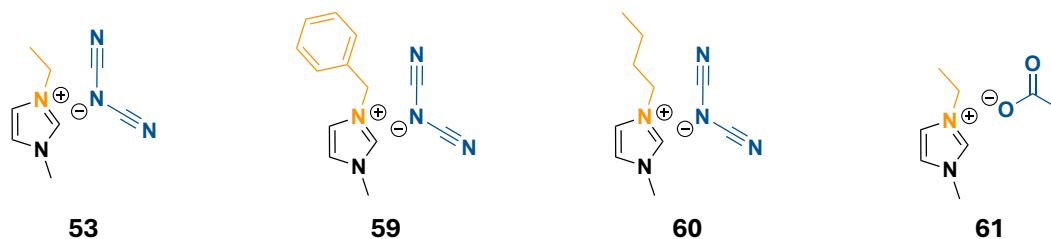
Rysunek 14. Wykres przedstawiający wartości szczytu termicznego oraz entalpii procesu utwardzania dla mieszanin badanych w pracach [A4] oraz [A5] oraz związków odniesienia.

5.4. UKŁADY ZAWIERAJĄCE WYPEŁNIENIE

Kolejnym podejściem do osiągnięcia wielofunkcyjności cieczy jonowych w układach z żywicami epoksydowymi były badania opisane w pracach [A6] oraz [A7], które skupiły się na połączeniu funkcji utwardzacza z funkcją nośnika wypełnienia do kompozytu. Wybrano dwa niezależne podejścia do realizacji tego celu:

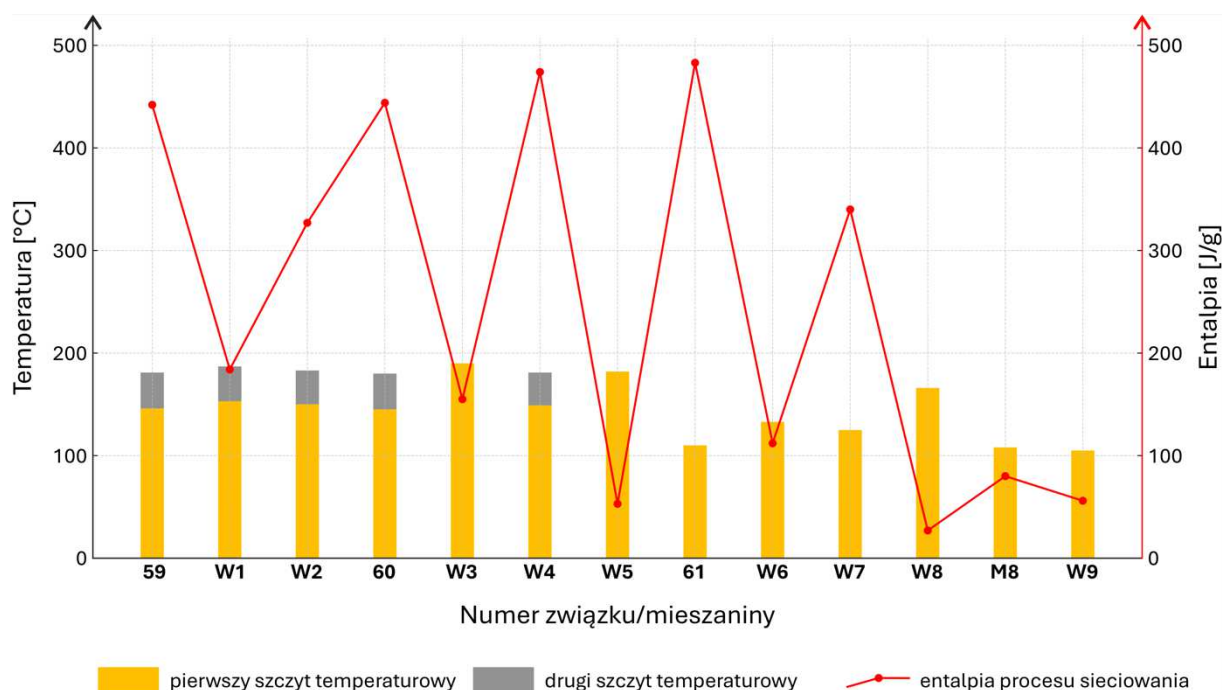
- / wykorzystanie materiałów typu SILP (ang. *Supported Ionic Liquid Phase*) jako sposobu wprowadzenia do kompozytu wypełnienia krzemionkowego;
- / wykorzystanie zjawiska rozpuszczania celulozy w cieczach jonowych jako sposobu wprowadzenia do kompozytu wypełnienia celulozowego.

W pracy [A6] wytworzono szereg materiałów typu SILP na bazie trzech krzemionek, różniących się wielkością porów oraz trzech ILs, których struktury przedstawiono na Rysunku 15, w kilku stężeniach. Materiały SILP wykorzystano do wytworzenia układów z żywicą epoksydową EnviPOXY® 530 w stężeniu 3 phr. Z kolei w pracy [A7] wykorzystano wcześniej przebadaną mieszaninę rozpuszczającą celulozę, w której zmieniono jedną z cieczy jonowych na bardziej aktywną jako inicjator utwardzania żywicy epoksydowej, zachowując w mieszaninie dimetylosulfotlenek (DMSO) jako substancję zmniejszającą lepkość mieszaniny ILs. Struktury wykorzystanych cieczy przedstawiono na Rysunku 15. Po wytworzeniu mieszaniny, rozpuszczono w niej celulozę mikrokryształiczną w ilości 5% wagowych, a następnie wykorzystano do przygotowania układów z żywicą epoksydową LH 301, w stężeniu 4 phr.



Rysunek 15. Struktury cieczy jonowych wykorzystanych w badaniach przedstawionych w pracach [A6] oraz [A7].

Na wykresie przedstawiającym wyniki badań DSC wspomnianych układów (Rysunek 16), zestawiono wartości szczytu temperaturowego dla związków odniesienia, czyli w przypadku pracy [A6] cieczy jonowych nieosadzonych na powierzchni krzemionki, oznaczonych numerami: 59 – 61. Natomiast w przypadku pracy [A7], wartością odniesienia jest mieszanina cieczy jonowych z DMSO bez rozpuszczonej w niej celulozy. Mieszanina M8 składała się ze związków 53 oraz 61, jak również DMSO w stosunkach molowych 15:35:50.



Rysunek 16. Wykres przedstawiający wartości szczytu termicznego oraz entalpii procesu utwardzania dla układów badanych w pracach [A6] oraz [A7] oraz związków odniesienia.

Ciecze jonowe 59 oraz 60, niezależnie od użytej do przygotowania na ich bazie materiałów typu SILP krzemionki jak i stężenia, zachowały wartości szczytu temperaturowego na podobnym poziomie, niekiedy wykazując dwa szczyty termiczne, szczególnie w przypadku związku 59. Z kolei w przypadku związku 61, zanotowano wpływ krzemionki na wzrost wartości szczytu temperaturowego, co może sugerować, że

osadzona na powierzchni krzemionki ciecz jonowa zwiększyła swoją stabilność termiczną. Układy W2, W4 oraz W7 powstały z wykorzystaniem krzemionki Davisil Grade 635 i jako jedyne zachowały wysokie wartości entalpii procesu co sugeruje, że to właśnie ten rodzaj krzemionki pozwala osiągnąć wysoką jakość procesu utwardzania, przy jednoczesnym skutecznym wprowadzeniu do układu wypełnienia. Natomiast opisana w pracy [A7] mieszanina, zawierająca celulozę, utrzymała w badaniach DSC zbliżoną wartość szczytu temperaturowego co próbka odniesienia, notując nieznaczny spadek wartości entalpii procesu.

WŁAŚCI- WOŚCI STRUKTUR KOMPOZY- TOWYCH/

Badania opisane w pracach [A1] – [A7] obejmują szerokie spektrum analizowanych właściwości otrzymanych materiałów. W zależności od specyficznego celu każdego artykułu, wybierano różnorodne metody badawcze, aby dokładnie scharakteryzować otrzymane materiały i struktury. W pracach [A1] i [A2] skupiono się głównie na procesie utwardzania żywicy epoksydowej, nie wytwarzając dalszych struktur kompozytowych. W tych badaniach szczególną uwagę poświęcono ocenie twardości usieciowanej żywicy jako podstawowego parametru właściwości materiału.

Pozostałe prace [A3] – [A7] zawierają również etap wytwarzania materiałów kompozytowych, które wzmacniano różnymi typami włókien: (i) włóknem węglowym, (ii) włóknem lnianym, oraz (iii) kombinacją

włókien węglowych lub lnianych z dodatkiem wypełniaczy na bazie krzemionki lub celulozy. W zależności od oczekiwanych efektów modyfikacji, dobrano różnorodne techniki badawcze, które pozwoliły na uzyskanie jak najbardziej kompletnych danych o właściwościach materiałów badanych w poszczególnych pracach. Szczegółowe informacje o przeprowadzonych badaniach oraz metodach badawczych zostały zebrane i przedstawione w Tabeli 5.

Tabela 5. Techniki badań właściwości materiałów otrzymanych w pracach [A1] - [A7].

Praca	Obszar badań	Struktury kompozytowe	Techniki badawcze
[A1]	ciecze jonowe	nie	/ twardość Shore’a (PN-EN ISO 868:2005)
[A2]	ciecze jonowe z glikolem etylenowym	nie	/ twardość Shore’a (PN-EN ISO 868:2005)
[A3]	ciecze jonowe	wzmacniane włóknem lnianym (180g/m ² , UD)	/ wytrzymałość na rozciąganie
[A4]	mieszaniny cieczy jonowych	wzmacniane włóknem węglowym (600g/m ² , 2×2)	/ dynamiczna analiza mechaniczna (DMA, ang. <i>dynamic mechanical analysis</i>) / badania palności UL-94 (ASTM D3081 oraz ASTM D635) LOI ^a (ASTM D2863) MLC ^b (ISO 13927)
[A5]	mieszaniny cieczy jonowych	wzmacniane włóknem lnianym (200g/m ² , 2×2)	/ wytrzymałość na rozciąganie (EN ISO 527-4) / wytrzymałość na zginanie (EN ISO 178) / dynamiczna analiza mechaniczna / temperatura ugięcia pod obciążeniem (HDT, ang. <i>heat deflection temperature</i>) (PN-EN ISO 75-2)
[A6]	materiały typu SILP oraz ciecze jonowe jako odniesienie	wzmacniane włóknem lnianym (180g/m ² , UD) wzmacniane włóknem węglowym (200g/m ² , 2×2)	/ wytrzymałość na rozciąganie
[A7]	mieszanina cieczy jonowych z DMSO z	wzmacniane włóknem lnianym (200g/m ² , 2×2)	/ dynamiczna analiza mechaniczna

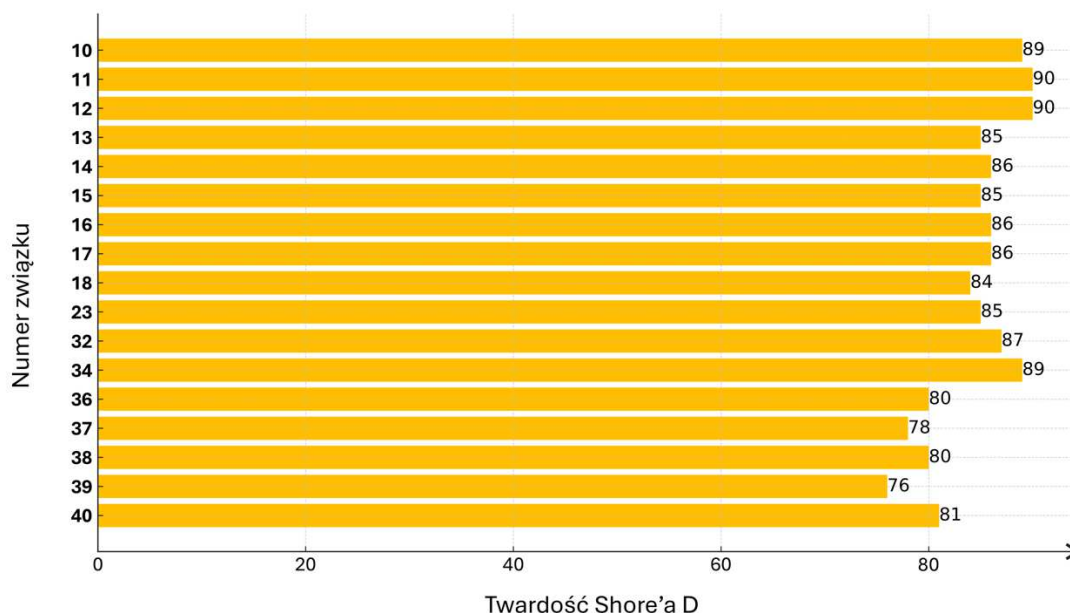
rozpuszczoną
celulozą oraz
mieszanina bez
celulozy jako
odniesienie

/ temperatura ugięcia pod
obciążeniem
(PN-EN ISO 75-2)
/ temperatura mięknięcia
metodą Vicat'a
(PN-EN ISO 306, A120)
/ udarność metodą
Charpy'ego
(PN-EN ISO 179-1)

^a LOI – ograniczony indeks tlenowy (ang. *Limiting Oxygen Index*), ^b MLC – kalorymetria stożkowa utraty masy (ang. *Mass Loss Cone test lub Mass Loss Calorimetry*).

6.1. CIECZE JONOWE

W pracach [A1] oraz [A2] nie wytwarzano struktur kompozytowych wzmacnianych włóknami, więc za parametr różnicujący poszczególne utwardzone układy żywiczne wybrano twardość Shore'a w skali D. Na Rysunku 17 przedstawiono wyniki dla poszczególnych ILs. W pracy [A1], użyto systemów utwardzania opartych na DABCO z różnymi długościami łańcuchów alkilowych. Wyniki wskazują, że twardość materiałów utwardzanych wzrosła średnio o 20% w porównaniu do materiałów referencyjnych (żywica utwardzana standardowym utwardzaczem na bazie trietylenotetraaminy, 79D), osiągając najwyższe wartości przy krótszych łańcuchach alkilowych, takich jak 90D dla łańcucha propylowego i butylowego w związkach 11 oraz 12.



Rysunek 17. Wykres przedstawiający twardość w skali Shore'a D dla utwardzonej cieczami jonowymi żywicy epoksydowej.

W drugiej pracy, [A2], przeanalizowano twardość żywic epoksydowych utwardzanych ILs na bazie urotropiny z różnymi anionami. Wyniki wskazują, że systemy z anionami [DCA] osiągnęły wyższe wartości twardości (średnio 85D) w porównaniu do systemów z anionami [NTf₂] (średnio 79D). Ponadto, zauważono, że wydłużenie łańcucha alkilowego w strukturze kationu zwiększało kruchość materiału, co w niektórych przypadkach uniemożliwiało pomiar twardości.

W pracy [A3] otrzymane struktury kompozytowe wzmacniane włóknem lnianym poddano badaniu pod kątem wytrzymałości na statyczne rozciąganie, którego wyniki zebrano i przedstawiono w Tabeli 6. Ciekawe wyniki uzyskano dla powłok epoksydowych utwardzanych ILs z anionami [OTf], które wykazały znaczącą wytrzymałość na rozciąganie oraz wysoki stopień sieciowania, szczególnie w systemach zawierających związki 47 i 49. Powłoki te charakteryzowały się stopniowym uszkodzaniem struktury pod wpływem obciążeń, co sugeruje obecność dodatkowego wzmocnienia w trakcie utwardzania. Ta obserwacja zainicjowała rozważania nad możliwym powstawianiem małych łańcuchów polianilinowych (PANI) podczas utwardzania. W pracy [A3] zaproponowano wniosek, że pozostałości anilinowe po polimeryzacji żywicy mogą tworzyć krótkie łańcuchy PANI, wpływając na właściwości mechaniczne powłok. Obserwacja nie była widoczna na pochodnych z kationem zawierającym trzy grupy etylowe.

Tabela 6. Wyniki badań wytrzymałości na rozciąganie próbek kompozytów epoksydowych utwardzanych cieczami jonowymi na bazie aniliny.

Numer związku	Stopień nasycenia włókien [%]	Wydłużenie przy zerwaniu [%]	Wytrzymałość na rozciąganie [N/mm ²]	Siła przy zerwaniu [N]	Moduł sprężystości [GPa]	Stopień usieciowania [%]
44	53	1.2	26	246	2.1	55
45	52	1.2	32	324	2.6	69
46	55	1.2	36	453	3.0	78
47	51	1.8	43	432	2.4	93
48	53	0.9	37	466	3.9	80
49	54	1.5	41	526	2.7	88

6.2. MIESZANINY CIECZY JONOWYCH

W pracy [A4] przedmiotem badań był wpływ mieszanin modyfikujących na bazie cieczy jonowych na właściwości epoksydowych struktur kompozytowych wzmacnianych włóknem węglowym. Wyniki analizy z wykorzystaniem DMA, przedstawione w Tabeli 7, dla mieszanin M1 – M5, którym poświęcona była praca [A4], pokazują znaczący wzrost temperatury zeszklenia w porównaniu do materiału referencyjnego (niezawierającego

mieszanin cieczy jonowych), co sugeruje zwiększoną gęstość sieciowania w polimerze. Modyfikacje z użyciem cieczy jonowych, takie jak systemy M1, M2 i M3, wykazały wzrost T_g o prawie 50%, a system M5 wykazał wzrost o 75%. Wykazano, że ciecz jonowa stabilizuje rotację wiązań, co prowadzi do usztywnienia i wzmocnienia materiału. Z kolei dla mieszanin ILs opisanych w pracy [A5] zanotowano dwie wartości temperatur zeszklenia co sugeruje niejednorodność polimeru (M6) lub bardzo niską wartość dla M7, co świadczy o tym, że kompozyt przechodzi w stan bardziej elastyczny w niskich temperaturach, tracąc przez to swoją sztywność i ogranicza to jego praktyczne zastosowanie. Uzupełnieniem badań przy użyciu DMA było w przypadku M6 oraz M7 badanie temperatury ugięcia pod obciążeniem. Wartość HDT dla mieszaniny M6 to 44.6°C, natomiast dla M7 uzyskano założone odkształcenie w temperaturze pokojowej (RT, ang. *Room Temperature*). Wyniki wskazują, że te mieszaniny cieczy jonowych wpłynęły na parametry sztywności struktur kompozytowych w podwyższonej temperaturze, obniżając je. Ogranicza to zastosowanie tych dwóch mieszanin w aplikacjach wymagających stabilności w temperaturze.

Tabela 7. Wyniki badań z użyciem dynamicznej analizy mechanicznej dla mieszanin cieczy jonowych opisywanych w pracach [A4] oraz [A5].

Mieszanina	Temperatura zeszklenia [°C]		Temperatura ugięcia pod obciążeniem HDT [°C]
	Moduł stratności G''	Tan δ	
Referencja	89	94	
M1	109	118	-
M2	114	113	-
M3	110	120	-
M4	71	84	-
M5	127	131	-
M6	51 / 114	59 / 109	44,7
M7	-	40	<RT

Badania wytrzymałości próbek kompozytów utwardzanych mieszaninami M6 oraz M7 w podwyższonej temperaturze, uzupełniono określeniem wytrzymałości przy statycznym rozciąganiu i zginaniu, której wyniki przedstawiono w Tabeli 8. W temperaturze pokojowej, kompozyty z mieszaniną M6 osiągnęły wytrzymałość na zginanie wynoszącą 28,6 MPa, przy umiarkowanej zdolności do deformacji i dużej sztywności (moduł przy zginaniu 1900,0 MPa). Natomiast kompozyty zawierające M7 wykazały znacznie niższą wytrzymałość na zginanie oraz większą zdolność do odkształcania i niższą sztywność. Podobne różnice zaobserwowano w przypadku wytrzymałości na rozciąganie. Kompozyty zawierające mieszaninę M6 wykazały wysoką wytrzymałość na rozciąganie, osiągając 55,0 MPa, oraz charakteryzowały się wysokim modułem Younga (5,9 GPa), co wskazuje na dość dużą sztywność materiału. Wartość wydłużenia przy zerwaniu wyniosła 1,6%, sugerując stosunkowo małą elastyczność. Z kolei kompozyty

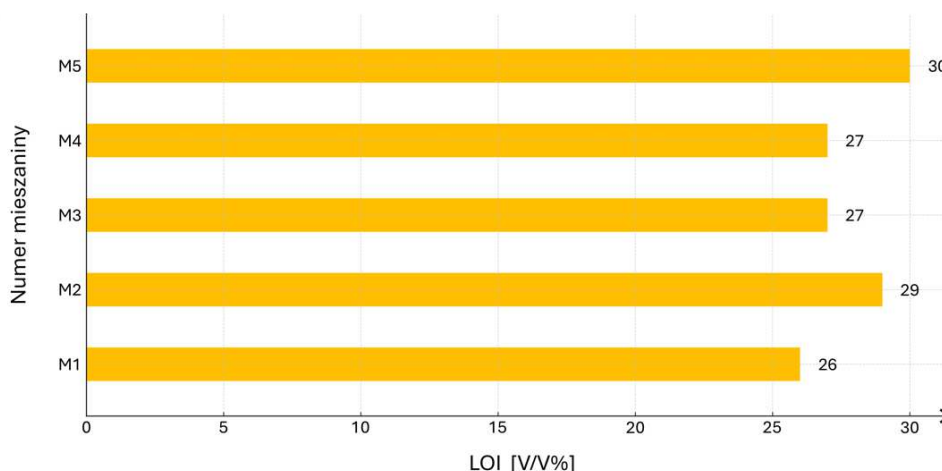
zawierające układ ILs M7 miały niższą wytrzymałość na rozciąganie oraz niższy moduł Younga.

Tabela 8. Wyniki badań wytrzymałości na rozciąganie oraz zginanie kompozytów epoksydowych utwardzanych mieszaninami opisanymi w pracy [A5].

Mieszanina	Wytrzymałość na zginanie [MPa]	Odształcenie przy wytrzymałości [%]	Strzałka ugięcia przy wytrzymałości [mm]	Moduł przy zginaniu (0,05-0,25%) [MPa]
M6	28,6 ± 7,2	5,7 ± 0,6	9,4 ± 0,9	1900,0 ± 422,0
M7	3,2 ± 0,3	6,2 ± 1,5	9,4 ± 2,3	138,0 ± 28,0
	Wytrzymałość na rozciąganie [MPa]	Napężenie przy zerwaniu [MPa]	Wydłużenie przy zerwaniu [%]	Moduł sprężystości (0,05- 0,25%) [GPa]
M6	55,0 ± 1,3	54,9 ± 1,3	1,6 ± 0,1	5,9 ± 0,3
M7	40,4 ± 5,0	39,2 ± 5,7	2,4 ± 0,1	1,7 ± 0,1

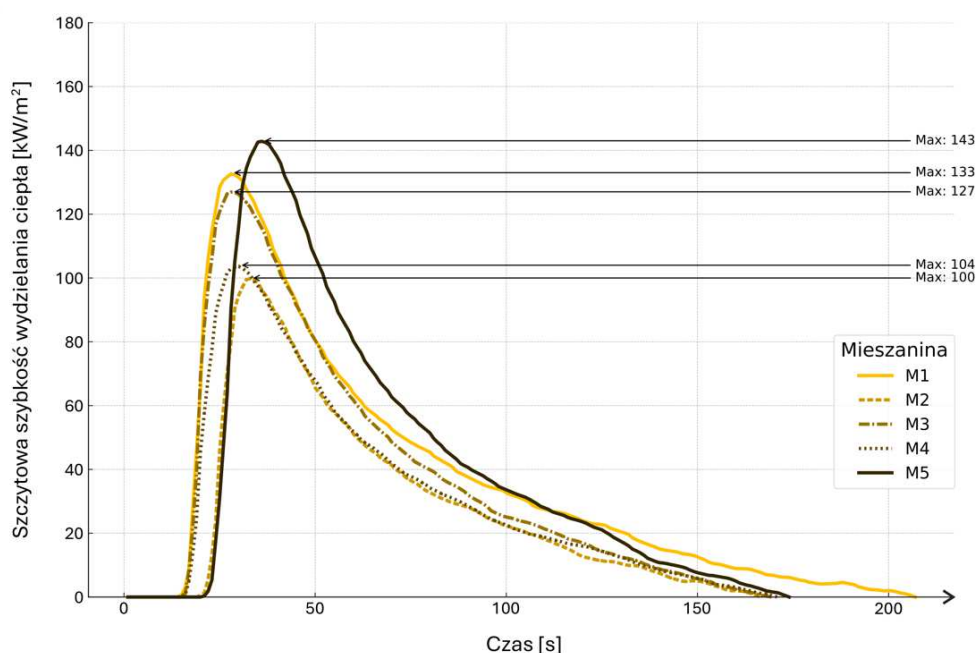
Właściwości uniepalniające

Mieszaniny ILs zastosowane jako modyfikatory systemów żywicznych w pracy [A4] zbadano również pod kątem zdolności zmniejszania palności struktur kompozytowych wzmacnianych włóknem węglowym. W tym celu przeprowadzono szereg analiz, w tym między innymi test UL-94, polegający na określeniu klasy palności materiału oraz wyznaczono indeks tlenowy próbek. Wyniki testu UL-94 wykazały, że żadne z modyfikowanych systemów nie wykazały znaczących właściwości uniepalniających, a wszystkie próbki otrzymały ocenę HB (ang. *Horizontal Burning*), czyli jedną z najniższych klas oceny w skali palności, wskazującą na niską odporność materiałów na rozprzestrzenianie się ognia. Niemniej jednak mieszanina M5 osiągnęła najwyższy indeks tlenowy na poziomie 30% V/V. Wartości LOI dla wszystkich próbek przedstawiono na Rysunku 18.



Rysunek 18. Wykres przedstawiający wyniki pomiaru indeksu tlenowego dla struktur kompozytowych modyfikowanych mieszaninami opisywanymi w pracy [A4]

Bardziej dokładne badanie palności przeprowadzono z użyciem kalorymetrii utraty masy, która pozwala ilościowo scharakteryzować proces spalania danego materiału. Zależność szczytowej szybkości wydzielania ciepła (pHRR, ang. *peak of heat release rate*) od czasu dla mieszanin M1 – M5 przedstawiono na Rysunku 19. Zauważono, że M5 zwiększa pHRR o 34% w porównaniu z próbką referencyjną, przy jednoczesnym przesunięciu czasu osiągnięcia pHRR z 32 do 36 sekund. Z kolei M1 wykazała wzrost pHRR o 24%. Podczas badań nie zaobserwowano znaczącego wpływu systemów modyfikujących na ilość pozostałości po spalaniu. Wyniki wskazują, że mimo pewnych zmian w poszczególnych wartościach, ilość użytych cieczy jonowych oraz całkowita zawartość w nich atomu fosforu i krzemu, nie były wystarczające, aby znacznie opóźnić rozwój ognia.



Rysunek 19. Wykres zależności szczytowej szybkości wydzielania ciepła od czasu dla próbek kompozytów epoksydowych modyfikowanych mieszaninami opisywanymi w pracy [A4].

6.3. UKŁADY ZAWIERAJĄCE WYPEŁNIENIE

Badania wytrzymałości na statyczne rozciąganie przeprowadzone w pracy [A6] dotyczyły zastosowania materiałów typu SILP jako utwardzaczy i wypełniaczy w kompozytach epoksydowych wzmacnianych włóknami węglowymi i lnianymi. Wyniki przeprowadzonych prac zebrano i przedstawiono w Tabeli 9. Każdy układ zawierający materiał typu SILP (W2, W4 i W7) odniesiono do materiału referencyjnego, w którym zastosowano samą ciecz jonową, nienaniesioną na powierzchnię krzemionki. Zaobserwowano tendencję do zmniejszenia wartości wydłużenia próbki w momencie zerwania, wzrostu wartości modułu sprężystości oraz spadku wytrzymałości na rozciąganie w przypadku próbek zawierających materiały SILP. Można wywnioskować, że dodatek krzemionki w kompozycie wpłynął na zwiększenie sztywności i kruchości otrzymanych struktur kompozytowych. Cechą charakterystyczną dla kompozytów wykorzystujących materiały typu SILP jest stochastyczne rozmieszczenie krzemionki na powierzchni materiału co pokazano w pracy [A6] wykorzystując skaningową mikroskopię elektronową (SEM, ang. *Scanning Electron Microscopy*).

Tabela 9. Wyniki badań wytrzymałości na rozciąganie próbek kompozytów epoksydowych wzmacnianych włóknem węglowym oraz lnianymi, opisywanych w pracy [A6].

Numer związku/ próbki	Stopień nasycenia włókien [%]	Wydłużenie przy zerwaniu [%]	Wytrzymałość na rozciąganie [N/mm ²]	Siła przy zerwaniu [N]	Moduł sprężystości [GPa]	Rodzaj wzmocnienia
59	45	1,4	131	1544	9,2	wzmocnienie na bazie włókna węglowego
W2	48	1,0	121	1283	11,9	
60	46	0,9	124	1313	13,3	
W4	45	0,6	97	1183	15,2	
61	47	1,2	143	1428	12,2	
W7	48	0,7	89	1204	12,7	Wzmocnienie na bazie włókna lnianego
59	56	1,5	43	541	2,8	
W2	58	0,7	36	493	5,5	
60	55	1,7	48	556	2,9	
W4	57	0,9	42	557	4,5	
61	58	1,6	39	488	2,4	
W7	59	0,7	36	490	4,9	

Natomiast badania nad wprowadzaniem do układu celulozy poprzez rozpuszczenie jej w mieszaninie cieczy jonowych, zdolnych do jednoczesnego utwardzania żywicy epoksydowej, przyniosły obserwację w postaci zjawiska generowania się celulozy lub też jej rekonstruowania podczas mieszania układu żywica: ciecz jonowa.

Rekonstruowana celuloza różni się morfologicznie od surowca rozpuszczanego uprzednio w mieszaninie ILs co potwierdziły badania SEM, opisane w pracy [A7]. Wykazano, że w trakcie mieszania z żywicą epoksydową dochodzi do *in situ* generowania włókien celulozy. Włókna te mają dużą długość i są równomiernie rozproszone w matrycy żywicy, co zapewnia wysoką kompatybilność bez defektów takich jak pęcherzyki powietrza czy cząsteczki wody. Obecność tych włókien wpływa na właściwości mechaniczne kompozytów, które zebrano i przedstawiono w Tabeli 10. Znotowano między innymi wzrost HDT do poziomu prawie 61°C, podczas gdy dla samej mieszaniny ILs, struktura osiągnęła zadane odkształcenie w temperaturze pokojowej. Co więcej, celuloza spowodowała znaczący wzrost temperatury mięknienia, co oznacza, że w praktyce, materiał może być używany w bardziej wymagających warunkach termicznych bez utraty swoich właściwości mechanicznych. Jednocześnie materiały te były bardziej kruche co potwierdza się w wynikach udarności.

Tabela 10. Wyniki badań wytrzymałościowych struktur kompozytowych utwardzanych mieszaniną cieczy jonowych z oraz bez rozpuszczonej celulozy.

Układ	Temperatura zeszklenia [°C]			Temperatura ugięcia pod obciążeniem [°C]	Temperatura mięknienia metodą Vicat'a [°C]	Udarność Charpy'ego [kJ/m ²]
	Moduł stratności G''	Tan δ	Moduł zachowawczy G'			
M8	51	42	58	<RT	59,7 ± 1,6	40,4 ± 3,6
W9	61	79	99	60,9 ± 1,7	219,7 ± 1,4	20,5 ± 3,2

WNIOSKI I PODSU- MOWANIE/

Rozdział ten podsumowuje kluczowe wyniki badań przeprowadzonych w ramach niniejszego cyklu publikacji. Celem głównym było nie tylko zbadanie, ale przede wszystkim zrozumienie roli i eksploracja właściwości cieczy jonowych w układach z żywicami epoksydowymi oraz ich wpływ na końcowe materiały kompozytowe wzmacniane włóknami. Eksplorowanie różnych aspektów zastosowania cieczy jonowych z żywicami jonowymi jako takimi, ale także w kompozytach epoksydowych wzmacnianych włóknami węglowymi lub lnianymi, przeprowadzono w oparciu o cele szczegółowe badań.

Realizacja zarówno celu głównego jak i celów szczegółowych uzupełniona została także badaniami nad syntezą, właściwościami czy stabilnością cieczy jonowych oraz ich mieszanin. W trakcie analizy zgromadzonych danych udało się osiągnąć szereg istotnych wniosków, które mają potencjalnie szerokie znaczenie zarówno teoretyczne, jak i praktyczne.

Wnioski wynikające z badań przeprowadzonych w cyklu publikacji

W odniesieniu do celów szczegółowych można zidentyfikować wnioski wynikające z cyklu publikacji, które zebrano poniżej.

- / Otrzymane z wysoką wydajnością pochodne DABCO, świadczą o dużej reaktywności tej aminy i szerokim potencjale do otrzymywania cieczy jonowych w łagodnych warunkach.
- / Wykorzystanie I etapu reakcji Delépine’a jest efektywną metodą syntezy czwartorzędowych soli halogenkowych urotropiny, w łagodnych warunkach i z wysoką wydajnością oraz czystością.

- / Synteza czwartorzędowych soli na bazie pochodnych aniliny zachodzi w warunkach podwyższonej temperatury i jej optymalizacja pozwoliła na osiągnięcie wysokich wydajności procesu przy jednoczesnym zachowaniu dużej czystości związków.
- / Otrzymano wszystkie założone pochodne w reakcjach metatezy, z anionami [DCA], [OTf] oraz [NTf₂] co świadczy o dobrze dobranych warunkach reakcji.
- / Ciecze jonowe na bazie urotropiny to związki o niskich temperaturach rozpadu i charakteryzujące się niską stabilnością w warunkach przechowywania w temperaturze pokojowej.
- / ILs w całym cyklu prac okazały się skutecznymi latentnymi czynnikami utwardzającymi, umożliwiającymi kontrolowaną polimeryzację żywic epoksydowych.
- / Temperatura utwardzania żywicy epoksydowej inicjowana przez ciecze jonowe może być kontrolowana poprzez dobór optymalnej struktury cieczy jonowych.
- / ILs zapewniały doskonałą stabilność przechowywania mieszanek żywic epoksydowych z cieczami jonowymi, co pozwalało na wydłużenie okresu trwałości bez przedwczesnego utwardzania.
- / Ciecze jonowe o bardzo długich łańcuchach, jak np. związek 52, obniżają temperaturę początku polimeryzacji w układach z żywicami epoksydowymi, co wskazuje na wpływ długości łańcucha na proces utwardzania.
- / Ciecze jonowe zawierające anion [DCA] to najbardziej aktywne inicjatory utwardzania żywicy epoksydowej i to właśnie ten anion powinien być obecny w strukturze ILs, aby zapewnić dobre właściwości sieciujące.
- / Aniliniowe ciecze jonowe z anionami [OTf] charakteryzują się szybką polimeryzacją i silnym sieciowaniem wyrażonym poprzez wysoką entalpię procesu. Są to aniony, dla których kontrolowanie procesu polimeryzacji jest trudne i w przypadku nawet lekkiego podniesienia temperatury w kierunku piku termicznego, może dojść do samozapłonu.
- / Wybór kationu i anionu znacznie wpływa na gęstość sieciowania i zachowanie podczas polimeryzacji, co uwidoczniły badania nad cieczami jonowymi będącymi pochodnymi aniliny.
- / ILs mogą być praktycznym rozwiązaniem dla zastosowań wymagających opóźnionego utwardzania i stabilnego przechowywania mieszanki żywicy z utwardzaczem.
- / Mieszaniny cieczy jonowych charakteryzują się zmniejszeniem całkowitej entalpii przemiany termicznej w stosunku do pojedynczych ILs, co wskazuje na bardziej efektywny proces utwardzania.

- / Ciecze jonowe w porównaniu do klasycznych utwardzaczy, stosuje się w znacznie mniejszej ilości, wystarczającej do zapewnienia skutecznego usieciowania żywicy epoksydowej. Zwykle stosunek aminy do żywicy wynosi pomiędzy 10 a 15% wagowych, z kolei dla ILs wartości te zawierają się w przedziale od 2 do 5% wagowych. Wpływa to na efektywne wykorzystanie surowców.
- / Utwardzone żywice epoksydowe wykazywały wysokie wartości twardości Shore'a w stosunku do referencji co oznacza, że mogą być stosowane w bardziej wymagających obszarach aplikacyjnych, w których kluczowa jest duża twardość.
- / Rodzaj i stężenie ILs wpływają na temperaturę zeszklenia i moduł zachowawczy kompozytów.
- / Długość łańcucha alkilowego cieczy jonowych wpływa na efektywność sieciowania i elastyczność kompozytów.
- / Ciecze jonowe jako modyfikatory mogą zwiększać stopień sieciowania i temperaturę przejścia szklстого kompozytów epoksydowych.
- / Wolniejszy proces polimeryzacji, obserwowany dla cieczy jonowych z anionem [DCA], wpływa korzystnie na właściwości mechaniczne struktur kompozytowych, umożliwiając powstawanie gęstej sieci połączeń wewnątrz matrycy epoksydowej.
- / Struktura kationów, w tym w szczególności długości łańcuchów alkilowych, determinują właściwości mechaniczne otrzymanych struktur kompozytowych.
- / Wykorzystanie mieszanin ILs poprawiło właściwości mechaniczne kompozytów, szczególnie w zakresie elastyczności i odporności na zginanie.
- / Właściwości mechaniczne, takie jak wytrzymałość na rozciąganie i zginanie, poprawiły się dzięki mieszaninom cieczy jonowych w porównaniu do systemów z pojedynczymi ILs.
- / Obecność atomów fosforu i krzemu w strukturach cieczy jonowych może wpływać na właściwości uniepalniające mieszanin w strukturach kompozytowych.
- / Kompozyty modyfikowane mieszaninami ILs wykazują zwiększoną odporność na ogień, ale do znaczącego uniepalnienia wymagane są dalsze badania.
- / Materiały typu SILP skutecznie pełniły podwójną rolę utwardzaczy i wypełniaczy.
- / Rodzaj cieczy jonowej osadzonej na krzemionce ma znaczenie w kontekście procesu polimeryzacji, w tym temperatur początku procesu i szczytu.

- / Rodzaj krzemionki ma istotne znaczenie we właściwościach kompozytów epoksydowych oraz w samym procesie utwardzania, co przedstawiono na przykładzie trzech krzemionek w pracy [A6], gdzie dla krzemionki DG635 uzyskano najlepsze wyniki.
- / Wprowadzenie cieczy jonowej osadzonej na krzemionce, inicjowało polimeryzację żywicy bezpośrednio przy powierzchni wypełniacza krzemionkowego, co gwarantowało maksymalną redukcję szansy powstawania defektów strukturalnych w porównaniu do klasycznej metody wprowadzania wypełniacza krzemionkowego.
- / Wypełnienie krzemionkowe wprowadzone do kompozytu przy pomocy materiału typu SILP wpłynęło na zwiększenie sztywności struktur kompozytów wzmacnianych włóknem lnianym i węglowym.
- / Rozpuszczanie celulozy w ILs zapewniło skuteczną metodę wprowadzania celulozy jako wypełniacza w biokompozytach epoksydowych, stanowiąc nowe podejście do zastosowania rozpuszczonej w ILs celulozy. Wykazano znaczący wpływ na właściwości mechaniczne struktur kompozytowych, w tym na zwiększenie wartości HDT oraz znaczący wzrost temperatury mięknięcia.
- / Włókna celulozowe generowane *in situ*, wprowadzone do układu żywicznego przy pomocy cieczy jonowych, poprawiły statyczne właściwości mechaniczne, w tym wytrzymałość na rozciąganie i moduł elastyczności.

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Mono N-Alkylated DABCO-Based Ionic Liquids and Their Application as Latent Curing Agents for Epoxy Resins

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Cite This: *ACS Appl. Polym. Mater.* 2021, 3, 5481–5493

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ABSTRACT: Research on ionic liquids is constantly providing information on their new and more advanced applications. Undoubtedly, the use of latent curing agents for epoxy resins is one of the most interesting applications of this group of compounds. In this work, a detailed description of the synthesis and physicochemical studies of DABCO-based (1,4-diazabicyclo[2.2.2]octane) ionic liquids is presented. Their most valuable feature is that they can be latent curing agents for polymerization of epoxy resins, which in turn can be used, when combined with fibers, as composites with special, new properties. The research includes detailed discussion of synthesis of new DABCO-ILs, focusing on obtaining pure compounds and expanding current knowledge on the subject. Thermal (DSC) and chromatographic (IC) properties have been discussed for all presented salts. Furthermore, ionic liquids with dicyanamide and triflate anion have demonstrated the ability to initiate polymerization of epoxy resins. Subsequently, all mixtures were cured into cubical shape and were subjected to the Shore hardness test (SHT). The main advantages of the obtained ILs are (i) the ability to store ionic liquids/epoxy resin mixture for prolonged periods of time without deterioration of curing properties and (ii) a significantly lower quantity of ionic liquids used in the process of curing epoxy resins.

KEYWORDS: ionic liquids, ion chromatography, DABCO, dicyanamide, epoxy resin, latent cure, initiators, polymerization mechanism

INTRODUCTION

For many years, we observed a continuous interest in ionic liquids' (ILs) research. ILs owe their interest due to their versatility and unique properties, which allowed them to find wide utilization in various fields.¹ A very low level of volatility, an ionic structure in the liquid state below 100 °C, and a great variety of combinations of cations and anions are just some of them.² In addition to the common features that allow these compounds to be called ionic liquids, they have various specific properties which determine their applications, for example, in electrochemistry,^{3,4} as catalysts,^{5,6} or as unique solvents in chemical reactions⁷ or for dissolution of biomass, for example, cellulose⁸ or lignin.^{9,10} On the other hand, ILs can successfully increase the efficiency of enzymes such as β -galactosidase,¹¹ enable the immobilization of enzymes on cellulose carriers¹² or finally, can be combined with enzymes in order to create an efficient extraction system for valuable organic compounds.¹³ Many applications of ILs are embedded in agriculture where they are a useful bioactive chemical tool as, for example, adjuvants in pesticides¹⁴ and many more.¹⁵ Consequently, there are wide classes of task-specific ionic liquids, like porous^{16,17} or polymerizable ILs,¹ which are valuable chemicals in formation of functional materials.

Similarly, ILs for a past decade or so are successfully implemented in epoxy composite technologies as a curing agent.^{18–23} Many classic amine-based hardeners initiate the epoxy resin polymerization process at room temperature, which is characterized by declining activity with an increasing number of carbon atoms adjacent to the nitrogen in an amine.²³ In contrast, one of the reactions that amines undergo is the alkylation reaction, leading to the quaternary ammonium salts, which can decompose under the influence of temperature. Amine derivative cations in ionic liquids have full and effective hardening activity at elevated temperatures.^{24,25} In particular, this is due to the need to supply energy capable of initiating the process of the IL cation decomposition, with the simultaneous release of the active amine.²⁴ Notwithstanding, ionic liquids consist of a cation and an anion, and both of them can initiate the curing process of the epoxy resin, using both

Received: July 7, 2021
Accepted: September 15, 2021
Published: October 1, 2021



the cationic and anionic polymerization mechanisms.²⁶ For this reason, it is observed that in the case of using the ILs-based hardening system, the necessary curing agent amount is mostly a couple of times lower than in the case of classic amine systems. Simultaneously, the pot life of epoxy composition is significantly extended.^{27,28} In detail, many factors must be taken into account for an ILs curing system, both the structure of the cation and the matched anion but also the decomposition temperature, which must be provided to initiate the curing process.

At the same time, because of possible modifications of the chemical structure, they bring to the final materials a number of functionalities, such as flame retardancy,^{29–33} wear and tear self-healing,²² better mechanical^{34–38} and thermal^{31,37} properties, or increased strength^{33,39} and toughness.^{39,40} Moreover, IL can act as a sizing agent, compatibilizer for aramid fibers,⁴¹ with epoxy resins or filler functionalizing factor in production of conducting polymer composites.⁴²

One more interesting but largely unexplored amine is 1,4-diazabicyclo[2.2.2]octan (DABCO). Recently presented routes for the synthesis of quaternary salts of DABCO, both monoalkylated^{43–46} and dialkylated,^{43,44} have made DABCO an unexplored source of new ionic liquids (DABCO ILs) in the field of their utilization. Thus, ionic liquids containing a DABCO cation in their structure, have found application as electrolytes for electrochemical,^{3,46} catalysts,^{47–53} surfactants.^{54–56} They were used in synthesis of functionalized magnetic nanoparticles,⁵⁷ while deep eutectic solvents, DABCO ILs, were used as the reaction medium.⁵⁸ In biology, they can be used in peptide coupling⁴⁷ or as potent alkaline phosphatase inhibitors.⁵⁹ They are also known in applications such as herbicidal and deterrent compounds^{45,60} or as potent antimicrobial agents.⁶¹

Herein, we would like to present the syntheses and characterization of a series of DABCO ILs with dicyanamide anion, substituted with alkyl chains with an even and odd number of carbon atoms ranging from C₂ to C₁₂. All compounds were first synthesized as bromide quaternary ammonium intermediates. The methods of synthesis for DABCO-based quaternary salts reported in the literature was upgraded in the case of highly hygroscopic compounds. Then, all obtained salts underwent a metathesis reaction to form dicyanamide DABCO ILs. Furthermore, our research plan was to show numerous dependencies between: (i) alkyl chain length, (ii) even or odd number of carbon atoms in alkyl chain and (iii) relationship between other anions. Ultimately, to present a complete research concept, we proposed an application for the obtained new compounds, confirming their effectiveness and also emphasizing their advantage over conventionally used amines, as hardening agents in the context of epoxy resins.

RESULTS AND DISCUSSION

The first objective was to obtain quaternary ammonium bromide salts of DABCO with the highest possible yields and the highest purity (Figure 1). In order to emphasize the completeness of the research, alkylating agents with both even and odd number of carbon atoms were selected. However, in order to achieve the highest possible efficiency of the process and the purity of the compounds, alkyl bromides as an alkylating agents were selected. An equally important reason for selecting bromide alkylating agents was the fact that N-

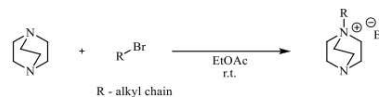


Figure 1. Reaction route to obtain mono N-alkylated bromide salts of DABCO.

monoalkylated DABCO bromides salts are formed as precipitate and could be easily isolated from the system.

The next step was to modify DABCO bromides and transform them into dicyanamide ionic liquids, with the use of a metathesis reaction. The choice of the dicyanamide anion provides: (i) an increase in number of potential sources of nitrogen atoms that are able to initiate epoxy polymerization and (ii) additional data to compensate for insufficient literature reports available on N-monoalkylated DABCO cations combined with dicyanamide anion. Another advantage of this choice is that most ILs with this anion are liquid at room temperature, which makes them easier to mix with epoxy resin without additional use of solvents. Furthermore, such compounds can be easily obtained by the metathesis reaction with high yields and purity. Above all, we present two ways of obtaining dicyanamide ionic liquids with and without silver salt. Lastly, on the basis of literature reports,²⁵ we expected that DABCO-based dicyanamide ILs will be able to initiate curing process at satisfying temperatures because of anion involvement in the curing process. In order to further investigate the curing process and the anion influence, the research plan also included synthesis of a series of quaternary salts based on the most effective DABCO cation paired with other typical anions used for ionic liquids. However, a N-mono quaternization reaction was applied, using slightly modified synthesis routes, as reported in the literature.^{43,47,60,62–68} Thereupon, nine N-mono alkylated bromide salts with alkyl chain lengths from C₂ to C₁₂ were prepared. Concurrently, to obtain highly hygroscopic bromides (C₆ to C₁₂), a reaction between DABCO and the corresponding alkyl bromide was carried out in neat. Thus, the goal was achieved by delivering a series of bromide compounds with high yields, in the range from 93% to 98% and a total purity above 96% (Table 1). All compounds were purified by melt crystallization, according to the procedure described in the literature.⁶⁹ The progress of each reaction was monitored by using ion chromatography. As a result, using cationic analysis and comparing the ratio of unreacted DABCO and N-monoalkylated product, the reaction time was optimized for each of the obtained salts, respectively. To illustrate the differences in susceptibility to quaternization reactions, between DABCO and alkylating agents of different chain length, a detailed experiment was carried out. For this purpose, four reaction systems based on DABCO with (i) ethyl bromide, (ii) propyl bromide, (iii) butyl bromide, and (iv) decyl bromide were evaluated using ion chromatography by collecting reaction samples after a specified period of time. Thus, the necessity to extend the reaction time, depending on the chain length of the alkylating agent, was confirmed. As a rule, longer alkyl chains require longer reaction times, but the exception is decyl bromide, for which the time required for complete conversion differs from the rule and is comparable to that for short alkyl chains (Figure 2).

Furthermore, there are no significant differences in reaction time between even and odd number of carbons present in alkyl chains. Ion chromatography was also used to determine the

Table 1. Synthesis Parameters and Purity of the Synthesized Substances

DABCO- C_n X

no.	compound	molecular mass [g/mol]	reaction time [h]	yield [%]	purity [%]
1	DABCO- C_2 Br	221.1	7	98	98.4
2	DABCO- C_3 Br	235.2	8	97	99.4
3	DABCO- C_4 Br	249.2	14	96	96.8
4	DABCO- C_5 Br	263.2	16	94	99.8
5	DABCO- C_6 Br	277.2	16	98	97.4
6	DABCO- C_7 Br	291.3	18	98 ^a	99.3
7	DABCO- C_8 Br	305.3	24	96 ^a	98.3
8	DABCO- C_{10} Br	333.4	9	96 ^a	97.9
9	DABCO- C_{12} Br	361.4	16	93 ^a	96.3
10	DABCO- C_2 DCA	207.3	6	92	97.2
11	DABCO- C_3 DCA	221.3	6	91	98.7
12	DABCO- C_4 DCA	235.3	6	96	97.7
				78 ^a	86.0 ^a
13	DABCO- C_5 DCA	249.4	6	88	96.3
14	DABCO- C_6 DCA	263.4	6	86	97.1
15	DABCO- C_7 DCA	277.4	6	92	99.0
16	DABCO- C_8 DCA	291.5	7	81	98.1
17	DABCO- C_{10} DCA	319.5	6	83	97.8
18	DABCO- C_{10} DCA	347.6	7	79	96.5
19	DABCO- C_6 Cl	232.9	12	95	98.3
20	DABCO- C_6 BF ₄	284.2	3	98	99.1
21	DABCO- C_6 NTf ₂	477.5	0.5	99	98.1
22	DABCO- C_6 OTf	368.6	2	97	98.6
23	DABCO- C_6 OTf	346.4	2	97	98.6
24	DABCO- C_6 MeSO ₃	292.5	2	96	99.1
25	DABCO- C_6 PF ₆	342.3	3	99	99.2
26	DABCO- C_6 MeSO ₄	308.3	2	97	98.2

^aReaction in neat with sodium dicyanamide.

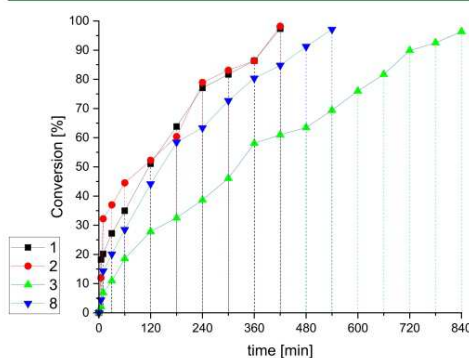


Figure 2. Optimization of the quaternization reaction using ion chromatography; (1) DABCO- C_2 Br, (2) DABCO- C_3 Br, (3) DABCO- C_4 Br, (8) DABCO- C_{10} Br.

purity of N-alkylated DABCO salts. In this case, both cationic and anionic ion chromatography analyses were conducted, and an overall purity of chemical compounds was determined as reported in the literature.² In addition, DABCO bromides with an odd number of carbons in alkyl chains are much purer than

the compounds with an even number of carbons in alkyl chains, obtained in the same way. Furthermore, for highly hygroscopic salts with longer alkyl chain substituents (5–9), no relationship between the synthesis route and the purity of the compounds was found, but products obtained in neat contain much less absorbed water in their structure and are less susceptible to its absorption, which in turn facilitates their isolation, purification, and vacuum drying. However, this effect can be simply a result of using ethyl acetate as a solvent in standard procedure, which itself contains some water and is difficult to dry. Consequently, during the reaction between DABCO and the alkylating agent in ethyl acetate at room temperature, the present trace amount of water solvates the hygroscopic quaternary ammonium product, making it difficult to remove, even when applying high vacuum.

The next step was to carry out a series of metathesis reactions to obtain N-mono alkylated DABCO ionic liquids (DABCO ILs) with dicyanamide anion (DCA, Figure 2). Metathesis reactions were conducted using two different routes: (i) main reaction route with freshly prepared silver dicyanamide (AgDCA) in distilled water and (ii) reaction with sodium dicyanamide (NaDCA) in neat. To explain, the use of silver salt allowed to obtain compounds of high purity, in a fast and highly efficient way. Synthesized from corresponding bromides, dicyanamides, in most cases present purity above 95%, without significant differences between even and odd alkyl chains and with high yields (Table 1). Similarly, as with the bromides, the progress of the both used metathesis reactions was monitored using ion chromatography. Thus, termination of all reactions was observed after about 6 h, with about 50% conversion in the first hour. Because of the amorphous form of silver dicyanamide, the reaction does not fully develop in the first hour. In the first step, the exchange takes place on the silver dicyanamide surface between the dicyanamide and bromide, and then by continued stirring in dark and the gradual washing of the silver bromide precipitate by the water present in system, the reaction continues. In addition, all synthesized compounds are liquid at room temperature, with no signs of high hygroscopicity. However, the neat method was used to present another route for the synthesis of dicyanamides. For this purpose, 1-butyl-1,4-diazabicyclo[2.2.2]octan-1-ium bromide was melted and underwent a metathesis reaction with NaDCA without solvent, with simultaneous ion chromatography progress controlling. After a series of purification experiments with solvents (tetrahydrofuran and dichloromethane), the final purity of 1-butyl-1,4-diazabicyclo[2.2.2]octan-1-ium dicyanamide was 86%, contaminated with 14% of other ions, including bromide and sodium (Figure 3).

In order to comprehensively investigate the application potential of DABCO ILs, a series of metathesis reactions were carried out to determine the influence of various anions on the application activity of the N-alkylated DABCO cation. For this purpose, we chose 1-hexyl-1,4-diazabicyclo[2.2.2]octan-1-ium cation core which, as shown in later sections dealing with the curing properties of various DABCO derivatives, proved to be the most effective cation derivative. For this purpose, the 1-hexyl-1,4-diazabicyclo[2.2.2]octan-1-ium bromide underwent a metathesis reaction with lithium bis(trifluoromethanesulfonyl)imide [NTf₂][−], potassium hexafluorophosphate [PF₆][−], and sodium tetrafluoroborate [BF₄][−]. At the same time, the procedure described in the literature² was used, and a number of derivatives based on sulfur-containing anions p-toluenesul-

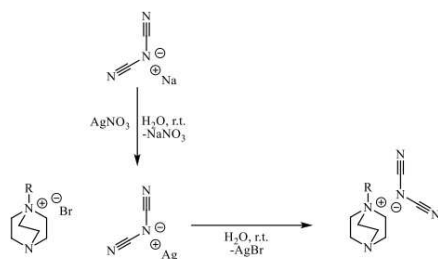


Figure 3. General route of metathesis reaction.

fonate [OTs][−], trifluoromethanesulfonate [OTf][−], methyl sulfate [MeSO₄][−], and methanesulfonate [MeSO₃][−] were obtained. For a direct comparison of the different halogen anions, 1-hexyl-1,4-diazabicyclo[2.2.2]octan-1-ium chloride was also obtained in the N-alkylation reaction of DABCO with hexyl chloride. The progress of all experiments and the

purity of the products were determined using ion chromatography. In addition, all solid products were purified by melt crystallization. As a result, eight different DABCO salts with (i) [NTf₂][−], (ii) [PF₆][−], (iii) [BF₄][−], (iv) [OTs][−], (v) [OTf][−], (vi) [MeSO₄][−], (vii) [MeSO₃][−], and (viii) [Cl][−] were obtained with yields above 95% and purity in the range from 95% to 99% (Table 1). The ion chromatograms show the absence of a bromide anion and a lack of formation of dialkylated DABCO derivatives under mild reaction conditions.

THERMAL PROPERTIES

The second objective was to determine the thermal properties (Table 2) of obtained substances using differential scanning calorimetry (DSC). As a general rule, mono N-alkylated DABCO bromide salts tend to decrease the melting point (*T_m*) with increasing chain length. However, compounds with an odd number of carbon atoms (2, 4, 6) in the alkyl chain show slightly lower melting points with respect to the same parameter for chains with an even number of carbon atoms (1,

Table 2. Thermal Properties of Compounds (DSC) and Water Content (KF)

no.	compound	alkyl chain	anion	water content [%]	<i>T_m</i> [°C]	<i>T_{on}</i> [°C]	<i>T_g</i> [°C]
1	DABCO-C ₂ Br	C ₂	Br	0.51	192.3	183.0	-
2	DABCO-C ₃ Br	C ₃	Br	0.22	190.0–194.1 ^{65,70}	69.8	-
3	DABCO-C ₄ Br	C ₄	Br	0.26	149.3	43.2	-
4	DABCO-C ₅ Br	C ₅	Br	0.58	144.0–146.0 ⁷⁰	126.7	-
5	DABCO-C ₆ Br	C ₆	Br	0.43	128.0–130.0 ⁷⁰	36.7	-
6	DABCO-C ₇ Br	C ₇	Br	1.08	121.8	83.5	-
7	DABCO-C ₈ Br	C ₈	Br	0.98	108.0–110.0 ⁶⁰	36.7	-
8	DABCO-C ₁₀ Br	C ₁₀	Br	1.26	94.3	36.5	-
9	DABCO-C ₁₂ Br	C ₁₂	Br	0.97	89.9	70.9	-
10	DABCO-C ₂ DCA	C ₂	DCA	0.81	84.0–86.0 ⁶⁰	21.1	-
11	DABCO-C ₃ DCA	C ₃	DCA	0.69	103.7	-	-79.5
12	DABCO-C ₄ DCA	C ₄	DCA	0.86	58.7	-	-74.1
13	DABCO-C ₅ DCA	C ₅	DCA	0.43	106.0–108.0 ⁶⁰	-	-60.2
14	DABCO-C ₆ DCA	C ₆	DCA	0.79	81.3	-	-60.7
15	DABCO-C ₇ DCA	C ₇	DCA	0.64	84.0 ⁷²	-	-59.0
16	DABCO-C ₈ DCA	C ₈	DCA	1.16	34.3	-	-57.6
17	DABCO-C ₁₀ DCA	C ₁₀	DCA	0.92	35.8 ⁷³	-	-55.2
18	DABCO-C ₁₂ DCA	C ₁₂	DCA	1.34	98.1	-	-54.7
19	DABCO-C ₆ Cl	C ₆	Cl	0.13	97.0–99.0 ⁷¹	40.9	-
20	DABCO-C ₆ BF ₄	C ₆	BF ₄	0.26	81.3	-	-
21	DABCO-C ₆ NTf ₂	C ₆	NTf ₂	0.04	84.0 ⁷²	-10.7	-
22	DABCO-C ₆ OTs	C ₆	OTs	0.18	34.3	78.9	-
23	DABCO-C ₆ OTf	C ₆	OTf	0.10	89.2	62.0	-
24	DABCO-C ₆ MeSO ₃	C ₆	MeSO ₃	0.09	62.8	0.2	-
25	DABCO-C ₆ PF ₆	C ₆	PF ₆	0.21	53.6	119.6	-
26	DABCO-C ₆ MeSO ₄	C ₆	MeSO ₄	0.16	133.0	-	-

^aReaction in neat.

Table 3. Curing Process Properties (DSC)

no.	compound	alkyl chain	anion	T_{onset} [°C]	T_{max} [°C]	T_{end} [°C]	ΔH [J/g]
10	DABCO- C_2 DCA	C_2	DCA	113.1	186.9	246.8	113.6
11	DABCO- C_3 DCA	C_3	DCA	119.2	165.0	215.1	2.9
					182.1		11.5
12	DABCO- C_4 DCA	C_4	DCA	94.3	127.1	233.6	17.3
					188.2		169.2
13	DABCO- C_5 DCA	C_5	DCA	95.4	129.3	239.1	79.5
					191.6		54.9
14	DABCO- C_6 DCA	C_6	DCA	123.7	187.5	226.4	121.3
15	DABCO- C_7 DCA	C_7	DCA	123.3	189.3	228.1	140.4
16	DABCO- C_8 DCA	C_8	DCA	133.0	185.5	225.8	85.5
17	DABCO- C_{10} DCA	C_{10}	DCA	131.2	183.1	227.4	53.4
18	DABCO- C_{12} DCA	C_{12}	DCA	124.5	188.7	227.7	118.6
23	DABCO- C_6 OTf	C_6	OTf	88.4	190.1	214.9	317.4
27	DABCO	-	-	63.5	104.7	169.8	315.4

3, 5, 7, 8, 9). Instead, 1-dodecyl-1,4-diazabicyclo[2.2.2]octan-1-ium bromide shows the lowest melting point with determined temperature 58.7 °C. In contrast, the highest melting point, 192.3 °C, is observed for 1-ethyl-1,4-diazabicyclo[2.2.2]octan-1-ium bromide. Similarly, there are differences in the crystallization temperature (T_c), which is in particular lower for substances with odd numbers of carbon atoms than for their even counterparts. Crystallization temperatures (during the cooling process) below 50 °C are observed for the compounds with C_4 , C_5 , C_7 , C_8 , and C_{12} with the lowest value determined for C_{12} (21.1 °C). Then, the same thermal tests were carried out for dicyanamide DABCO ILs. Because of the liquid form of the compounds, only the appearance of the glass transition temperatures (T_g) were observed in the thermograms. In principle, for all dicyanamide DABCO ILs, this value is very similar and ranges from −54.7 °C to −79.4 °C, with the overwhelming majority at the level of −60 °C. Moreover, none of the salts exhibited any signs of decomposition (exothermic peak in DSC analysis) over the temperature range of DSC measurements (up to 200 °C). A direct dependence of the length of the alkyl chain in the cation on the glass transition temperature was observed. Regardless of an even or odd number of carbons in the alkyl chain, there is a dependency; the more carbon atoms in the alkyl chain, the lower glass transition temperature. In addition, thermal analyses were performed for organic salts of 1-hexyl-1,4-diazabicyclo[2.2.2]octan-1-ium with different anions. The vast majority of the melting points for the compounds obtained are within the range below 100 °C, with one exception in the case of 1-hexyl-1,4-diazabicyclo[2.2.2]octan-1-ium hexafluorophosphate (133 °C). The lowest value was observed for bis(trifluoromethanesulfonyl)imide anion (34.3 °C), aside the lack of the observable melting transition for the dicyanamide derivative (14) which only presents glass transition at −60.7 °C. Large differences were also observed in the case of the crystallization temperature (during cooling process) of the obtained salts, in particular between bis(trifluoromethanesulfonyl)imide salt (−10.7 °C), methanesulfonate salt (0.2 °C), and the rest of the compounds. An exception to all the synthesized substances was methyl sulfate, without any recorded thermal transformation under the condition of DSC experiment.

CURING PROCESS

The final goal of the research was (i) to examine the properties of the obtained compounds in terms of their activity as hardeners of commercially available epoxy resins (Epidian 53, Ciech Sarzyna S.A.) and (ii) to determine the basic hardness parameters of the obtained materials. The choice of resin was dictated by proving the versatility of ionic liquids as hardeners and their compatibility with modified epoxy raw material, available on the market. Epidian 53 is typically used in applications such as (i) bonding wood, metals, glass, and plastics (except for PE and PP). Also, it is used in preparation of epoxy-glass laminates, flooding and impregnation of various materials. All obtained substances were tested for their curing activity using DSC measurements. Also, neutral DABCO (10% w/w) was used in the same experiment, to confirm its curing activity as a pure amine (27). At the same time, ILs were used in concentration 2.5 times lower than pure DABCO. The correlation of curing temperature parameters with tested compounds is summarized in Table 3. For dicyanamide DABCO ILs, the starting temperatures of the polymerization process are directly related to the length of the alkyl chain of the liquid, and their values vary alternately. There was a characteristic shift from higher values for short -ethyl and -propyl alkyl chains to temperatures below 100 °C for -butyl (94.3 °C) and -pentyl (95.4 °C) chains and then a further increase in the polymerization start temperature for the -hexyl and -octyl chains, reaching the maximum temperature recorded for the C_8 chain (133 °C). Finally, for -decyl and -dodecyl alkyl chains, the polymerization initiation temperature to lower values was again observed, reaching for C_{12} (124.5 °C) a similar value to C_6 (123.7 °C). Moreover, correlations between the length of the alkyl chain in the cation and the maximum temperature of the epoxy resin curing process were also observed. Similarly, the lowest values were noticed for C_4 and C_5 alkyl chains; however, in the case of determining the maximum temperature, no characteristic alternating shifts were observed. Furthermore, for -propyl, -butyl and -pentyl alkyl chains (11, 12, 13), two temperature peaks were observed on DSC thermograms. This suggest that two different polymerization processes occur during the first heating cycle (Figure 4). Next, temperatures for the end of the cross-linking process were designated. The tested epoxy resin systems with DABCO ionic liquids with DCA anion have, regardless of the chain length, a similar value of the temperature of the end of the hardening process, and it is in the range from 224 to 228 °C.

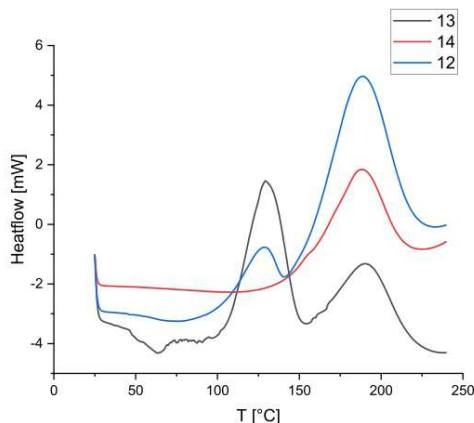


Figure 4. DSC thermograms of polymerization process; (12) DABCO- C_4 DCA, (13) DABCO- C_5 DCA, (14) DABCO- C_6 DCA.

However, 1-hexyl-1,4-diazabicyclo[2.2.2]octane trifluoromethanesulfonate, as the only one among other tested anions (19–26) combined with 1-hexyl-1,4-diazabicyclo[2.2.2]octan-1-ium cation (with the exclusion of DCA), exhibits activity as an initiator of epoxy resin polymerization. This suggests that the epoxy resin polymerization was more frequently initiated by an anion in ionic liquids rather than a cation. In addition, the temperatures of the individual thermal transitions of the resin system cured with this compound differ from those observed for dicyanamides and are 88.36 °C at the start point of the curing process, 190 °C at the maximum point, and 214.9 °C at the end point. To summarize, all values collected were directly pooled and referenced to the temperature reference values recorded for the pure DABCO cured resin system, 63.5 °C at the start point of the curing process, 104.7 °C at the maximum point, and 169.8 °C at the end point. Thus, of all the substances tested, all dicyanamide DABCO ILs and 1-hexyl-1,4-diazabicyclo[2.2.2]octan-1-ium trifluoromethanesulfonates are effective in the process of initiating the polymerization of epoxy resin. In comparison with other research on ionic liquids as curing agents, presented results exhibit higher maximum

temperature of polymerization. For example, simple ILs (1-ethyl-3-methylimidazolium thiocyanate or acetate) have a significantly lower maximum point (121, 114 °C, respectively).²⁵ In addition, for phosphonium ionic-liquid-based epoxy systems, the maximum temperature of the process is closely related to the concentration of IL and is within the range of 128–157 °C.⁷⁴

INITIATION AND PROPAGATION OF EPOXY POLYMERIZATION

Presented DABCO ILs can simultaneously initiate polymerization of epoxy resin by three possible pathways (Figure 5), which is similar to that suggested in a report by Binks et al.²⁴ Two of them present a cationic mechanism, which results in obtaining adducts 1:1 and 1:2, using nitrogen atoms in a cation structure. The cationic 1 polymerization pathway is based on the use of a tertiary nitrogen atom in the cation of an ionic liquid, already enabling a slow start of the polymerization process at room temperature. Formation of adducts 1:1, 1:2, and the following ends with branched polymer and IL as a byproduct. However, the curing process initiated by tertiary nitrogen atoms is very slow. Moreover, because of the nature of an ionic liquid, their ability to undergo the dealkylation reaction under increased temperature conditions, second tertiary nitrogen atom may become available for the polymerization process. Thus, suggesting that the second cationic polymerization process (cationic 2) may also take place simultaneously. As a result, direct formation of adduct 1:2 is suggested. The cationic 2 pathway ends with similarly branched polymer and pure DABCO as a byproduct, which in itself is capable of initiating further polymerization of epoxy resin. Furthermore, anionic polymerization is also possible. In this case, epoxy resin molecule reacts with a nitrogen atom in a dicyanamide anion, resulting in formation of adduct 1:1 and then 1:2. This process ends with a similar branched polymer and DCA anion molecule. Nitrogen atoms, depending on their order, can initiate polymerization of epoxy resin with different speed. Thus, why we suggest that increased number of nitrogen atoms in hardener structure can promote better curing activity. Hence, the simplest common anion with three nitrogen atoms in the structure is dicyanamide. Its activity relates to the commonly used commercial hardener 2-cyanoguanidine (Dicy), which is similar in structure to DCA anion. Nonetheless, as to triflate anion, its reactivity can be

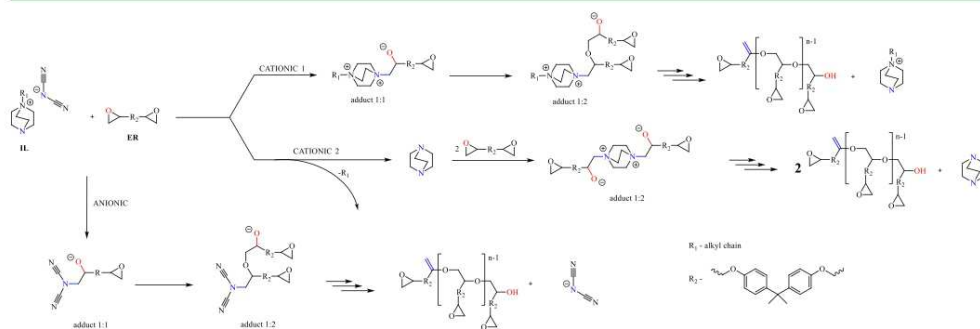


Figure 5. Proposed pathway of epoxy resin polymerization, initiated by DABCO ILs.

explained by trifluoromethyl group present in its structure. High temperature can promote generation of highly active radical $\cdot\text{CF}_3$, which can also form adducts with epoxy resin molecules. In addition, when energy is supplied to the system in the form of heat, the anion curing processes take place first (anionic polymerization, Figure 5), and in our research it is the DCA anion due to its highly nucleophilic nature. In the case of other tested anions, their nucleophilic character is not that strong, thus, the curing process occurs through cationic polymerization (Figure 5), which requires higher temperatures to start decomposition of IL and formation of neutral amine. To the best of our knowledge, one of the key elements contributing to the lack of activity of ionic liquids with anion other than DCA may be the very high stability of these compounds and the lack of activity of the anion itself. Nevertheless, our experience shows that such substances may also be capable of initiating polymerization, but it requires a significant increase in temperature and sometimes the concentration of the ionic liquid (taking into account that the active initiator will be only the cation after the decomposition process). Our research had clearly defined curing boundary conditions, which allowed us to select systems that will be able to be used industrially in the future and will prove to be the most interesting from a practical point of view.

SHORE HARDNESS TEST (SHT)

For all cured samples based on DSC experiments, a Shore hardness test was carried out. Properly prepared samples of the hardened material (Figure 6), based on two different commercially available epoxy resins (Epidian 53, Ciech Sarzyna S.A., ER₁ and EnviPOXY 530, SPOLCHEMIE a.s., ER₂) combined with dicyanamide DABCO ILs, were subjected

to hardness measurement in order to determine the influence of the use of an ionic liquid on the basic parameters of the material quality and to exclude the negative influence of ionic liquids on the hardness of the products (Table 4). To Epidian

Table 4. Hardness of the Cured Materials (SHT)

no.	compound	ER ₁ [D]	ER ₂ [D]
10	DABCO-C ₂ DCA	88	89
11	DABCO-C ₃ DCA	89	90
12	DABCO-C ₄ DCA	95	90
13	DABCO-C ₅ DCA	89	85
14	DABCO-C ₆ DCA	90	86
15	DABCO-C ₇ DCA	88	85
16	DABCO-C ₈ DCA	87	86
17	DABCO-C ₁₀ DCA	85	86
18	DABCO-C ₁₂ DCA	86	84
23	DABCO-C ₆ OTf	86	85
27	DABCO	73	71
28	Commercial amine system	74	79

53, other epoxy resin was added to examine versatility of synthesized DABCO curing agents. EnviPOXY resin is typically used in casting and tooling, civil engineering, coatings, adhesives, composites, encapsulation, and potting. The reference material was cured with commercial amine (triethylenetetramine, TETA) curing resin system (28) and a pure DABCO cured system (27). A significant increase in the hardness of the hardened materials was confirmed for all the compounds obtained, compared with the reference materials. This suggests that the DABCO based curing systems provide better materials' parameters in terms of their hardness, which can translate into increased stiffness and crush and impact resistance. The average recorded increase in material hardness remains at the level of 20%, regardless of the type of epoxy resin used. Namely, the highest results in terms of material hardness were achieved with shorter alkyl chains, respectively 88D and 89D for -ethyl, 89D and 90D for -propyl and 95D and 90D for -butyl, for which this result is the highest among the others. As the chain length increased, the material hardness decreased and the result for -decyl (85D) chain was the lowest among the tested compounds in case of ER₁, while for -dodecyl (84D) was the lowest among tested compounds in case of ER₂. Figure 3 presents samples of cured materials with DABCO ILs and DABCO as reference. It can be observed that Epidian 53 systems show a tendency to color changing (from orange to brown) during the polymerization process. This can be explained by the anion influence on the polymerization process (advantage of anionic pathway). Reference material stays orange because only cationic polymerization occurs.

CONCLUSIONS

A series of mono N-alkylated DABCO bromides and dicyanamides with even and odd numbers of carbon atoms in the alkyl chain have been synthesized and fully characterized (NMR, IC, DSC). Furthermore, the group of tested compounds has been extended by a series of anion modifications for the 1-hexyl-1,4-diazabicyclo[2.2.2]octan-1-ium cation. The method of synthesis of all compounds has been precisely optimized through the use of ion chromatography technique, bringing accurate information about the time of chemical reactions and the purity of the compounds obtained. Thus, thermal properties of the obtained compounds



Figure 6. Shore samples of cured epoxy resins with dicyanamide DABCO ILs (curing systems as described in Table 4).

were discussed, showing differences in compounds with even and odd numbers of carbon atoms in the alkyl chain. Subsequently the synthesized substances were used as latent curing agents for two commercial epoxy resins, the parameters of the curing process were discussed in detail, indicating the differences between the individual compounds. Finally, the samples of epoxy resins cured with the compounds presented in this paper were subjected to the Shore hardness test (SHT), which showed an average increase in hardness of the cured resins, of 20% in compared with the reference materials. 1-Butyl-1,4-diazabicyclo[2.2.2]octan-1-ium dicyanamide and 1-pentyl-1,4-diazabicyclo[2.2.2]octan-1-ium dicyanamide can be considered as the best curing systems among the tested ones, and they will be used in further works as hardeners in the technology of producing prototype composite materials. For carbon reinforced composites and preregs, dedicated for curing with large vacuum autoclaves, hardeners with lowest activation temperature are desirable; thus, compounds **12** and **13** are suited the best. In addition, choice of systems with the lowest activation temperatures guarantees higher security with using vacuum autoclave and decrease risk of the uncontrollable combustion of the curing material. The conducted research shows that ionic liquids based on the DABCO cation are not only effective as curing agents but also have a positive effect on the hardness of the cured materials.

EXPERIMENTAL SECTION

Materials. 1,4-Diazabicyclo[2.2.2]octane, DABCO (>99%), 1-bromoethane (>99%), 1-bromopropane (99%), 1-bromobutane (99%), 1-bromopentane (98%), 1-bromohexane (98%), 1-bromoheptane (99%), 1-bromooctane (99%), 1-bromodecane (98%), 1-bromododecane (97%), 1-chlorohexane (99%), silver nitrate (>99%), sodium dicyanamide (96%), potassium hexafluorophosphate (>99%), sodium tetrafluoroborate (98%), lithium bis-(trifluoromethanesulfonyl)imide (>99%), methyl *p*-toluenesulfonate (98%), methylmethanesulfonate (99%), dimethyl sulfate (>99%), and methyl trifluoromethanesulfonate (>98%) were purchased from Sigma-Aldrich (Sigma-Aldrich Co. LLC, St. Louis, U.S.A.) and used without further purification. All organic solvents used were HPLC grade. Styrene modified epoxy resin, Epidian 53 was purchased from Ciech Sarzyna S.A. (Joint-stock company), epoxy resin containing no modifiers, EPD certified significant savings in CO₂, low crude oil content, and high renewable content, EnviPOXY 530 was purchased from SPOLCHEMIE Spolek pro chemickou a hutní výrobu, a.s. (Joint-stock company).

Methodology. *Melt Crystallization.* Ionic liquid was placed in a glass vial and then put in a thermal block tightly adjacent to the vessel walls. Thereafter, the block temperature was increased following a temperature ramp of 1 degree. After the melting process was observed, the sample was thermostated at a constant temperature for a period of 60 min. Crystallization occurred on the walls of the vial with simultaneous temperature decrease.

Differential Scanning Calorimetry (DSC). Pure Ionic Liquids/Organic Salts Samples. Melting point/glass transition analyses were determined according to slightly modified method, as reported in previous work.¹ The first heating cycle was up to 130 °C, and the second heating cycle was up to 200 °C.

Ionic Liquid/Epoxy Resin System. All of the samples were freshly prepared by mixing ionic liquids (0.2 g) with epoxy resin (5 g) in a glass vial. Each sample (5–10 mg) was analyzed using differential scanning calorimetry with a heat/cool cycle from 25 to 250 °C at 10 °C·min⁻¹. The data were collected by the same calorimeter as for melting points.

Ion Chromatography. Ion chromatography experiments were carried out according to method reported in previous work.¹

Water Content Analysis. Water content was determined using Karl Fischer type titration apparatus according to method reported in previous work.¹

NMR Spectroscopy. NMR spectra were recorded using 400 and 500 MHz spectrometer in commercially available CDCl₃ solvent. The value of standard measurement uncertainty did not exceed ±0.02 ppm.

Method for Testing the Hardness of Cured Epoxy Resins—Shore Test. To measure the hardness of cured materials, the Shore D durometer was used. Prepared samples of the cured resin with dimensions of 1.0 × 1.0 cm and a homogeneous surface were tested by a series of hardness measurements at room temperature, while maintaining the distance from the edge of the material (minimum 1.0 mm). The final result, expressed on the Shore D scale, is the average of three repetitions. Before testing, all samples were conditioned at room temperature for 24 h.

Synthesis of Compounds. General Procedure of DABCO Bromides Salts' Synthesis [A]. To obtain products **1–5**, a solution of 1,4-diazabicyclo[2.2.2]octane (DABCO, 1.0 equiv) in ethyl acetate was placed in a round-bottomed flask with simultaneous stirring on a magnetic stirrer. Then corresponding alkyl bromide (1.0 equiv) was added dropwise at room temperature. After that, product in a form of precipitate or a new phase, was observed immediately. After the time required to complete the reaction (controlled by ion chromatography, Table 1), bromide salt was separated, then washed with ethyl acetate (3 × 10.0 mL) and diethyl ether (3 × 10.0 mL). Product was dried under vacuum (72 h).

Synthesis of 1-Ethyl-1,4-diazabicyclo[2.2.2]octan-1-ium Bromide (1). Compound **1** was obtained according to general procedure A with the use of DABCO (11.2 g, 0.1 mol), 1-bromoethane (10.9 g, 0.1 mol), and ethyl acetate (150.0 mL). Reaction time was equal to 7.0 h, and the reaction gave pure product as a white crystalline solid (21.7 g, 98%). Purity [IC]: 98.4%.

¹H NMR (400 MHz, CDCl₃) δ 3.64 (t, *J* = 7.2 Hz, 6H), 3.50 (m, 2H), 3.23 (t, *J* = 7.6 Hz, 6H), 1.40 (t, *J* = 7.3 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 59.71 (s), 51.94 (s), 45.40 (s), 8.06 (s). IC⁺ (min): *t*_R = 23.86, IC⁻ (min): *t*_R = 4.16. Water content (KF) = 0.51%.

Synthesis of 1-Propyl-1,4-diazabicyclo[2.2.2]octan-1-ium Bromide (2). Compound **2** was obtained according to general procedure A with use of DABCO (11.2 g, 0.1 mol), 1-bromopropane (12.3 g, 0.1 mol), and ethyl acetate (150.0 mL). Reaction time was equal to 8.0 h, and the reaction gave pure product as a white solid (22.8 g, 97%). Purity [IC]: 99.4%.

¹H NMR (400 MHz, CDCl₃) δ 3.66 (t, *J* = 7.2 Hz, 6H), 3.44 (m, 2H), 3.24 (t, *J* = 7.9 Hz, 6H), 1.82 (sextet, *J* = 7.7 Hz, 2H), 1.00 (t, *J* = 7.3 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 65.91 (s), 52.48 (s), 45.43 (s), 15.68 (s), 10.85 (s). IC⁺ (min): *t*_R = 22.83, IC⁻ (min): *t*_R = 4.13. Water content (KF) = 0.22%.

Synthesis of 1-Butyl-1,4-diazabicyclo[2.2.2]octan-1-ium Bromide (3). Compound **3** was obtained according to general procedure A with use of DABCO (11.2 g, 0.1 mol), 1-bromobutane (13.7 g, 0.1 mol), and ethyl acetate (150.0 mL). Reaction time was equal to 14.0 h, and the reaction gave pure product as a light yellow solid (23.9 g, 96%). Purity [IC]: 96.8%.

¹H NMR (400 MHz, CDCl₃) δ 3.65 (m, *J* = 7.2 Hz, 6H), 3.47 (m, 2H), 3.23 (t, *J* = 7.9 Hz, 6H), 1.74 (pentet, *J* = 7.5 Hz, 2H), 1.38 (sextet, *J* = 7.5 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 64.36 (s), 52.45 (s), 45.42 (s), 23.94 (s), 19.74 (s), 13.69 (s). IC⁺ (min): *t*_R = 29.95, IC⁻ (min): *t*_R = 4.14. Water content (KF) = 0.26%.

Synthesis of 1-Pentyl-1,4-diazabicyclo[2.2.2]octan-1-ium Bromide (4). Compound **4** was obtained according to general procedure A with use of DABCO (11.2 g, 0.10 mol), 1-bromopentane (15.1 g, 0.10 mol), and ethyl acetate (150.0 mL). Reaction time was equal to 16.0 h, and the reaction gave pure product as a white finely crystalline solid (24.7 g, 94%). Purity [IC]: 99.8%.

¹H NMR (400 MHz, CDCl₃) δ 3.61 (t, *J* = 7.7 Hz, 6H), 3.41 (m, 2H), 3.19 (t, *J* = 7.3 Hz, 6H), 1.71 (m, 2H), 1.29 (m, 4H), 0.83 (t, *J* = 6.9 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 64.50 (s), 52.39 (s),

45.39 (s), 28.34 (s), 22.17 (s), 21.72 (s), 13.80 (s). IC^+ (min): $t_R = 28.27$, IC^- (min): $t_R = 4.15$. Water content (KF) = 0.58%.

Synthesis of 1-Hexyl-1,4-diazabicyclo[2.2.2]octan-1-ium Bromide (5). Compound 5 was obtained according to general procedure A with use of DABCO (11.2 g, 0.10 mol), 1-bromohexane (16.5 g, 0.10 mol), and ethyl acetate (150.0 mL). Reaction time was equal to 16.0 h, and the reaction gave pure product as a white solid (27.1 g, 98%). Purity [IC]: 97.4%.

1H NMR (400 MHz, $CDCl_3$) δ 3.70 (t, $J = 7.4$ Hz, 6H), 3.53 (m, 2H), 3.28 (t, $J = 7.4$ Hz, 6H), 1.78 (m, 2H), 1.34 (m, 6H), 0.90 (t, $J = 7$ Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 64.61 (s), 52.51 (s), 45.47 (s), 31.28 (s), 26.05 (s), 22.40 (s), 22.11 (s), 13.90 (s). IC^+ (min): $t_R = 37.23$, IC^- (min): $t_R = 4.15$. Water content (KF) = 0.43%.

General Procedure of DABCO Bromides Salts' Synthesis [B]. To obtain products 6–9, 1,4-diazabicyclo[2.2.2]octane (DABCO, 1.0 equiv) was placed in two-necked round-bottomed flask equipped with drying tube (filled with calcium chloride) with simultaneous stirring on magnetic stirrer. Then corresponding alkyl bromide (1.0 equiv) was added dropwise at room temperature. After that, product in a form of precipitate was observed. After time required to complete the reaction (controlled by ion chromatography, Table 1), precipitate was separated with diethyl ether as auxiliary solvent. Product was washed with diethyl ether (3×10.0 mL) and dried under vacuum (72 h).

Synthesis of 1-Heptyl-1,4-diazabicyclo[2.2.2]octan-1-ium Bromide (6). Compound 6 was obtained according to general procedure B with the use of DABCO (11.2 g, 0.10 mol) and 1-bromooctane (17.9 g, 0.10 mol). Reaction time was equal to 18.0 h, and the reaction gave pure product as a white solid (28.5 g, 98%). Purity [IC]: 99.3%.

1H NMR (400 MHz, $CDCl_3$) δ 3.69 (t, $J = 7.4$ Hz, 6H), 3.53 (m, 2H), 3.28 (t, $J = 7.9$ Hz, 6H), 1.78 (m, 2H), 1.31 (m, 8H), 0.89 (t, $J = 6.9$ Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 64.61 (s), 52.51 (s), 45.47 (s), 31.52 (s), 28.86 (s), 26.35 (s), 22.46 (s), 22.16 (s), 14.02 (s). IC^+ (min): $t_R = 35.98$, IC^- (min): $t_R = 4.18$. Water content (KF) = 1.08%.

Synthesis of 1-Octyl-1,4-diazabicyclo[2.2.2]octan-1-ium Bromide (7). Compound 7 was obtained according to general procedure B with the use of DABCO (11.2 g, 0.10 mol) and 1-bromooctane (19.3 g, 0.10 mol). Reaction time was equal to 24.0 h, and the reaction gave pure product as a white solid (29.3 g, 96%). Purity [IC]: 98.3%.

1H NMR (400 MHz, $CDCl_3$) δ 3.69 (t, $J = 7.4$ Hz, 6H), 3.51 (m, 2H), 3.28 (t, $J = 7.4$ Hz, 6H), 1.77 (m, 2H), 1.35 (m, 4H), 1.28 (m, 6H), 0.88 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 64.62 (s), 52.51 (s), 45.46 (s), 31.61 (s), 29.16 (s), 29.03 (s), 26.40 (s), 22.56 (s), 22.16 (s), 14.05 (s). IC^+ (min): $t_R = 46.49$, IC^- (min): $t_R = 4.28$. Water content (KF) = 0.98%.

Synthesis of 1-Decyl-1,4-diazabicyclo[2.2.2]octan-1-ium Bromide (8). Compound 8 was obtained according to general procedure B with use of DABCO (11.2 g, 0.10 mol) and 1-bromodecane (22.1 g, 0.10 mol). Reaction time was equal to 9.0 h, and the reaction gave pure product as a white solid (32.0 g, 96%). Purity [IC]: 98%.

1H NMR (400 MHz, $CDCl_3$) δ 3.68 (t, $J = 7.4$ Hz, 6H), 3.49 (m, 2H), 3.27 (t, $J = 7.4$ Hz, 6H), 1.78 (m, 2H), 1.35 (m, 4H), 1.26 (m, 10H), 0.88 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 64.62 (s), 52.51 (s), 45.46 (s), 31.82 (s), 29.40 (d, $J = 1.3$ Hz), 29.22 (s), 26.41 (s), 22.64 (s), 22.18 (s), 14.10 (s). IC^+ (min): $t_R = 57.79$, IC^- (min): $t_R = 4.16$. Water content (KF) = 1.26%.

Synthesis of 1-Dodecyl-1,4-diazabicyclo[2.2.2]octan-1-ium Bromide (9). Compound 9 was obtained according to general procedure B with the use of DABCO (11.2 g, 0.10 mol) and 1-bromododecane (24.9 g, 0.10 mol). Reaction time was equal to 16.0 h, and the reaction gave pure product as a white solid (33.6 g, 93%). Purity [IC]: 96.3%.

1H NMR (400 MHz, $CDCl_3$) δ 3.69 (t, $J = 7.4$ Hz, 6H), 3.56 (m, 2H), 3.29 (t, $J = 7.4$ Hz, 6H), 1.77 (m, 6H), 1.33 (s, 14H), 0.90 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 64.62 (s), 52.45 (s), 44.95 (d, $J = 68.0$ Hz), 31.86 (s), 29.57 (s), 29.45 (d, $J = 4.6$ Hz), 29.26 (d, $J = 7.2$ Hz), 26.41 (s), 22.64 (s), 22.12 (s), 14.09 (s). IC^+ (min): $t_R = 69.17$, IC^- (min): $t_R = 4.19$. Water content (KF) = 0.97%.

General Procedure of Metathesis Reaction [C]. To obtain products 10–18, a solution of the corresponding bromide (1.0 equiv) in water was placed in round-bottomed flask with simultaneous stirring on magnetic stirrer. Then freshly prepared silver dicyanamide (1.0 equiv) was added at room temperature. After that, appearing of yellow precipitate of silver bromide was observed immediately. Reaction was carried out without light access. After time required to complete the reaction (controlled by ion chromatography), silver bromide was separated using a glass fiber filter and then washed with distilled water (3×25.0 mL). Combined aqueous phase was evaporated on rotary evaporator to obtain pure product. Product was dried under vacuum (72 h).

Synthesis of Silver Dicyanamide. To obtain silver dicyanamide, a solution of sodium dicyanamide (1.0 equiv) in water was placed in round-bottomed flask with simultaneous stirring on magnetic stirrer. Then, silver nitrate (1.0 equiv) was added at room temperature, and a white precipitate of silver dicyanamide was observed immediately. Reaction was carried out without light access. After 1.0 h, silver dicyanamide was separated using glass fiber filter and then washed with distilled water (6×25.0 mL). Product was obtained with quantitative yield and used in next step without any purification.

Synthesis of 1-Ethyl-1,4-diazabicyclo[2.2.2]octan-1-ium Dicyanamide (10). Compound 10 was obtained according to general procedure C with the use of 1 (4.4 g, 0.02 mol), silver dicyanamide (3.5 g, 0.02 mol), and water (40.0 mL). Reaction time was equal to 6.0 h, and the reaction gave pure product as a colorless liquid (3.8 g, 92%). Purity [IC]: 97.2%.

IC^+ (min): $t_R = 23.01$, IC^- (min): $t_R = 6.62$. Water content (KF) = 0.81%.

Synthesis of 1-Propyl-1,4-diazabicyclo[2.2.2]octan-1-ium Dicyanamide (11). Compound 11 was obtained according to general procedure C with use of 2 (4.7 g, 0.02 mol), silver dicyanamide (3.5 g, 0.02 mol), and water (40.0 mL). Reaction time was equal to 6.0 h, and the reaction gave pure product as a light yellow liquid (4.0 g, 91%). Purity [IC]: 98.7%.

IC^+ (min): $t_R = 22.41$, IC^- (min): $t_R = 6.59$. Water content (KF) = 0.69%.

Synthesis of 1-Butyl-1,4-diazabicyclo[2.2.2]octan-1-ium Dicyanamide (12). Compound 12 was obtained according to general procedure C with use of 3 (5.0 g, 0.02 mol), silver dicyanamide (3.5 g, 0.02 mol), and water (40.0 mL). Reaction time was equal to 6.0 h, and the reaction gave pure product as a light yellow liquid (4.5 g, 96%). Purity [IC]: 97.7%.

IC^+ (min): $t_R = 29.02$, IC^- (min): $t_R = 6.68$. Water content (KF) = 0.86%.

To obtain product 12, compound 3 (2.5 g, 0.01 mol) was melted (130.0 °C) in the pressure tube without any solvent. After melting, sodium dicyanamide (2.7 g, 0.03 mol) was added in one portion. The resulting mixture was stirred on a magnetic stirrer for 72.0 h; subsequently, the reaction was cooled to room temperature, and tetrahydrofuran (50.0 mL) was added. The white precipitate of sodium bromide and residual sodium dicyanamide was removed with filtration on a Buchner funnel. The organic phase was then evaporated under reduced pressure and washed with dichloromethane (50.0 mL). Finally, residual sodium salts were removed with filtration, and dichloromethane was evaporated under reduced pressure to give pure product (1.8 g, 78%). Purity [IC]: 86%.

IC^+ (min): $t_R = 29.48$, IC^- (min): $t_R = 7.39$. Water content (KF) = 0.17%.

Synthesis of 1-Pentyl-1,4-diazabicyclo[2.2.2]octan-1-ium Dicyanamide (13). Compound 13 was obtained according to general procedure C with the use of 4 (5.3 g, 0.02 mol), silver dicyanamide (3.5 g, 0.02 mol), and water (40.0 mL). Reaction time was equal to 6.0 h, and the reaction gave pure product as a yellow liquid (4.4 g, 88%). Purity [IC]: 96.3%.

IC^+ (min): $t_R = 28.49$, IC^- (min): $t_R = 6.68$. Water content (KF) = 0.43%.

Synthesis of 1-Hexyl-1,4-diazabicyclo[2.2.2]octan-1-ium Dicyanamide (14). Compound 14 was obtained according to general procedure C with the use of 5 (5.5 g, 0.02 mol), silver dicyanamide

(3.5 g, 0.02 mol), and water (40.0 mL). Reaction time was equal to 6.0 h, and the reaction gave pure product as a crystallizing colorless liquid (4.5 g, 86%). Purity [IC]: 97.1%.

IC⁺ (min): t_R = 37.19, IC[−] (min): t_R = 6.65. Water content (KF) = 0.79%.

Synthesis of 1-Heptyl-1,4-diazabicyclo[2.2.2]octan-1-ium Dicyanamide (15). Compound 15 was obtained according to general procedure C with the use of 6 (5.8 g, 0.02 mol), silver dicyanamide (3.5 g, 0.02 mol), and water (40.0 mL). Reaction time was equal to 6.0 h, and the reaction gave pure product as a light yellow liquid (5.1 g, 92%). Purity [IC]: 99%.

IC⁺ (min): t_R = 36.02, IC[−] (min): t_R = 6.64. Water content (KF) = 0.64%.

Synthesis of 1-Octyl-1,4-diazabicyclo[2.2.2]octan-1-ium Dicyanamide (16). Compound 16 was obtained according to general procedure C with the use of 7 (6.1 g, 0.02 mol), silver dicyanamide (3.5 g, 0.02 mol), and water (40.0 mL). Reaction time was equal to 7.0 h, and the reaction gave pure product as a light yellow liquid (4.7 g, 81%). Purity [IC]: 98%.

IC⁺ (min): t_R = 46.89, IC[−] (min): t_R = 6.62. Water content (KF) = 1.16%.

Synthesis of 1-Decyl-1,4-diazabicyclo[2.2.2]octan-1-ium Dicyanamide (17). Compound 17 was obtained according to general procedure C with the use of 8 (6.7 g, 0.02 mol), silver dicyanamide (3.5 g, 0.02 mol), and water (40.0 mL). Reaction time was equal to 6.0 h, and the reaction gave pure product as a yellow viscous liquid (5.3 g, 83%). Purity [IC]: 97.8%.

IC⁺ (min): t_R = 58.03, IC[−] (min): t_R = 6.68. Water content (KF) = 0.92%.

Synthesis of 1-Dodecyl-1,4-diazabicyclo[2.2.2]octan-1-ium Dicyanamide (18). Compound 18 was obtained according to general procedure C with the use of 9 (7.2 g, 0.02 mol), silver dicyanamide (3.5 g, 0.02 mol), and water (40.0 mL). Reaction time was equal to 7.0 h, and the reaction gave pure product as a light yellow viscous liquid (5.5 g, 79%). Purity [IC]: 96.5%.

IC⁺ (min): t_R = 68.97, IC[−] (min): t_R = 6.66. Water content (KF) = 1.34%.

Synthesis of Other Ionic Liquids. Synthesis of 1-Hexyl-1,4-diazabicyclo[2.2.2]octan-1-ium Chloride (19). Compound 19 was obtained according to general procedure A with the use of DABCO (11.2 g, 0.10 mol), 1-chlorohexane (12.1 g, 0.10 mol), and ethyl acetate (150.0 mL). Reaction time was equal to 12.0 h, and the reaction gave pure product after evaporation of solvent and reactants, as a white solid (22.1 g, 95%). Purity [IC]: 98.3%.

IC⁺ (min): t_R = 36.96, IC[−] (min): t_R = 3.58. Water content (KF) = 0.13%.

Synthesis of 1-Hexyl-1,4-diazabicyclo[2.2.2]octan-1-ium Tetrafluoroborate (20). To the solution of 5 (2.8 g, 0.01 mol) in distilled water (50.0 mL) was added dropwise an aqueous solution of sodium tetrafluoroborate (1.1 g, 0.01 mol) with simultaneous stirring on magnetic stirrer. The white precipitate of 20 was observed immediately. Reaction time was equal to 3.0 h; subsequently, the white precipitate was separated using Buchner funnel and washed with distilled water (3 × 15.0 mL) and ethyl acetate (3 × 15.0 mL). The product was dried under vacuum and obtained as a white solid (2.8 g, 98%). Purity [IC]: 99.1%.

IC⁺ (min): t_R = 37.06, IC[−] (min): t_R = 5.70. Water content (KF) = 0.26%.

Synthesis of 1-Hexyl-1,4-diazabicyclo[2.2.2]octan-1-ium Bis(trifluoromethylsulfonyl)imide (21). The solution of 5 (2.8 g, 0.01 mol) in distilled water was transferred into a separating funnel. Then, methylene chloride (50.0 mL) was added followed by aqueous solution of lithium bis(trifluoromethylsulfonyl)imide (80%, 3.6 g, 0.01 mol). The obtained mixture was vigorously shaken for a few minutes, and then the separated organic layer was washed with deionized water (3 × 20.0 mL) and deionized water with small portion of LiNTf₂ (80%, 0.001 mol) (1 × 20.0 mL). The washing procedure was finished in an absence of bromide anion in water layer (silver nitrate test). To obtain pure product, methylene chloride from organic layer was evaporated under reduced pressure, and bis-

(trifluoromethylsulfonyl)imide ionic liquid as a yellow solid (4.73 g, 99%) was dried under vacuum (24h). Purity [IC]: 98.1%.

IC⁺ (min): t_R = 37.18, IC[−] (min): t_R = 17.27. Water content (KF) = 0.04%.

Synthesis of 1-Hexyl-1,4-diazabicyclo[2.2.2]octan-1-ium p-Toluenesulfonate (22). Compound 22 was obtained according to literature procedure² with the use of 5 (2.8 g, 0.01 mol), methyl p-toluenesulfonate (1.9 g, 0.01 mol), and acetonitrile (50.0 mL). Reaction time was equal to 2.0 h, and the reaction gave pure product as a slightly yellow solid (3.5 g, 97%). Purity [IC]: 98.6%.

IC⁺ (min): t_R = 37.58, IC[−] (min): t_R = 4.98. Water content (KF) = 0.18%.

Synthesis of 1-Hexyl-1,4-diazabicyclo[2.2.2]octan-1-ium Trifluoromethanesulfonate (23). Compound 23 was obtained according to literature procedure² with the use of 5 (2.8 g, 0.01 mol), methyl trifluoromethanesulfonate (1.6 g, 0.01 mol), and acetonitrile (50.0 mL). Reaction time was equal to 2.0 h, and the reaction gave pure product as a yellow solid (3.4 g, 97%). Purity [IC]: 98.6%.

IC⁺ (min): t_R = 37.01, IC[−] (min): t_R = 6.03. Water content (KF) = 0.10%.

Synthesis of 1-Hexyl-1,4-diazabicyclo[2.2.2]octan-1-ium Methanesulfonate (24). Compound 24 was obtained according to literature procedure² with the use of 5 (2.8 g, 0.01 mol), methylmethanesulfonate (1.1 g, 0.01 mol), and acetonitrile (50.0 mL). Reaction time was equal to 2.0 h, and the reaction gave pure product as a white solid (2.8 g, 96%). Purity [IC]: 99%.

IC⁺ (min): t_R = 37.48, IC[−] (min): t_R = 5.37. Water content (KF) = 0.09%.

Synthesis of 1-Hexyl-1,4-diazabicyclo[2.2.2]octan-1-ium Hexafluorophosphate (25). To the solution of 5 (2.8 g, 0.01 mol) in distilled water (50.0 mL) was added dropwise an aqueous solution of potassium hexafluorophosphate (1.8 g, 0.01 mol) with simultaneous stirring on magnetic stirrer. The white precipitate of 25 was observed immediately. Reaction time was equal to 3.0 h; subsequently, the white precipitate was separated using vacuum funnel and washed with distilled water (3 × 15.0 mL) and ethyl acetate (3 × 15.0 mL). The product was dried under vacuum and obtained as a white solid (3.4 g, 99%). Purity [IC]: 99.2%.

IC⁺ (min): t_R = 37.86, IC[−] (min): t_R = 11.96. Water content (KF) = 0.21%.

Synthesis of 1-Hexyl-1,4-diazabicyclo[2.2.2]octan-1-ium Methyl Sulfate (26). Compound 26 was obtained according to literature procedure² with the use of 5 (2.8 g, 0.01 mol), dimethyl sulfate (1.3 g, 0.01 mol), and acetonitrile (50.0 mL). Reaction time was equal to 2.0 h, and the reaction gave pure product as a white solid (3.0 g, 97%). Purity [IC]: 98.2%.

IC⁺ (min): t_R = 37.49, IC[−] (min): t_R = 3.76. Water content (KF) = 0.16%.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors acknowledge financial support from the National Science Centre (Poland), project SONATA BIS 7 (No. 2017/26/E/ST8/01059) entitled “Multifunctional composite systems based on epoxy resins with ionic liquids as a crosslinking initiators”. The authors acknowledge financial support from the National Science Centre (Poland), project OPUS 18 (No. 2019/35/B/ST8/03736) entitled “High resolution optical and electron beam patterning processes with new ionic liquid based resists”.

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Article

Synthesis and Behavior of Hexamethylenetetramine-Based Ionic Liquids as an Active Ingredient in Latent Curing Formulations with Ethylene Glycol for DGEBA

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Abstract: The paper presents the preparation of new ionic liquids based on hexamethylenetetramine with bis(trifluoromethanesulfonyl)imide and dicyanamide anion, which were characterized in detail in terms of their purity (Ion Chromatography) and thermal properties (Differential Scanning Calorimetry), as well as stability. The obtained substances were used to develop curing systems with ethylene glycol, which were successfully tested for their application with bisphenol A diglycidyl ether molecule. In addition, the curing process and its relationship to the structure of the ionic liquid are characterized in detail. The research showed that hexamethylenetetramine-based new ionic liquids can be successfully designed using well-known and simple synthetic methods—the Delepine reaction. Moreover, attention was paid to their stability, related limitations, and the application of hexamethylenetetramine-based ionic liquids in epoxy-curing systems.

Keywords: hexamethylenetetramine; ionic liquids; epoxy resin; ethylene glycol; curing agent; composites



Citation: Zielinski, D.; Szpecht, A.; Hinc, P.; Smiglak, M. Synthesis and Behavior of Hexamethylenetetramine-Based Ionic Liquids as an Active Ingredient in Latent Curing Formulations with Ethylene Glycol for DGEBA. *Molecules* **2023**, *28*, 892. <https://doi.org/10.3390/molecules28020892>

Academic Editor: Francesca D'Anna

Received: 30 November 2022

Revised: 11 January 2023

Accepted: 12 January 2023

Published: 16 January 2023



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1. Introduction

It is commonly believed that ready-made composite materials are neutral to the environment and due to the lack of direct interactions at the molecular level, are not toxic [1]. This theorem is fulfilled for properly prepared composites, in which the network of connections between resins and the hardener are closed, well-known, predictable, and stable, and the resin itself does not contain solvents and other volatile organic compounds (VOCs) before the curing process [2].

The aim of this work was to provide new solution in the field of multifunctional initiating systems for the polymerization of epoxy resins. To be more precise, this solution is based directly on previously unknown ionic liquids, designed with well-known raw materials, reactions, and processes. The proposed cross-linking systems must be easy to prepare, stable and predictable in the context of their application and most importantly, well thought out. In addition, it is important to bring added value to the final products in the form of changing their mechanical properties and/or application potential through new functionalities. In the era of ecological awareness and social responsibility, an extremely important element of research is the use of substances for which the details of their environmental impact, toxicity and methods of obtainment are known. This is one of the ways to limit the emergence of new, unpredictable, and not fully tested substances in the industry, while still developing science and improving existing solutions, which this work was also intended to prove.

Ionic liquids (ILs) are chemical compounds with an ionic structure, consisting of a cation and an anion and having several specific properties. The cation of the ionic liquid is usually of organic origin and has a varied structure. On the other hand, anions of ionic liquids can be both organic and inorganic, and their nature significantly affects

the properties of the entire compound. The most important feature of this group of compounds is undoubtedly an extremely wide range of applications, in which the following should be distinguished: (i) dissolution and processing of biomass [3–5], (ii) catalytic reactions [6–8], (iii) active ingredients in pharmaceutical preparations [9,10] or (iv) design of polymerizable monomers intended for modern material solutions [11–13]. The wide area of application of ionic liquids is due to their properties, among which the following should be mentioned: high thermal stability [14], high electrochemical window [15], low volatility [16] and flammability [17]. At the same time, it turns out that these compounds can successfully replace, among others, hardeners (as a latent curing agents) of epoxy resins [18–21] as well as a large group of property modifiers: (i) flame retardants [22–24], (ii) hydrophobizers [25,26] and (iii) compounds that increase the mechanical parameters of the composite [21,27–30].

However, despite so many literature reports and numerous confirming the unique applications of ionic liquids, there are still groups of these compounds that require further research. One of these understudied groups is the non-aromatic polycyclic amines with catalytic properties, which can potentially be used as structures of ionic liquid cations. The most important substances in this group include: (i) 1,4-diazabicyclo[2.2.2]octane (DABCO), (ii) 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), (iii) 1-azabicyclo[2.2.2]octane (ABCO), (iv) 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) and hexamethylenetetramine (HMTA). The first two, DABCO and DBU, remain in the interest of many researchers, especially as new ionic liquids with catalytic properties [21]; DBN is not very popular due to its high similarity to DBU, while ABCO, because of its very high price, is practically not studied at all. In contrast, the simplest, best known and most easily available, as well as the cheapest polycyclic amine—HMTA, remains to this day the most unexplored source of ionic liquids, which may have a few unique properties, from catalytic, electrochemical and anti-corrosion to fuel applications. There are only a few reports of HMTA-based ionic liquids being obtained and used as components for the production of strong catalysts for obtaining hexahydroquinolines [31] and pyrido[2,3-d:5,6-d']dipyrimidines [32]. In addition, it was confirmed that HMTA-ILs exhibit high ionic conductivity, which increases significantly with temperature [33]. A huge impact on the importance of HMTA in chemistry was the discovery of the Delepine reaction in 1895, which allows for a simple and easy synthesis of primary amines through the intermediate product, which is a quaternary ammonium derivative of HMTA. The key here is the fact that this intermediate product can be easily isolated and shows very high stability [34,35].

Another view is ethylene glycol (EG), which is a well-known, simple chemical compound that is constantly gaining new applications based on the excellent knowledge of the properties of this substance. Especially in combination with ILs there is an interesting set of reports about its applications as a microemulsifier [36,37], co-solvent [38–40] and a substance able to stabilize ionic liquids through a specific interaction [41].

All the literature reports cited above were an inspiration to conduct this research, the results of which will be presented in the following subsections.

2. Results

2.1. Synthesis of Ionic Liquids

The research proposed a portfolio of new HMTA derivatives, differing in the length of the carbon chain attached to the nitrogen atom. Structures of all cations are shown in the Figure 1. As part of the research, alkyl chains with both an even and an odd number of carbon atoms were used to precisely determine the influence of the chain length on the properties of the obtained compounds. Moreover, two groups of anions were selected and combined with cation structures to obtain new ionic liquids. The bis(trifluoromethanesulfonyl)imide (TFSI) anion is highly hydrophobic [42], while the dicyanamide (DCA) anion is inherently more hydrophilic [43]. Such a correlation between anions allows for a thorough look at the nature of the compounds obtained and opens up more application possibilities and areas (mainly those indicated in the introduction) where new substances may prove value. To obtain the proposed substances, it was necessary to conduct quaternization reactions first, leading to the

desired halogen derivatives, which were then subjected to metathesis reactions leading to the final products. Afterward, all obtained substances were subjected to a thorough analysis of physicochemical properties before they were subjected to application tests.

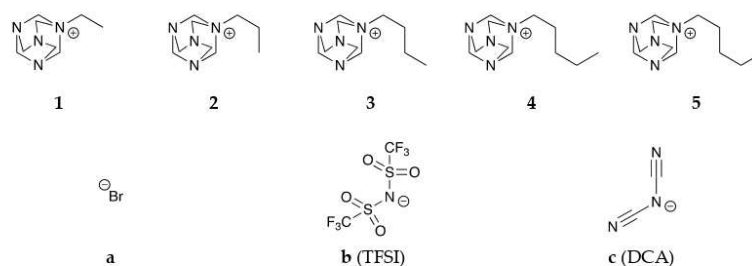


Figure 1. Chemical structures of the obtained compounds.

2.1.1. Quaternization

The first step of the Delepine reaction is the attachment of an alkylated chain to the nitrogen atom, followed by a quaternary ammonium salt (QAS) of HMTA formation. The reaction proceeds at room temperature in chloroform, from which the product is easily separated by simple filtration. Thus, the process was highly efficient, and the products were recrystallized to obtain QASs of very high purity (Table 1). On the other hand, the obtained products do not show strong hygroscopicity in contrast to analogous derivatives for, e.g., DABCO [17]. Determination of the purity of the obtained substances was carried out using ion chromatography, considered to be the best method for determining the purity of ionic compounds [12,17,40–42]. In addition, the same technique was used to monitor the progress of the reaction. Through routine analysis of product increment and substrate depletion, the reaction time was precisely determined to enable high process yields to be obtained in the shortest possible time. As a result of the conducted experiments, five bromide derivatives were successfully obtained, reaching the efficiency exceeding 99% and the purity of the obtained substances at the average level of 99.2%. To fully identify the obtained compounds, they were subjected to NMR and mass spectrometry analysis. Another equally important value for ILs is their water content, especially for halides, which are a key step on the way for obtaining the desired further products. None of the salts obtained exceeded the level of 1% of water; moreover, compounds **1a**, **2a** and **5a**, did not exceed the level of 0.5% water. The lowest value was recorded for the derivative having a propyl chain (**2a**) in its structure.

Table 1. Parameters of the synthesis of HMTA derivatives.

Compound	Yield [%]	Purity [%]	Water Content [wt%]
1a	99.6	99.6	0.47
2a	99.0	99.0	0.17
3a	99.1	99.1	0.68
4a	99.1	99.1	0.57
5a	99.0	99.1	0.42

2.1.2. Metathesis Reaction

However, ten new TFSl and DCA ionic liquids were selected for research. The bromide salts obtained earlier were precursors on the way to their preparation and required further processing. For this purpose, two different pathways of the metathesis reaction were used between the bromide anion in the HMTA quaternary salt and (i) the dicyandiamide anion derived from the freshly prepared (according previously published work [21]) silver salt, or the (ii) bis(trifluoromethanesulfonyl)imide anion derived from lithium salt. Each pathway

was analyzed at room temperature, however, using different process conditions, as shown in Figure 2, and synthetic techniques, as described in detail in the synthesis section. In the case of hydrophobic ionic liquids, the average yield of the metathesis reaction was 98.4%, while the purity of the obtained compounds ranged from 99.1 to 99.8%, with the lowest values for ionic liquids **4b** and **5b**, with the longest alkyl chains. Similar results were recorded for the synthesis of dicyandiamide derivatives, for which the average yield of the reaction was 94.5%, with the lowest values of 87.9% for compound **2c** and 93.9% for compound **4c**, for compounds with an odd number of carbon atoms in the alkyl chain. On the other hand, the purity of all dicyandiamide derivatives exceeded 97.5%, reaching the highest value of 98.1% for compounds **1c** and **3c** containing ethyl and butyl alkyl chains, respectively.

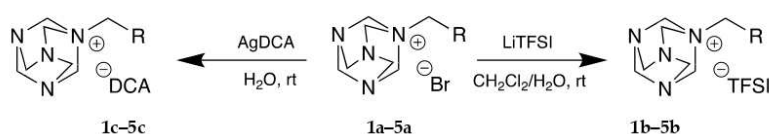


Figure 2. Scheme of metathesis reaction leading to HMTA derivatives with TFSI anion and DCA.

2.1.3. Thermal Properties of the Compounds

Measurements of thermal properties of the obtained substances (thermograms from analyzes available in Supplementary Materials), show numerous differences between both individual groups of compounds (depending on the anion present in the IL structure) and depending on the length of the carbon chain, in particular the relationship between the even and odd number of carbon atoms in the alkyl chain (Table 2). Namely, for quaternary ammonium salts with a bromide anion, only an onset exothermic peak (T_{decomp}) was observed in the thermogram, characteristic of the process of partial decomposition of the salt with the release of a large portion of energy. Differences in the decomposition temperature were observed, depending on whether an alkyl chain with an even or an odd number of carbon atoms was present in the structure. Compounds **2a** and **4a**, which contain a propyl and a pentyl chain structure, have onset peak decomposition temperatures of 146.5 °C and 143.6 °C, respectively. Between this group of compounds and analogs containing even carbon chains in the structure, an average temperature difference of 14 °C was observable. The highest decomposition temperatures, 168.3 °C and 155.4 °C, respectively, were recorded for compounds **1a** and **3a**, i.e., those with an ethyl or butyl chain. On the contrary, all ionic liquids obtained in the metathesis reaction, both DCA and TFSI, are characterized by lower crystallization/decomposition peak temperatures (T_{decomp}) observed during the measurements. The lowest values were recorded for compounds **1b**, **4b**, **1c** and **3c** and amounted to the following: 119.3 °C, 121.6 °C, 120.3 °C and 101.6 °C, respectively. However, the highest values were for the derivatives **2b** (126.8 °C), **5b** (134.7 °C), **2c** (135.3 °C) and **5c** (126.8 °C). There was no clear relationship between the chain length and the parameters obtained. In addition, glass transition temperature (T_g) data were collected for ILs with the TFSI anion, and melting point temperatures (T_m) were collected for ILs with the DCA anion. For the glass transition temperature, there is a general shift towards lower temperatures with increasing chain length, resulting in the lowest temperature values for **4b** and **5b** being −29.1 °C and −19.9 °C, respectively. Similarly, the melting temperatures observed for the dicyandiamides also show a shift towards higher temperatures with increasing chain length, except for compound **2c** (57.4 °C), which decreases relative to a compound **1c** (69.1 °C) with a shorter alkyl chain. All collected values are below 100 °C, reaching the highest value of 75.5 °C and 86.6 °C for **4c** and **5c** compounds, respectively.

Table 2. Thermal properties of the HMTA-based compounds obtained in this research.

Compound	T _m [°C]	T _g [°C]	T _{decomp} [°C]
1a	-	-	168.3 ^a
2a	-	-	146.5 ^a
3a	-	-	155.4 ^a
4a	-	-	143.6 ^a
5a	-	-	152.4 ^a
1b	-	−5.0	119.3 ^b
2b	-	−16.6	126.8 ^b
3b	-	−17.1	126.3 ^b
4b	-	−29.1	121.6 ^b
5b	-	−19.9	134.7 ^b
1c	69.1	-	120.3 ^b
2c	57.4	-	135.3 ^b
3c	72.1	-	101.6 ^b
4c	75.5	-	124.0 ^b
5c	86.6	-	126.8 ^b

^a Decomposition onset peak, ^b Start of exothermic decomposition during DSC measurement.

2.2. Curing Process

In the next stage of the research, a selected group of ten ILs was used to prepare ten curing mixtures intended for cross-linking the epoxy resin (Figure 3). The combinations were prepared by mixing the ionic liquid with ethylene glycol in a molar ratio of 1:2 in such a way as to ensure the highest possible curing activity in relation to the resin while maintaining high stability of the mixture itself. By experimenting with different ratios of IL to ethylene glycol, a system was selected in which there are two equivalents of EG for one equivalent of ionic liquid. Such a relationship between these substances resulted in the most stable mixtures, whose stability was validated by observing phase separation over a period of up to 60 days. Moreover, it was confirmed that ethylene glycol forms more stable systems with DCA-based ionic liquids, which successfully maintain their homogeneity beyond 60 days, while TFSI anion ionic liquids lose their homogeneity after about 2 weeks, requiring re-mixing. EG, due to its emulsifying properties, allowed us to prepare homogeneous curing systems with a high degree of compatibility with the resin, which in this case was the Bisphenol A diglycidyl ether (DGEBA, M = 340 g/mol) molecule. An important feature here is the fact that ethylene glycol creates much more stable emulsions in combination with more hydrophilic ionic liquids such as DCA ILs. It has been observed that TFSI causes emulsions to become heterogenous rather quickly. Specifically, to thoroughly study the curing process and compatibility, a system consisting of unmodified DGEBA molecules was used, thus eliminating the influence of possible modifiers and solvents that could be present in commercially available epoxy resins. Next, the prepared curing systems were mixed with a resin particle in a ratio that guaranteed full cross-linking (detailed data on sample preparation of resin systems are provided in the chapter Methods and in the reference [17]), degassed, and then cured in a vacuum oven with process temperature, developed based on data from simultaneously conducted tests using Differential Scanning Calorimetry (DSC). An important property of the curing mixtures is their initiating effect occurring only at elevated temperatures. At room temperature, they remain weakly active against the DGEBA molecule. In particular, this is a property observed with many ionic liquids used as curing initiators for epoxy resins and is fairly well explained [18–21].

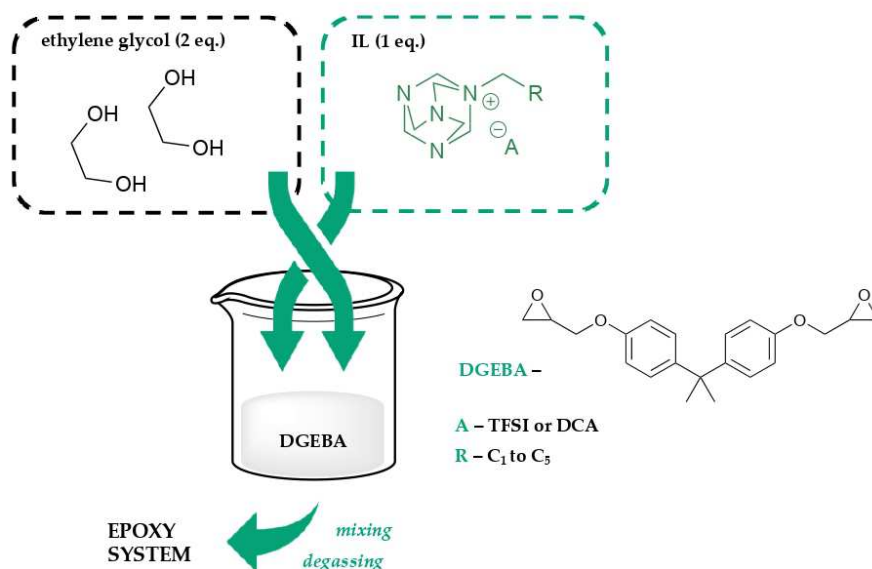


Figure 3. Scheme of the process of preparing resin systems with ionic liquids.

2.2.1. Thermal Analysis

Subsequently, ten curing systems were used to prepare mixtures with DGEBA, which were subjected to tests of curing process nature. For this purpose, Differential Scanning Calorimetry was again used (thermograms from analyzes available in Supplementary Materials), and several parameters of the process (Table 3) were determined, such as polymerization start temperature (T_{onset}), temperature peak (T_{max}) and polymerization end temperature (T_{end}). At the same time, the amount of energy released (ΔH) during the process was monitored. In the case of curing systems based on ionic liquids with the TFSI anion, comparable results for individual parameters were obtained, which remained at a similar level of values, regardless of the type and length of the alkylated chain in the cation structure. The exception is the derivative with an ethyl chain (1b), for which a lower polymerization start temperature (109.4 °C) and a much higher process energy (84.4 J/g) were recorded. At the same time, for the polymerization initiated by these curing systems, the appearance of two independent areas of temperature peaks in the form of two thermal processes occurring in the sample was observed. The highest temperature values of the first thermal peak, respectively 154.4 °C and 149.0 °C, were obtained for systems containing compounds 3b and 5b, however, these differences are insignificant. Similarly, in the case of the second thermal peak, the highest values were recorded for systems containing compounds 2b (224.4 °C) and 4b (229.5 °C). Simultaneously, with the increase in the length of the alkyl chain in the cation structure, the amount of energy released during the second thermal process occurring in the sample decreases. On the other hand, polymerization initiated by systems based on dicyanamide ionic liquids proceeds in the form of a single thermal transformation process. In this case, the relationship between the polymerization starting temperature and the energy released during the process, dependent on an odd or even number of carbon atoms in the alkyl chain, is clearly visible. Thus, with an odd number of carbon atoms in the cation structure, relatively lower values of the process start temperature were observed, while the amount of released energy decreases with the increase in the length of the odd alkyl chain. In contrast, if there is an even number of carbon atoms in the alkyl chain of the ionic liquid, the energy of thermal transformation increases with its length, reaching a maximum of 151.5 J/g for the system containing compound 5c,

for which the lowest polymerization initiation temperature (101.3 °C) and polymerization peak temperature (151.8 °C) were also recorded. To summary, all characteristic temperature points of the cross-linking process are within the range of the decomposition temperature of ionic liquids.

Table 3. Thermal properties of the curing process.

System	Anion	T _{onset} [°C]	T _{max} [°C]	T _{end} [°C]	ΔH [J/g]
1b/EG/DGEBA	TFSI	109.4	137.0	164.8	84.4
		200.7	223.5	236.9	24.3
2b/EG/DGEBA		122.2	148.1	201.5	26.5
		215.9	224.4	236.4	11.0
3b/EG/DGEBA		122.1	154.4	185.6	19.8
		210.3	218.9	239.5	11.7
4b/EG/DGEBA		119.1	147.0	205.7	29.3
		221.0	229.5	242.3	8.9
5b/EG/DGEBA		119.8	149.0	193.2	28.5
		209.3	221.7	223.0	7.2
1c/EG/DGEBA	DCA	140.8	170.7	224.0	49.5
2c/EG/DGEBA		123.6	164.7	213.2	81.6
3c/EG/DGEBA		140.0	163.9	188.1	49.8
4c/EG/DGEBA		129.5	165.1	199.1	23.0
5c/EG/DGEBA		101.3	151.8	210.6	151.5

2.2.2. Hardness of the Cured Resin

Afterward, the prepared samples of the cured DGEBA were tested for the basic assessment of their hardness/brittleness depending on the curing system used. Such a quick experiment made it possible to determine the relationship between the structure of the IL and the behavior of the hardened material in laboratory conditions. Furthermore, the samples were evaluated 48 h after hardening and after 7 and 14 days to determine the effect of aging of the samples on the basic parameter, which was hardness. For comparison, analogous samples cured with two amines commonly used as initiators of epoxy resin polymerization, triethylenetetramine (TETA, RM1) and isophorone diamine (IPDA, RM2), whose hardening properties have already been thoroughly investigated [44], were made. The samples are tabulated and related to the results obtained for the new curing systems. With the passage of time, the changes in the hardness parameters of the samples did not change beyond 2D, therefore the Table 4 summarizes the collected data as average values for all measurements carried out for a given sample. The average value of the hardness of the samples in which systems with TFSI ILs were used was 79D, while systems with DCA IL was 85D and all these values are higher than the reference samples. The influence of the type of anion in the ionic liquid on the obtained hardness results is visible. DCA IL-based systems show a relatively higher hardness of the obtained materials than TFSI IL-based systems. However, in the case of these DCA systems, composed of ILs with an odd number of carbon atoms in the alkyl chain, they were characterized by significant brittleness, which made measurement impossible. Systems containing TFSI ILs have a smaller increase in hardness in relation to reference samples and at the same time, slightly higher values were observed for compounds **2b** (80D) and **4b** (81D), in which their structures contain chains with an odd number of carbon atoms.

Table 4. Hardness measurements results.

Compound	Hardness [D]
RM1/RM2	74/71
1b	78
2b	80
3b	76
4b	81
5b	n/a
1c	87
2c	n/a
3c	89
4c	n/a
5c	80

n/a—not available due to too high brittleness of the samples.

3. Discussion and Conclusions

3.1. Synthesis and ILs Stability

Hexamethylenetetramine is an unusual amine, obtained by the reaction of formaldehyde and ammonia. It does not melt, only sublimates, and is very sensitive to any changes in pH. Improperly stored or contaminated, it slowly decomposes to formaldehyde and ammonia. The decomposition phenomenon is probably caused by the hygroscopicity of the amine itself and by the presence of water, initiating a slow hydrolysis process that leads to the formation of formaldehyde and ammonia [45]. On the other hand, under the influence of temperature or during combustion (with access to oxygen), the HMTA decomposition pathways change. To illustrate, thermal decomposition mainly leads to nitrogen oxides, carbon dioxide, carbon monoxide and formaldehyde, while the combustion process generates carbon dioxide, nitrogen, nitrogen oxides and trace amounts of ammonia. Based on studies of the kinetics of HMTA decay conducted to understand the behavior of this molecule in the human body, the following conclusions can be drawn: (i) HMTA solution in water has a pH of 9.5, (ii) pH values lower than 9.5 initiate the decomposition process, (iii) no release of formaldehyde is observed up to pH 7.4, (iv) at a pH around 2.0, formaldehyde is released in higher quantities [46]. We assume that during the thermal curing of the resin with HMTA-based ionic liquids, formaldehyde is not released due to the high process temperature, and carbon oxides are released in its place. Nevertheless, there is a risk that residual unreacted ionic liquid in the cured resin structure will be able to release formaldehyde during storage. This is not the subject of the presented research, but in the case of further experiments, it may be advisable to carry out tests in the direction of determination of volatile organic compounds (VOCs) from the cured material.

In this work, several new chemical compounds are presented. From our point of view, the key aspect to discuss here is undoubtedly the very high purity of the salts obtained and the high efficiency of the reactions. This shows how useful the first step of the Delepine reaction is for the synthesis of new potential ionic liquids. However, this reaction is limited to the amine substrate—HMTA. While the halide salts obtained directly in it show high stability, signs of lower stability appear in the case of metathesis reaction products. The spatial structure of the quaternary HMTA cation, especially as a product of only a single chain attachment, is likely to be energetically highly unstable. Moreover, the liquid form of the compound, which allows the migration of molecules and the presence of, for example, anions derived from strong acids, additionally affects the stability of the compounds obtained due to high impact on pH. As HMTA quaternary ammonium salts, the products are highly sensitive to any changes in pH that may occur through spontaneous partial decomposition of the cation, which will shift the ionic balance. In addition, the nature of ionic liquids favors the absorption of even small amounts of water, which is absorbed in the compounds and facilitates the hydrolysis of the compound. In the case of HMTA, this leads directly to the release of ammonia, the smell of which is observable in the case of TFSI and DCA ionic liquids over time of their storage at room temperature. Undoubtedly,

this phenomenon is influenced primarily by the presence of water, but also by the fact that along with the breakdown of the cation structure, the concentration of anions increases, which results in a decrease in pH. In the case of the synthesis of quaternary ammonium salts based on HMTA, it is very important to monitor the purity of the obtained compounds, e.g., using ion chromatography. In this way, it is possible to quickly detect the potential presence of ammonia or other ionic structures that could be formed by the decomposition of the compound and, consequently, affect the possibility of using a given substance. On the one hand, the synthesis of this type of derivatives is exceptionally simple and gives a very wide field for the introduction of many alkylating agents from all groups of this type of compounds. However, one should be always carefully analyze the stability of the obtained substances and consider the possibility of changes in pH, which, by initiating the degradation process of the compound, may sometimes make it impossible to use them in specific application areas. In the case of application presented in this paper, the phenomenon of slow decay does not have a significant impact, and sometimes it is in favor of our solution.

3.2. Role of Ethylene Glycol

Ionic liquids are compounds with very different rheological parameters. Depending on many factors, such as (i) the length of the alkylated chain used or (ii) the type of anion, they can be compounds of very low viscosity as well as those with a viscosity resembling glue [47]. In fact, in some application areas, it is necessary to introduce additional substances that are designed to adjust the ionic liquids to a specific application, not only by changing the rheological properties, but sometimes also by additional interactions with ILs [48].

Ethylene glycol was not accidentally used in this work, which was supposed to fulfill the following tasks: (i) to reduce the viscosity of long-chain ionic liquids and at the same time increase their compatibility in combination with the epoxy resin molecule, (ii) due to its emulsifying properties [36,37], to form stable curing mixtures, (iii) be a substance capable of absorbing ammonia [49] and formaldehyde or eventually carbon dioxide [50] that could be released from the IL over time of its storage and (iv) remain in the structure of the cured resin, thanks to its high boiling point exceeding the temperature of the cross-linking process. In addition, during the study, the effect of ethylene glycol on slowing down the pH change process was observed, which was systematically controlled before each application experiment, using simple strip tests. Moreover, no ammonia odor was observed in mixture samples stored for 60 days. We suppose that through emulsification and connection with the structure of the IL, the EG undergoes a specific incorporation into the structure of the cation through a network of hydrogen bonds. Thus, this stabilizes the quaternary structure of HMTA and slows down the process of its breakdown. However, this is only an assumption requiring much extended research and theoretical calculations that would not affect the application presented in the work.

3.3. Curing Process and the Mechanism

The aim of this work was to demonstrate the use of new ionic liquids as active ingredients in the curing of epoxy resins. For this purpose, studies of the curing process were carried out, drawing key conclusions: (i) HMTA-based ionic liquids can successfully initiate the curing of epoxies, (ii) the low stability of these compounds favors their use in this area, resulting in lower temperatures of the curing process, (iii) the choice of anion affects the curing process itself, in particular the temperature range of the process. The quaternary hexamethylenetetramine cation can disintegrate under the influence of temperature into a whole spectrum of different types of molecules. Most of them are highly reactive, energetically unstable molecules, and able to react quickly with the epoxide groups of the resin. In Figure 4 several potential transition structures that may be generated during the process of thermal decomposition of HMTA-ILs have been proposed. The presented structures were inspired by the Delepine reaction mechanism, but also by data on HMTA decay directions [40,41]. The process generates, among others, primary amines based on an

alkyl chain that was attached to the generic cation structure. In addition, the process may also produce ammonia, which is easily reacted with the epoxy group to form a quaternary adduct, which is unstable and quickly initiates a chain reaction leading to full cross-linking of the resin structure.

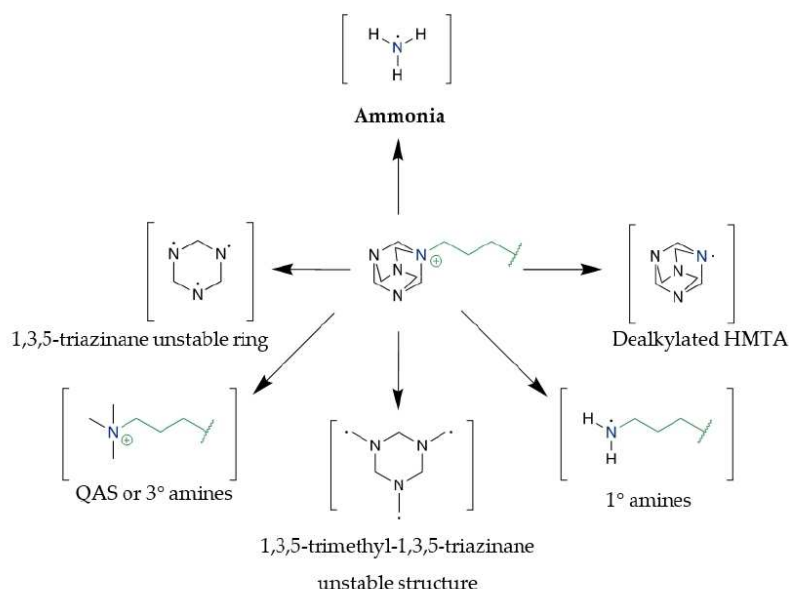


Figure 4. Proposed pathways of thermal decomposition of HMTA-based ILs.

Undoubtedly, in the case of curing the resin with ionic liquids based on HMTA, we are dealing with independently occurring processes of disintegration and simultaneous reaction with the epoxy groups present in the DGEBA molecule. In addition, the epoxy group can react with both basic (amines) and acidic compounds, which means that the anions present in the ionic liquid also react with the resin, leading to the formation of fully cross-linked structures. This phenomenon can be defined as cationic or anionic polymerization depending on which part of the ionic liquid is reacting with the epoxide at a given moment [21]. Both processes usually take place simultaneously, but if they occur at different temperatures, they are sometimes observable as separate polymerization peaks in thermal analysis. From the considerations regarding the ability to initiate the epoxy resin curing process, (i) due to their high thermal stability, and (ii) the lack of ionic liquid characteristics that would allow these compounds to be classified into this group, halide derivatives were excluded. So, the curing process of epoxy resin initiated by systems based on ionic liquids with TFSI anion is a process independent of the structure of the cation and its chain length. For all the tested compounds, the polymerization start, peak and end temperatures were similar, with the only exception being the derivative with an ethyl chain, which, probably due to its short chain, quickly joins the curing process and does not require the time necessary to generate appropriate, active transitional structures. What is more, this thesis becomes more likely with the information that a much greater amount of energy is released in the thermal process than in the case of analogous structures with longer carbon chains. In general, it can be concluded that the initiators based on HMTA–TFSI-ILs are characterized by a predictable and independent curing process. On the other hand, the polymerization reaction initiated by dicyanamides is characterized by a single thermal peak with a maximum temperature peak that depends on the chain length and generally decreases as it increases. More precisely, we assume that with the

increase in the length of the alkyl chain in the cation structure, the thermal stability of the compounds decreases, which means that active molecules directly participating in the reaction with epoxides are generated faster. At the same time, we noticed differences in the polymerization start temperature depending on whether the alkyl chain has an even or odd number of carbon atoms. We suggest that the reason for this phenomenon may be that structures with an odd number of carbon atoms in the chain will decay faster, especially at the very beginning of the process, through an energetically lower favorable structure. Against the background of all the tested substances, the **5c** derivative stands out the most, for which the polymerization start temperature is significantly lower than for the rest of the tested substances. However, the temperature peak for this substance is slightly lower than for the other representatives of this group, and the polymerization end temperature remains the same for all. We suggest that the reason for this may be the fact that the hexyl alkyl chain strains the cation structure significantly and the effect of ethylene glycol is not able to compensate for this phenomenon, so the molecule undergoes a slight disintegration, generating active initiators of resin polymerization, especially at the beginning after supplying temperature to the system, which can be seen by the recorded low polymerization start temperature and high process energy.

3.4. Hardness of the Materials

For additional characterization of the cured materials obtained, a simple measurement of the hardness of the resin after curing was chosen. Such a parameter allows one to quickly determine the effect of the tested substances on the final product and define certain regularities. The results showed that with the increase in the length of the carbon chain in the cation structure, the brittleness of the obtained material increases, which in some cases made it impossible to measure the hardness. We suggest that such a hardness test result correlates with the values of water absorbed by ionic liquids, and thus with the level of hygroscopicity of a particular ionic liquid. Moreover, as a rule, ionic liquids with TFSI anions are hydrophobic in nature, while dicyanamides are representatives of mainly hydrophilic compounds and it is for this group of compounds that information about significant brittleness has been reported more often. In addition, the brittle effect of the structure can sometimes also be caused by the presence of ethylene glycol.

In conclusion, it was proved during research that by using the first stage of the Delepine reaction, leading to the production of hexamethylenetetramine quaternary ammonium salts, it was possible to obtain a series of new ionic liquids that can be successfully used in epoxy resin curing mixtures operating only at elevated temperatures. What is more, the use of ethylene glycol as a component of such mixtures is presented, which simultaneously performs many functions important for the proposed area of application as well as for the obtained ionic liquids, especially in terms of their stability.

4. Materials and Methods

4.1. Materials

All reagents were purchased from suppliers: (i) Merck (alkylating agents, hexamethylenetetramine, triethylenetetramine, isophorone diamine, lithium bis(trifluoromethylsulfonyl)imide, sodium dicyanamide, ethylene glycol, organic solvents, reagents necessary to perform analyzes), and (ii) abcr GmbH (bisphenol A diglycidyl ether, DGEBA, silver nitrate). The minimum purity for alkylating agents, amines (beyond triethylenetetramine—97%) and compounds used for metathesis is 99%, while all solvents had a minimum HPLC grade. DGEBA was 85% purity.

4.2. Synthesis

4.2.1. Bromides

To obtain products **1a–5a**, a solution of hexamethylenetetramine (1.0 eq.) in chloroform was placed in a two-necked round-bottomed flask equipped with a reflux condenser with simultaneous stirring on magnetic stirrer. Then, corresponding alkyl bromide (1.0 eq.)

was added dropwise at room temperature. After that, a white precipitate was observed immediately. After the time required to complete the reaction (controlled with IC analysis), a large amount of white precipitate was filtered through a sintered funnel, then washed with hexane (3×10.0 mL) and diethyl ether (3×10.0 mL). Products were dried under vacuum (24 h) and recrystallized from a mixture of methanol and diethyl ether to furnish pure compounds.

Compound 1a

Product form: white solid; yield: 99.6%; water content: 0.47 wt%; IC: $t_R = 4.67$ min (cation), 4.14 min (anion), Purity: 99.6%; ^1H NMR (400 MHz, D_2O): $\delta = 5.05$ (s, 6H), 4.69 (d, $J = 12.4$ Hz, 3H), 4.54 (d, $J = 12.5$ Hz, 3H), 2.98 (q, $J = 7.5$ Hz, 2H), 1.25 (t, $J = 7.4$ Hz, 3H); ^{13}C (^1H) NMR (100 MHz, D_2O): $\delta = 77.72$, 70.14, 52.66, 4.95; MS (ESI): m/z (%) = 169 ($[\text{M}]^+$, 100), 155 ($[\text{HMTA}-\text{CH}_2]^+$), 140 ($[\text{HMTA}]^+$).

Compound 2a

Product form: white solid; yield: 99.0%; water content: 0.17 wt%; IC: $t_R = 4.89$ min (cation), 4.17 min (anion), Purity: 99.0%; ^1H NMR (400 MHz, D_2O): $\delta = 5.04$ (s, 6H), 4.63 (d, $J = 14.9$ Hz, 3H), 4.52 (d, $J = 13.4$ Hz, 3H), 2.81 (m, 2H), 1.67 (ddd, $J = 15.3$, 7.4, 5.3 Hz, 2H), 0.89 (t, $J = 7.3$ Hz, 3H); ^{13}C (^1H) NMR (100 MHz, D_2O): 77.65, 70.15, 58.32, 20.77, 13.63; MS (ESI): m/z (%) = 183 ($[\text{M}]^+$, 100), 155 ($[\text{HMTA}-\text{CH}_2]^+$), 140 ($[\text{HMTA}]^+$).

Compound 3a

Product form: white solid; yield: 99.1%; water content: 0.68 wt%; IC: $t_R = 5.12$ min (cation), 4.16 min (anion), Purity: 99.1%; ^1H NMR (400 MHz, D_2O): $\delta = 5.06$ (s, 6H), 4.65 (d, $J = 15.5$ Hz, 3H), 4.54 (d, $J = 13.0$ Hz, 3H), 2.87 (m, 2H), 1.65 (ddd, $J = 15.6$, 12.6, 7.5 Hz, 2H), 1.32 (dd, $J = 14.8$, 7.4 Hz, 2H), 0.89 (t, $J = 7.4$ Hz, 3H); ^{13}C (^1H) NMR (100 MHz, D_2O): 78.13, 70.14, 60.45, 26.82, 19.61, 14.03; MS (ESI): m/z (%) = 197 ($[\text{M}]^+$, 100), 168 ($[\text{HMTA}-\text{CH}_2-\text{CH}_2]^+$), 155 ($[\text{HMTA}-\text{CH}_2]^+$), 140 ($[\text{HMTA}]^+$).

Compound 4a

Product form: white solid; yield: 99.1%; water content: 0.57 wt%; IC: $t_R = 5.78$ min (cation), 4.12 min (anion), Purity: 99.1%; ^1H NMR (400 MHz, D_2O): $\delta = 5.05$ (s, 6H), 4.66 (d, $J = 13.5$ Hz, 3H), 4.55 (d, $J = 13.1$ Hz, 3H), 2.85 (m, 2H), 1.65 (dd, $J = 15.4$, 7.5 Hz, 2H), 1.31 (m, 4H), 0.83 (t, $J = 7.1$ Hz, 3H); ^{13}C (^1H) NMR (100 MHz, D_2O): 77.52, 70.93, 60.43, 31.57, 25.32, 19.70, 13.05; MS (ESI): m/z (%) = 211 ($[\text{M}]^+$, 100), 182 ($[\text{HMTA}-\text{CH}_2-\text{CH}_2-\text{CH}_2]^+$), 168 ($[\text{HMTA}-\text{CH}_2-\text{CH}_2]^+$), 155 ($[\text{HMTA}-\text{CH}_2]^+$), 140 ($[\text{HMTA}]^+$).

Compound 5a

Product form: white solid; yield: 99.0%; water content: 0.42 wt%; IC: $t_R = 6.34$ min (cation), 4.10 min (anion), Purity: 99.1%; ^1H NMR (400 MHz, D_2O): $\delta = 5.03$ (s, 6H), 4.67 (d, $J = 13.1$ Hz, 3H), 4.51 (d, $J = 12.7$ Hz, 3H), 2.84 (dd, $J = 11.9$, 5.5 Hz, 2H), 1.63 (dd, $J = 15.8$, 7.8 Hz, 2H), 1.26 (m, 6H), 0.80 (t, $J = 6.9$ Hz, 3H); ^{13}C (^1H) NMR (100 MHz, D_2O): 78.12, 70.12, 57.32, 30.25, 25.47, 21.64, 19.10, 13.15; MS (ESI): m/z (%) = 225 ($[\text{M}]^+$, 100), 182 ($[\text{HMTA}-\text{CH}_2-\text{CH}_2-\text{CH}_2]^+$), 155 ($[\text{HMTA}-\text{CH}_2]^+$), 140 ($[\text{HMTA}]^+$).

4.2.2. Bis(trifluoromethane)sulfonimides

Compounds **1b–5b** were obtained according to a slightly modified, previously reported procedure. Corresponding bromide (**1a–5a**, 1.0 eq.) was dissolved in deionized water (100.0 mL) and transferred into a separating funnel. Then, methylene chloride was added followed by an aqueous solution of lithium bis(trifluoromethylsulfonyl)imide (80%, 1.1 eq.). The obtained mixture was vigorously shook for a few minutes and then the separated organic layer was washed with deionized water (3×20.0 mL) and then deionized water with small portion of lithium bis(trifluoromethylsulfonyl)imide (80%, 0.1 eq., 1×20.0 mL). The washing procedure was finished in an absence of bromide anion in the water layer (silver nitrate test, and washed until no observable yellow silver bromide precipitation). To obtain pure product (**1b–5b**), methylene chloride from the organic layer was evaporated under reduced pressure and bis(trifluoromethylsulfonyl)imide ionic liquid was dried under vacuum (24 h).

Compound 1b

Product form: slightly yellow liquid; yield: 98.8%; water content: 0.31 wt%; IC: t_R = 4.57 min (cation), 18.58 min (anion), Purity: 99.8%.

Compound 2b

Product form: yellow liquid; yield: 97.7%; water content: 0.23 wt%; IC: t_R = 4.94 min (cation), 18.71 min (anion), Purity: 99.6%.

Compound 3b

Product form: transparent liquid; yield: 99.1%; water content: 0.28 wt%; IC: t_R = 5.19 min (cation), 18.73 min (anion), Purity: 99.5%.

Compound 4b

Product form: yellow liquid; yield: 98.9%; water content: 0.49 wt%; IC: t_R = 5.81 min (cation), 18.69 min (anion), Purity: 99.1%.

Compound 5b

Product form: yellow, viscous liquid; yield: 97.6%; water content: 0.38 wt%; IC: t_R = 6.31 min (cation), 18.71 min (anion), Purity: 99.1%.

4.2.3. Dicyanamides

Compounds **1c–5c** were obtained according to a slightly modified previous reported procedure. A precisely weighed amount of corresponding bromide (**1a–5a**, 1.0 eq.) was placed in the flask and dissolved in deionized water (30.0 mL). Then, freshly prepared silver dicyanamide was added (1.0 eq.) and the mixture was stirred on a magnetic stirrer, protected from a sunlight. The exchange process was monitored by ion chromatography. After completion of the reaction, the yellow precipitate of silver bromide was separated on a sintered funnel using a glass fiber filter, and washed with water (3×15.0 mL). The filtrate was evaporated in a vacuum evaporator, and then the obtained compound was purified by dissolution in anhydrous methylene chloride and repeated filtration. To obtain pure product (**1c–5c**), methylene chloride was evaporated under reduced pressure and dicyanamide ionic liquid was dried under vacuum (24 h).

Compound 1c

Product form: yellow solid; yield: 96.2%; water content: 0.73 wt%; IC: t_R = 4.59 min (cation), 6.66 min (anion), Purity: 98.1%.

Compound 2c

Product form: slightly yellow solid; yield: 87.9%; water content: 0.43 wt%; IC: t_R = 4.92 min (cation), 6.59 min (anion), Purity: 97.9%.

Compound 3c

Product form: yellow solid; yield: 97.5%; water content: 0.86 wt%; IC: t_R = 5.16 min (cation), 6.58 min (anion), Purity: 98.1%.

Compound 4c

Product form: yellow, viscous solid; yield: 93.9%; water content: 0.69 wt%; IC: t_R = 5.83 min (cation), 6.63 min (anion), Purity: 97.8%.

Compound 5c

Product form: yellow, viscous solid; yield: 97.0%; water content: 0.33 wt%; IC: t_R = 6.29 min (cation), 6.60 min (anion), Purity: 97.5%.

4.3. Ion Chromatography

All experiments were conducted with the use of ion chromatography, both regarding the control of the reaction course and the determination of the purity of the obtained compounds, which were performed using Eco-IC apparatus (Metrohm, Herisau, Switzerland) in accordance with the procedures published in previous works [12,21].

4.4. Thermal Analysis

4.4.1. Differential Scanning Calorimetry (DSC) for ILs

Melting point/glass transition/decomposition temperature analyses were determined using the DSC 3 apparatus (Mettler Toledo, Greifensee, Switzerland), according to the method reported in previous work [12,21] and described in Supplementary Materials.

4.4.2. Differential Scanning Calorimetry (DSC) for Epoxy Systems

The cross-linking process of the epoxy resin was tested using a DSC 8500 apparatus (PerkinElmer, Waltham, MA, USA), according to a slightly modified method described in the previous work [21] and described in Supplementary Materials.

4.5. Water Content

Determination of the water content in the obtained compounds was carried out using the Karl Fischer titration apparatus (Metrohm, Herisau, Switzerland) in accordance with the method described in previous works [12,21].

4.6. NMR Analysis

NMR spectra were recorded using a 400 MHz (^1H) and 100 MHz (^{13}C) Ascend spectrometer (Bruker, Billerica, MA, USA) in commercially available D_2O solvent. The value of standard measurement uncertainty did not exceed ± 0.02 ppm.

4.7. ESI-MS Analysis

ESI-MS analysis were conducted using a HPLC/MS apparatus (Waters Corporation, Milford, MA, USA), according to the procedure described in the previous work [12].

4.8. Curing Process

All experiments regarding the curing process were performed in accordance with the procedure described in the previous work [21]. For microscopic documentation of cured samples see the Supplementary Materials.

4.9. Hardness Measurements

All experiments regarding the hardness measurements were performed in accordance with the procedure described in the previous work [21].

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/molecules28020892/s1>, 1. NMR spectra; 2. DSC thermograms for ILs measurements; 3. DSC thermograms for curing process; 4. Microscopic pictures of cured samples; Figure S1. Microscopic pictures of cured samples.

Author Contributions: Conceptualization, D.Z. and A.S.; Formal analysis, D.Z.; Funding acquisition, M.S.; Investigation, D.Z., A.S. and P.H.; Methodology, D.Z. and A.S.; Software, D.Z. and A.S.; Supervision, M.S.; Validation, D.Z.; Visualization, D.Z.; Writing—original draft, D.Z.; Writing—review & editing, D.Z., A.S. and M.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by National Science Centre, grant number 2017/26/E/ST8/01059 and grant number 2019/35/B/ST8/03736.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

Sample Availability: Not available.

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Behavior, synthesis, and effectiveness of an activity of anilinium-based Ionic Liquids (AnILs) as a hardeners and modifiers for epoxy-coatings of flax biocomposites

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ARTICLE INFO

Keywords:

Epoxy resin
Epoxy resin coating
Ionic liquids
Composites
Flax-fiber reinforcement

ABSTRACT

This paper presents a comprehensive investigation of the synthesis and properties of anilinium-based ionic liquids (AnILs) incorporating dicyanamide [DCA] and trifluoromethanesulfonate [OTf] anions. This study systematically examines the thermal behavior of these AnILs, highlighting the influence of cation size on distinct thermal transitions. Crucially, detailed thermal analyses were conducted for both AnILs and their corresponding epoxy resin systems. AnILs featuring [DCA] anion exhibited lower enthalpy values, indicative of a gradual polymerization process with potential energy inefficiency. In contrast, AnILs with [OTf] anion displayed elevated enthalpy values, signifying accelerated polymerization and significant potential for crosslinking. The resulting epoxy coatings were subjected to meticulous mechanical analyses. Notably, AnILs with a dicyanamide anion exhibited a noteworthy correlation between increased strength, enhanced crosslinking, and heightened structural complexity. Conversely, anilinium-based ionic liquids with [OTf] anion displayed distinctive polymerization behavior, even at lower temperatures. Investigation of the curing mechanics uncovered distinct polymerization pathways influenced by factors such as anion strength, dealkylation initiation temperature, and structural branching. Tensile strength assessments of coatings with trifluoromethanesulfonate anion revealed intriguing behavior, indicating that additional reinforcement during curing, is essential for maintaining structural integrity in impact-prone scenarios. Moreover, this study proposed a novel mechanism involving residual aniline molecules that influence structural outcomes. Overall, this research provides valuable insights into the intricate interplay of AnILs structures, polymerization dynamics, and mechanical properties, providing a foundational understanding for future advancements in functional coating applications.

1. Introduction

In the ever-progressing field of chemistry, there is a constant development of chemical substances. One notable example of this rapid progress is seen in ionic liquids (ILs). Made up of positively and negatively charged parts, these compounds are becoming widely used in many scientific areas, such as catalysis [1–4], biomass dissolution [5–8], electrochemistry [9,10], modification of various types of materials [11–13] or pharmaceuticals [14–16]. It is impossible to list all the applications of ILs currently being explored around the world, which proves not only their extraordinary usefulness, but also shows that a number of their physicochemical properties are of importance in the context of various applications. Ionic liquids exhibit near-zero vapor pressure, high

thermal stability and, due to their ionic structure, high conductivity [17–20]. Importantly, they can be customized for specific applications. Analogous to the substrate-specificity of enzymes governed by the lock-and-key mechanism, ionic liquids can be carefully designed to optimize their functional potential, allowing them to perform various tasks effectively. The presence of positively charged nitrogen, sulfur, or phosphorus elements in the cationic structures of organic compounds, combined with the abundance of counter ions in the form of organic and inorganic anions, provides flexibility for precise adjustments to the physicochemical features of these compounds. This creates a broad range of opportunities for their use in different and independent areas, taking advantage of the unique qualities of ionic liquids. These custom-made mixtures, carefully designed to meet specific needs, often appear

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<https://doi.org/10.1016/j.porgcoat.2024.108353>

Received 21 November 2023; Received in revised form 30 January 2024; Accepted 20 February 2024

Available online 23 February 2024

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as highly effective solutions. Moreover, a significant aspect involves the easy obtainment of most ionic liquids through simple chemical transformations, allowing for the achievement of desired structural configurations in just two synthetic steps.

The progress in creating new materials with specific functions is driven by the need for advanced technologies. These needs require the development of materials with the exact qualities essential for their optimal performance in specific situations. Simultaneously, focusing on sustainability is crucial in exploring ways to recycle materials and creating strategies using renewable resources or compounds that naturally break down. This approach leads to the production of simple and environmentally friendly chemicals. In this context, epoxy resins (ER) are considered a good option for construction materials that align with the requirements of emerging technologies. Epoxy resins can be easily modified in terms of their entire volume [21,22] and coating [23–25], processed under specific conditions, and are compatible with various reinforcements such as carbon [26], flax [27–29], cellulose [30,31], basalt [27,28,32], and aramid fibers [11], as well as fillers such as silica [33–35], graphite [36] or inorganic compounds [37]. Their potential use of natural raw materials, such as cardanol [38–40], and the ongoing research into their recycling [41] make them a justified and advisable choice. Moreover, the utilization of hyperbranched polymers derived from itaconic anhydride has led to significant improvements in the toughness and flame-retardant properties of epoxy resins with low phosphorus contents [42]. Additionally, achieving high mechanical performance, recyclability, and maintaining thermal properties were accomplished through the adoption of ferulic acid-based hyperbranched epoxy resin (FEHBP) in the fabrication of catalyst-free epoxy vitrimers [43].

One important area of application for ionic liquids is composites and biocomposites, especially systems based on epoxy resins of various types, including new resins derived from natural raw materials [38,44]. The most important applications of ILs in this field are primarily latent cure initiators for epoxy resins [45–50], whose research began with a landmark publication in 2009 [51]. When combined with epoxy resin and exposed to temperature, ionic liquids with a positive charge on the nitrogen atom react with the resin molecules in a manner similar to that of tertiary amines. Furthermore, the anion of the ionic liquid may also be capable of curing the resin in its characteristic mechanism [45,52–55]. Moreover, ILs can also affect the mechanical properties of composites such as strength [56,57], hardness [45] and more [58]. An important property of ionic liquids is their ability to make composite materials flame retardant [57,59–61] or to impart anti-corrosion [62,63] or anti-fouling [64] properties. These compounds have also been successfully used to modify the structures of composite reinforcements such as aramid [11], carbon [65], or natural fibers [30,66,67]. Epoxy resins modified with ILs can be used in solid electrolytes, bringing this building material into a new field of application [68,69]. Appropriately designed ionic liquids can perform multiple functions simultaneously in composite systems [70], and recently, it has been confirmed that ILs can dissolve already cured epoxy resins, thus allowing them to be recycled [41].

In recent years, an array of imidazolium-based ionic liquids has been meticulously examined, serving dual roles as epoxy resin hardeners and coatings for steel surfaces. The coating, when applied to steel, has shown significant improvements in terms of interfacial adhesion, long-term durability, and its resistance to corrosion. Impressively, this coating has proven to endure exposure to salty conditions for an extended period, protecting the steel for up to 1500 h [46]. Another approach to address the same issue involves using a cross-linked ionic liquid network as a protective coating. This method has been suggested and used to prevent rust and corrosion. Its effectiveness comes from its ability to repel water solutions containing salt and moisture, which slows down the degradation process. This occurs because the ionic liquid structure contains large cationic and anionic components. In the reported study, the first step involves treating the imidazolium-based ionic liquid with a

polyamine compound through a condensation reaction. Subsequently, the resulting product is utilized as a hardening agent for epoxy resin formulations. When applied as specialized coatings for steel substrates, they undergo thorough evaluation of their inherent anti-corrosion properties and resistance to salt spray-induced deterioration [62]. Conversely, an inquiry into the influence of imidazolium-based ionic liquids (1-butyl-3-methylimidazolium chloride) on epoxy coatings modified with graphene has been undertaken. In this context, IL serves as a dispersant within this composite matrix, significantly improving the protective qualities of graphene in the coating. These improvements involve preventing corrosion and resisting moisture, which are achieved by the ionic liquid attaching to the surface of graphene nanosheets and strengthening the connections in the composite structure [71]. Mono- and bilayer configurations of epoxy coatings, integrating distinct IL formulations, namely, 1-octyl-3-methylimidazolium tetrafluoroborate and bis(2-hydroxyethyl)ammonium oleate, were subjected to experimental evaluation. These multifaceted coatings, with dispersed graphene in the ionic liquid, were assessed for their tribological performance concerning wear resistance and frictional mitigation. Interestingly, the ionic liquid with a fluorinated tetrafluoroborate anion showed effective performance when in a single layer, resulting in a significant 60 % reduction in the friction coefficient. On the other hand, the one with the oleate anion required a two-layer structure to achieve similar levels of reduced friction and wear resistance [72].

An interesting type of ILs is made from quaternary ammonium salts originating from aniline derivatives. The distinctive properties exhibited by this group of compounds have attracted significant attention, both for exploring their applications and for improving their synthetic methodologies. Research into these compounds follows two main paths. The first involves the synthesis of straightforward protonated salts through acid-base reactions between aniline derivatives and corresponding acids, yielding compounds with melting points below 100 °C [73–75]. On the other hand, the second path creates quaternary alkylated salts, which can be synthesized using the classical Menshutkin reaction, which involves the reaction of tertiary amines with suitable alkyl halides. The resulting halide salt can then undergo metathesis to replace the halogen anion with another that is more suitable for the intended application. Nevertheless, alternative synthetic pathways for AnILs have also been recognized [76,77]. In the example mentioned earlier, a quaternary salt with the [OTf] anion is synthesized in a single step, devoid of transition metals and requiring specialized conditions. This efficient synthesis reduces the time required for producing AnILs with the trifluoromethanesulfonate anion into a single step, eliminating the need to first prepare a halide salt.

After examining the existing literature and reports on the uses of anilinium-based ionic liquids (AnILs), it is evident that their applications are somewhat limited, mostly involving tasks beyond organic synthesis. In these contexts, AnILs function as catalysts or reagents that undergo subsequent transformations, often bypassing the isolation stage of the quaternary salt [77]. Particular attention is directed toward anilinium-based ionic liquids featuring the trifluoromethanesulfonate anion, as well as tosylate and various halide anions. Owing to their distinctive structural composition in which the quaternary nitrogen atom is directly linked to an aryl group and alkyl moieties, these compounds are used as both alkylation and arylation agents, with the reaction's direction influenced by the catalysts or reaction conditions [78,79]. Notably, important catalysts used with AnILs include metals such as palladium and nickel, enabling the synthesis of various organic compounds, including aryl ketones, esters, aldehydes, amides, and 1-aryl/alkyl substituted alk-1-yne [77,80].

However, the crucial aspect of anilines produced from this process is their inherent tendency to form polymers, specifically polyaniline (PANI), through both chemical and electropolymerization processes. The discussions mainly focus on thoroughly investigating this phenomenon, which includes understanding the conditions that govern the polymerization processes and explaining the material properties of the

resulting products. Moreover, AnILs, particularly protonated salts exhibits activity within the context of electropolymerization [74,75]. In the ongoing research, specific attention has been given to instances where PANI is combined with carbon nanotubes and ionic liquids. These studies confirm a noticeable improvement in the corrosion resistance of epoxy coatings across a wide pH range when PANI and ILs are combined. Moreover, the demonstrated increase in resistance is directly linked to how long the specimens are immersed in the solutions causing corrosion [87,88].

This research aims to explore methods for creating a new type of ionic liquids using aniline derivatives (AnILs). These liquids have *N,N*-dimethylaniline and *N,N*-diethylaniline as cation sources and dicyanamide [DCA] and trifluoromethanesulfonate [OTf] as anions. The synthesis is complemented by extensive evaluation of their physicochemical attributes. Subsequently, these synthesized compounds have been used in the formulation of coating systems with epoxy resin, and applied to flax fabric. Notably, within these developed systems, the ionic liquids assume a principal role as hardeners, and are administered in significantly reduced quantities - five times less than conventionally employed solutions such as triethylenetetramine. Despite the reduced quantity, the coatings still exhibit similar mechanical properties. Additionally, the ionic liquids help create stable IL/ER coating systems that undergo curing solely under controlled temperature conditions, in contrast to amine-cured systems that initiate crosslinking even at ambient temperatures. This study involves comprehensive analyses using Differential Scanning Calorimetry (DSC), revealing complex relationships between the anionic part of the ionic liquid and the epoxy coating's polymerization process. Moreover, an explanation of the initiation mechanism for curing, prompted by the synthesized ionic liquids, is described. Notably, AnILs with the [OTf] anion, due to their strong acidity, create favorable conditions during the coating's cooling phase that catalyze the polymerization of residual aniline derivative molecules. This leads to the formation of shorter polyaniline chains (PANI) in the coating structure after curing. This study lays the foundation for future investigations into this interesting class of compounds, suggesting their potential to bring various qualities to epoxy coatings.

2. Materials and methods

2.1. Materials

N,N-dimethylaniline >99 %, *N,N*-diethylaniline >99 %, Trimethylphenylammonium bromide <98 %, Silver nitrate >99 %, were purchased from Merck GmbH (Germany), Bromoethane >98 % and Benzyl bromide >99 % were purchased from Thermo Scientific Chemicals Inc. (USA), Sodium dicyanamide >97 % was purchased from IoLiTec-Ionic Liquids Technologies GmbH (Germany), Methyl trifluoromethanesulfonate >97 % was purchased from Ambeed Inc. (USA). Styrene modified epoxy resin, Epidian 53 was purchased from Ciech Sarzyna S. A. (Poland). Flax fabric, FLAXDRY-UD180 cross-stitched unidirectional flax fabric 180 g/m² was purchased from Hexcel Corporation Inc. (USA). All organic solvents used in synthesis and during chromatographic analysis were of HPLC grade and were purchased from Merck GmbH (Germany).

2.2. Synthesis of the halides

2.2.1. Triethylphenylammonium bromide [TEA][Br]

N,N-Diethylaniline (10 g, 0.067 mol, 1 eq.) was dissolved in acetonitrile (100 mL) and heated to 50 °C. Then, 1-bromoethane (7.39 g, 0.067 mol, 1 eq.) was added dropwise and the reaction mixture was stirred under reflux for 96 h. Afterwards, the acetonitrile was evaporated, and the resulting precipitate was washed with ethyl acetate (3 × 40 mL) and dried under vacuum. White solid was obtained (16.5 g, 95.4 %). *T*_m = 123.4 °C, *T*_c = 110.8 °C.

IC: *t*_R = 7.52 min (cation), 5.25 min (anion), Purity: 99.90 %. ¹H

NMR (400 MHz, CDCl₃): δ = 7.87 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 2H), 7.41 (t, *J* = 8.3 Hz, 2H), 7.30 (dd, *J* = 8.1 Hz, *J* = 6.9 Hz, 1H), 3.92 (q, *J* = 7.0 Hz, 6H), 1.01 (t, *J* = 7.2 Hz, 9H). ¹³C {¹H} NMR (100 MHz, CDCl₃): δ = 140.99, 130.47, 129.90, 122.18, 56.11, 8.00.

2.2.2. *N*-Benzyl-*N,N*-dimethylphenylammonium bromide [BenzDMA][Br]

N,N-Dimethylaniline (10 g, 0.083 mol, 1 eq.) was dissolved in acetonitrile (100 mL) and heated to 60 °C. Then, benzyl bromide (14.2 g, 0.083 mol, 1 eq.) was added dropwise, and the reaction mixture was stirred under reflux for 48 h. Afterwards, the acetonitrile was evaporated, and a dark blue, viscous liquid was obtained. Next, it was washed three times with acetone (3 × 50 mL) and evaporated. The obtained light blue solid was crystallized from acetone and a gray solid was obtained (7.23 g, 30 %). *T*_m = 88.6 °C.

IC: *t*_R = 9.61 min (cation), 5.22 min (anion), Purity: 99.97 %. ¹H NMR (400 MHz, CDCl₃): δ = 7.79 (d, *J* = 8.1 Hz, 2H), 7.44 (m, 3H), 7.20 (t, *J* = 7.2 Hz, 1H), 7.03 (m, 4H), 5.54 (s, 2H), 3.88 (s, 6H). ¹³C {¹H} NMR (100 MHz, CDCl₃): δ = 144.30, 132.67, 130.45, 130.39, 130.32, 128.52, 127.63, 121.62, 72.72, 53.46.

2.3. Methatesis

2.3.1. Dicyanamides

2.3.1.1. General procedure A. Dicyanamides were obtained according to a the previously reported procedure [81]. Briefly, corresponding bromide (1 eq.) was dissolved in deionized water. Then, freshly prepared silver dicyanamide was added (1 eq.) and the mixture, protected from sunlight, was stirred at room temperature. Next, silver bromide was separated, and the filtrate was evaporated. The obtained compounds were dried under vacuum.

Trimethylphenylammonium dicyanamide [TMA][DCA]

[TMA][DCA] was obtained according to the general procedure A as a white solid (Yield: 98 %). IC: *t*_R = 5.75 min (cation), 6.55 min (anion), Purity: 97.85 %.

Triethylphenylammonium dicyanamide [TEA][DCA]

[TEA][DCA] was obtained according to the general procedure A as an orange liquid (Yield: 97 %). IC: *t*_R = 7.55 min (cation), 6.61 min (anion), Purity: 98.44 %.

N-Benzyl-*N,N*-dimethylphenylammonium dicyanamide [BenzDMA][DCA]

[BenzDMA][DCA] was obtained according to the general procedure A as a brown liquid (Yield: 97 %). IC: *t*_R = 9.58 min (cation), 6.65 min (anion), Purity: 97.63 %.

2.3.2. Trifluoromethanesulfonates

2.3.2.1. General procedure B. Trifluoromethanesulfonates were obtained according to a previously reported procedure [82]. Briefly, the corresponding bromide (1 eq.) was dissolved in MeOH and methyl trifluoromethanesulfonate (1 eq.) was added dropwise. Next, the solvent was evaporated and obtained the products were dried under vacuum.

Trimethylphenylammonium trifluoromethanesulfonate [TMA][OTf]

[TMA][OTf] was obtained according to the general procedure B as a beige solid (Yield: 99 %). IC: *t*_R = 5.74 min (cation), 7.45 min (anion), Purity: 99.52 %.

Triethylphenylammonium trifluoromethanesulfonate [TEA][OTf]

[TEA][OTf] was obtained according to the general procedure B as a yellow liquid (Yield: 99 %). IC: $t_R = 7.53$ min (cation), 7.38 min (anion), Purity: 99.72 %.

N-Benzyl-*N,N*-dimethylphenylammonium trifluoromethanesulfonate [BenzDMA][OTf]

[BenzDMA][OTf] was obtained according to the general procedure B as a beige solid (Yield: 99 %). IC: $t_R = 9.63$ min (cation), 7.40 min (anion), Purity: 99.85 %.

2.4. Nuclear magnetic resonance spectroscopy (NMR) analysis

NMR Spectroscopic analyses were performed using a Bruker Ascend™ (USA) instrument. ^1H spectra recorded with a resolution of 400 MHz, while ^{13}C spectra were recorded with a resolution of 100 MHz. The deuterated solvent used in each analysis was indicated when describing the synthesis of each compound. The value of standard measurement uncertainty did not exceed ± 0.02 ppm.

2.5. Ion Chromatography (IC)

All chromatographic analyses, both progress of the reaction and purity of the compounds obtained, were performed on an Ion chromatograph EcoIC from Metrohm AG (Switzerland). The analytical methods used in the study were developed from the authors previous publications and a full description of them can be found in Supplementary materials.

2.6. Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA)

All tests using DSC, both for the analysis of ionic liquids and the study of the curing process of epoxy resin, were performed on a DSC-3 Mettler-Toledo (Switzerland) instrument. All thermogravimetric analyses of ionic liquids were performed on a Q50 TA Instruments (USA). All analytical protocols are based on the measurement parameters previously reported by the authors, a detailed description of which is provided in Supplementary materials.

2.7. Coating preparation

Systems of epoxy resin Epdian 53 with ILs (98:2) were used to produce monolayer composite structures reinforced with flax fibers. For

this purpose, the technique of hand lamination of fabric fibers using a previously degassed resin system was used. During the wetting of the fibers with resin, the degree of resin saturation was controlled and maintained at 50–55 %. The prepregates were cured in a vacuum oven at 130 °C for 5 h, in the form of composite sheets with dimensions of 30×30 cm.

2.8. Mechanical properties examination

The mechanical properties of the composite structures were tested using a Scanning Electron Microscope (SEM, Hitachi SU3500, Japan) equipped with a measuring table for mechanical testing of the materials (Deben Microtest MT5000 kit (United Kingdom)). For this purpose, measuring samples with dimensions of 2×3.5 cm and a thickness of 0.5–0.6 mm were prepared. Then, the samples were placed in the measuring jaws, with a jaw extension rate of 1.5 mm/min. During the measurement a 2KN single leadscrew tensile with 415:1 gearbox and 512-line encoder was used. The apparatus was calibrated at 2000 N, and a trip was set to 2000 N. The measurement was performed until the continuity of the composite structure was broken, observing a visible decrease in the force value. Based on the measurements carried out, the following were determined: (i) the force at break and (ii) the maximum elongation of the sample at break. The measurement data obtained were used to determine the following: (iii) tensile strength, defined as the stress corresponding to the highest tensile force F obtained during the static tensile test, related to the original cross-sectional area of the sample [83,84], (iv) modulus of elasticity, which quantifies the relationship between tensile stress (force per unit area) and axial strain (proportional deformation) [85–87], and (v) crosslinking degree presented as a linear relationship of ultimate tensile strength [88] with respect to a reference material with a degree of crosslinking at the level of 99.20 %. For each sample of material, 6 repetitions were made, the average result of which was used when presenting and discussing the results in the paper.

3. Results and discussion

3.1. Synthesis of AnILs

Two amines were used for the preparation of anilinium-based ionic liquids, namely *N,N*-dimethylaniline and *N,N*-diethylaniline, as well as one commercially available AnIL, trimethylphenylammonium bromide. For the preparation of halide salts, the Menshutkin reaction was conducted (Fig. 1), which is the formation of a quaternary ammonium salt. *N,N*-Dimethylaniline was reacted with benzyl bromide and *N,N*-diethylaniline with bromoethane. Both reactions were carried out at elevated

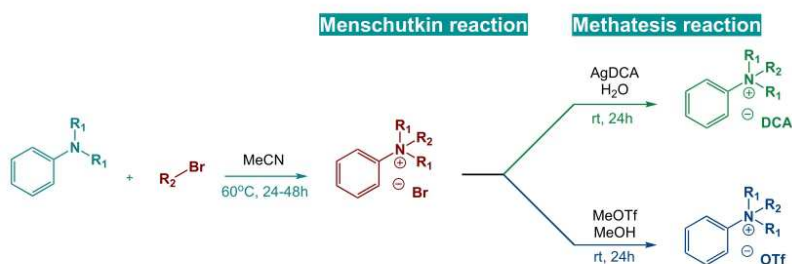


Fig. 1. Reaction scheme of the ionic liquids synthesis.

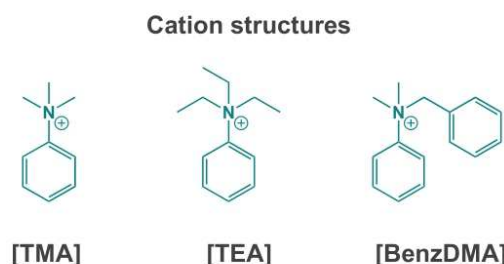


Fig. 2. Cation structures of the obtained ILs.

Table 1
Thermal properties of the obtained ILs.

No	IL	Thermal analysis			
		T _g [°C]	T _m [°C]	T _c [°C]	T _{cc} [°C]
1	[TMA][DCA]		109.7	44.2	
2	[TMA][OTf]		75.4	14.7	
3	[TEA][DCA]	−48.0			
4	[TEA][OTf]		5.5		−20.6
5	[BenzDMA][DCA] ^a				
6	[BenzDMA][OTf]	−45.0			

^a Polymerization occurs: T_{onset} = 136.0 [°C], T_{max} = 158.9 [°C], T_{endset} = 181.9 [°C], ΔH = 95.9 [J/g].

temperatures (60 °C), with acetonitrile as a solvent.

As described previously, aniline readily undergoes polymerization reactions, and during the synthesis of *N*-benzyl-*N,N*-dimethylanilinium bromide, the reaction mixture changed colors, and after 96 h it became dark blue, which indicated that some of the tertiary amine underwent thermal polymerization. Hence, a workup procedure was required to retrieve the quaternary salt. Furthermore, all three bromide salts were used in two different metathesis reactions. First, ILs with dicyanamide anion were obtained, by reaction of halide salts with freshly prepared silver dicyanamide. The structures of the ILs cations are shown in Fig. 2. Second, by employment of methyl trifluoromethanesulfonate, anilinium-based ionic liquids with trifluoromethanesulfonate as an anion were obtained. Both procedures have been previously reported by us. The purity of all obtained AnILs was characterized by Ion Chromatography (IC), both cationic and anionic.

The NMR analysis was conducted to confirm the chemical structures of the obtained halide salts. In the ¹H NMR spectrum of [TEA][Br], distinct resonances are observed (at δ = 7.87, 7.41 and 7.30), attributed to the aromatic protons of the phenyl ring. The complexity in the coupling constants suggests a non-trivial conformation of the phenylammonium moiety. In addition, signals at 3.92 and 1.01 ppm represent the methylene and methyl protons of the triethyl substituents, respectively. The ¹H NMR spectrum of [BenzDMA][Br] displays resonances at 7.79 and 7.44 ppm for the benzyl protons, whereas signals at 7.20 and 7.03 ppm are attributed to the phenyl ring. Notably, a singlet at 5.54 ppm corresponds to the benzylmethine protons, and a singlet at 3.88 ppm represents the dimethylammonium moiety. [TEA][Br] exhibits a more straightforward aromatic system with triethyl substituents, whereas [BenzDMA][Br] displays a more complex structure with benzyl and dimethylammonium groups.

3.2. Thermal analysis

3.2.1. Thermal properties of the AnILs

All obtained ionic liquids were analyzed using differential scanning calorimetry to determine their thermal properties. The results of the

analyses are summarized in Table 1.

From the data obtained, it can be observed that as the size of the cation of the ionic liquid increases, the thermal nature of the compound changes. The least expanded cation - [TMA], is characterized by thermal transitions corresponding to the melting point (T_m) and crystallization temperature. On the other hand, the cation having three ethyl chains - [TEA], shows a thermal transition corresponding to the glass transition temperature (T_g) or the melting point, depending on the anion. In addition, for [TEA][OTf] cold crystallization (T_{cc}) can be observed. It is a phase transition that is present between the glass and melting transitions temperatures. The cation with the largest spacial structure, [BenzDMA], with [DCA] as an anion undergoes thermal polymerization. On the other hand the same cation with [OTf] anion presents only T_g temperature.

3.2.2. Thermal analysis of AnILs with epoxy resins

The obtained ILs were used to prepare coating epoxy systems in which the ionic liquids acted as hardener for the epoxy resin. The produced systems were examined using differential scanning calorimetry to determine the parameters of the polymerization process, in particular, the temperature of the beginning of polymerization (T_{onset}), the temperature of maximum polymerization (T_{max}) and the temperature of the end of polymerization (T_{offset}). In addition, the enthalpy values of the individual thermal transformations were determined (ΔH). The results of the measurements were collected and are presented in Table 2.

For all ionic liquids with a [DCA] anion, thermal transformations were observed with low process enthalpy. This suggests a potential low energy efficiency of the process and implies that polymerization initiated by this group of compounds proceeds slowly and does not generate substantial heat. Moreover, in the case of [BenzDMA][DCA], two polymerization peaks were observed on the thermogram, indicating two distinct polymerization pathways. Additionally, the recorded enthalpy values for this ionic liquid were the lowest within this group of ILs. This may imply the occurrence of epoxy resin polymerization initiated by either a cation (1st pathway) or an anion (2nd pathway), or the occurrence of resin polymerization initiated by an ionic liquid (1st pathway, cation or anion) and polymerization of the ionic liquid itself.

The behavior differs for ionic liquids with the [OTf] anion, as evidenced by the high enthalpy values observed during the thermal process. This indicates that the process occurs rapidly when sufficient heat energy is supplied to the system, potentially influencing a high degree of cross-linking in the epoxy coating structure. However, no correlation was identified between an increase in the alkyl chain length in the ionic liquid. In the case of [TEA][OTf], the lowest enthalpy for the process was observed, along with the lowest values for the start, maximum, and end temperatures of polymerization within this group of compounds. Despite the structural similarities among these compounds, additional factors must influence both the temperature and enthalpy values for these specific cations and anions.

The glass transition temperature was determined for epoxy resins cured with various ionic liquids, ranging from 46.7 to 51.2 °C. The highest value was achieved for [BenzDMA][OTf], while the lowest was observed for [TMA][OTf]. It is noteworthy that, irrespective of the

Table 2
Thermal properties of ILs mixtures with epoxy resin.

No	IL	Thermal analysis				
		T _{onset} [°C]	T _{max} [°C]	T _{offset} [°C]	ΔH [J/g]	T _g [°C]
1	[TMA][DCA]	143.0	177.3	198.0	36.8	47.7
2	[TMA][OTf]	150.5	165.3	168.7	415.9	46.7
3	[TEA][DCA]	147.0	180.2	201.6	66.9	50.7
4	[TEA][OTf]	113.7	134.8	140.4	335.9	48.3
5	[BenzDMA][DCA]	135.8	154.8	172.2	3.7	49.0
6	[BenzDMA][OTf]	193.0	212.7	238.2	11.2	51.2

Table 3
Thermogravimetric properties of the cured resin samples.

No	IL	Thermogravimetric Analysis (TGA)			
		T _{5%} [°C]	T _{50%} [°C]	dTG _{max} [%/min]	T _{dTGmax} [°C]
1	[TMA][DCA]	376	440	26.4	439
2	[TMA][OTf]	293	369	20.1	315
3	[TEA][DCA]	376	443	28.1	447
4	[TEA][OTf]	255	352	14.1	296
5	[BenzDMA]	356	439	26.4	440
6	[BenzDMA][OTf]	254	362	13.6	287

specific ionic liquid employed, the glass transition temperature consistently remains at a similar level, indicating that the choice of ionic liquid does not exert a significant influence on this parameter.

Subsequently, TGA analysis was conducted on the cured resin samples, establishing the temperature values corresponding to 5 % mass loss (T_{5%}), 50 % of the initial mass (T_{50%}), and the maximum rate of the sample decomposition (dTG_{max}), along with the assigned temperature for this peak (T_{dTGmax}). All the data collected is presented in Table 3. The acquired data reveals that epoxy coatings formulated with [DCA] ionic liquids exhibit greater overall thermal stability, undergoing a 5 % mass loss within a temperature range of 356 to 376 °C. In contrast, coatings cured with ILs featuring the [OTf] anion display notably lower stability within the 255 to 293 °C range. Nevertheless, a distinction is observed in the maximum decomposition rate, with [OTf] anion ionic liquids demonstrating a lower value (from 13.6 to 20.1 %/min) than [DCA] ILs (from 26.4 to 28.1 %/min).

3.3. Mechanical properties of the obtained coatings

All coating systems, formed by combining epoxy resin and ionic liquids, were used to fabricate monolayer structures on linen fabric substrates. The epoxy resin, acting as a protective layer around the fibers, underwent curing alongside the ionic liquids. Afterward, the strength of the resulting composite was assessed using a scanning electron microscope attachment. The data collected from numerous measurements for each material were compiled to determine the average strength parameters, which are detailed in Table 4. Notably, these results were compared with those of a reference coating (denoted as "Ref"), created similarly using the same epoxy resin but with triethylenetetramine as the curing initiator. This reference coating entailed a resin-to-initiator ratio of 90:10, which is five times higher than the ionic liquids content.

An interesting correlation is observed in AnILs with a dicyanamide anion, where there is a notable link between the increase in the maximum strength and the degree of crosslinking, along with the rise in structural complexity. Specifically, the lowest extent of crosslinking and tensile strength is observed for the cation featuring the trimethylphenylammonium configuration. Analyzing these findings suggests that this behavior is due to the strong attraction of the [DCA] anion to the cationic structure, which hinders facile *N*-dealkylation when the system

is exposed to high temperatures. This inhibits the displacement of the anion and consequent initiation of the reaction. Furthermore, an additional observation is noted, as the cation's structure becomes more extended, a faster *N*-dealkylation transpires following the sequence Benz > Et > Me. This *N*-dealkylation is followed by further interaction with the resin's epoxy groups, facilitating concurrent participation of the [DCA] anion in the process. This idea is supported by the fact that AnILs containing the dicyanamide anion typically manifest two polymerization peaks in DSC thermograms, originating from cation-initiated and anion-initiated polymerization [45]. However, the examined samples exhibit a singular peak in the higher temperature range, suggesting that the predominance of cation-initiated polymerization, depends on the temperature-induced dealkylation as a precursor to the starting epoxy reactions. A different phenomenon occurs with AnILs featuring the [OTf] anion, where even at lower temperatures, the anion separates from the ionic liquid cation and initiates the polymerization of the resin. The expectation is that anion-initiated polymerization is predominant in the case of [OTf]. The reacting anion appears to affect the stability of the cationic structure, facilitating an altered dealkylation sequence compared to DCA, Me > Benz > Et. However, it is theorized that the relationship in this instance is more complex, requiring a more detailed discussion in subsequent sections of the article. Conclusions drawn from the obtained results indicate that two of the six tested ionic liquids, namely trimethylphenylammonium [OTf] and *N*-Benzyl-*N,N*-dimethylphenylammonium [OTf], exhibit marked similarity to the reference system, albeit at substantially lower concentrations within the resin matrix.

A crucial aspect is highlighted in Fig. 3, which illustrates the assessment of tensile strength for ionic liquids with the trifluoromethanesulfonate anion. To gain meaningful insights, it is essential to comprehensively evaluate the entire experimental process, not just focusing on the force needed for the initial damage to the structural integrity. The data reveal that even though the force required for the initial coating disruption is the lowest in the case of [TMA][OTf], the subsequent tearing process does not occur abruptly; instead, it progresses gradually. This suggests that additional reinforcement, likely formed during the curing process, exerts a noticeable influence in preventing the complete rupture of the coating structure. This aspect is crucial for maintaining the coating's integrity in scenarios such as structural components that are susceptible to impact, such as vehicle bumpers or athletic equipment parts. After exposure, the material would not experience total fracture; rather, it would undergo partial tearing while retaining a degree of structural stability. This outcome prompted a more comprehensive exploration into the mechanics of curing and the development of the polymer network, aiming to understand the origin of this additional reinforcement or any other contributory factor responsible for the distinct behavior exhibited by systems with [TMA][OTf]. A comparable phenomenon of gradual and modest intensity increase was also observed in the case of [BenzDMA][OTf], although it was slightly less prominent.

Table 4
Mechanical properties of the obtained epoxy coatings.

No	Coating saturation [%]	Thickness [mm]	Mechanical analysis				
			Max elongation at break [%]	Tensile strength [N/mm ²]	Force [N]	Modulus of Elasticity [GPa]	Crosslinking degree [%]
Ref	54	0.57	1.68	46	524	2.72	99.20
1	53	0.48	1.24	26	246	2.06	55.46
2	51	0.51	1.75	43	432	2.44	92.89
3	52	0.51	1.22	32	324	2.58	68.52
4	53	0.63	0.94	37	466	3.91	79.83
5	55	0.63	1.20	36	453	2.97	77.58
6	54	0.65	1.49	41	526	2.73	88.48

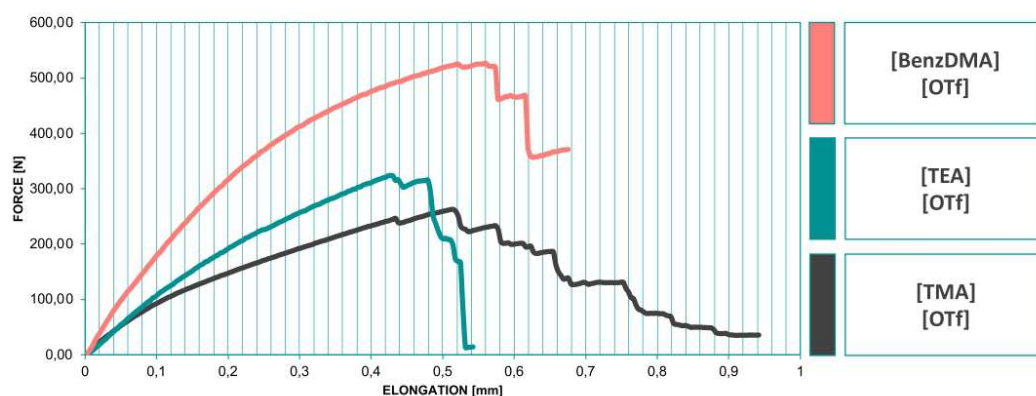


Fig. 3. Tensile strength analysis of the obtained epoxy coatings.

3.4. Mechanism of crosslinking network formation

The polymerization process of ER facilitated by the ionic liquid requires a specific temperature threshold for initiation; without this necessary temperature input, the process is slow and inefficient. The polymerization process can be divided into distinct pathways as shown in Fig. 4. One pathway involves the IL anion as the main initiator, whereas the other involves a dealkylated radical originating from the IL cation. This polymerization process follows a classical triphasic mechanism akin to that of tertiary amines (cation) and acid anhydrides (anion), including the initiation, propagation, and termination stages. The dominance of one pathway over the other depends on various factors, such as the strength of the acid anion, the temperature required for dealkylation initiation, the binding strength between the anion and cation, and the degree of structural branching. Notably, [TMA][OTf] has

an anion from the superacid category and falls into the class of weakly coordinating anions [89–91]. This anion-cation interaction is relatively weak, allowing facile dissociation under favorable conditions. In the case of [TMA][OTf], the anion-initiated polymerization pathway, which is driven by temperature and easy dissociation, takes precedence. This trajectory dominates the [TMA] cation-initiated polymerization pathway, which, during the ongoing [OTf]-mediated polymerization, undergoes dealkylation, thereby enabling its participation in the polymer structure assembly. Following the established mechanics of tertiary amine and acid anhydride reactions, both moieties regenerate after the propagation phase, and the terminating polymer can achieve chain extension through β -elimination or *N*-dealkylation. Nonetheless, [TMA] molecule entities and [OTf] superacid ions persist within the system. A decreasing temperature gradient within the material, coupled with reduced mobility of the aforementioned molecules suggests, that the

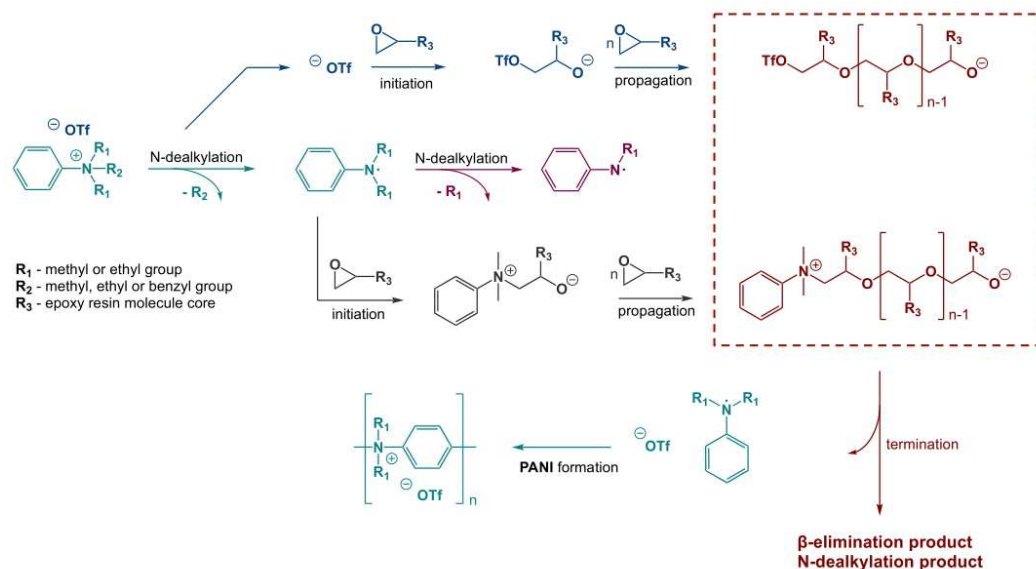


Fig. 4. Polymerization pathways.

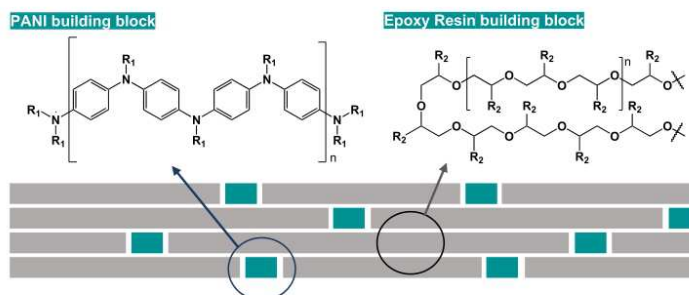


Fig. 5. Suggested architecture of the obtained PANI:Epoxy coating.

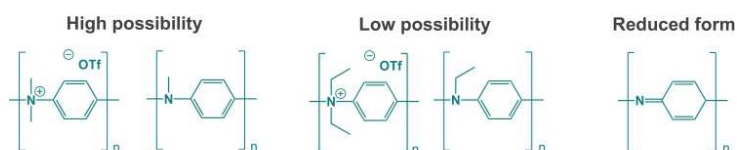


Fig. 6. Predicted structures of the PANI inside the epoxy matrix.

terminal stages of curing involve the polymerization of residual aniline radicals within the matrix, yielding distinct forms of PANI chains: ionic and reduced, with indications favoring the ionic configuration. The credibility of this phenomenon is supported by the preference for lower temperatures conducive to aniline polymerization, coupled with the presence of a superacid environment. The need to achieve lower temperatures for PANI reappearance—unattainable at elevated temperatures—implies that the polymerization process of aniline-derived entities must occur after ER polymerization [92].

If the suggested phenomenon occurs, especially regarding certain residual aniline molecules after the resin polymerization process, it suggests the presence of specific areas within the coating structure with varying distributions of shortened PANI chains. It is hypothesized that these localized areas play a crucial role in influencing the outcomes observed in the tensile testing process, orchestrating a progressive structural disruption instead of a comprehensive fracture. Fig. 5 provides a schematic representation of the epoxy-polyaniline composite coating, highlighting the specific regions containing PANI within the epoxy network. Furthermore, an illustrative example of the epoxy polymer structure after *N*-dealkylation and in the reduced PANI configuration is presented.

In terms of the mechanical properties of the coatings obtained, the presence of distinct zones with different distributions of short PANI chains could have a significant impact on the structural stability and mechanical performance of these coatings. These localized regions of truncated PANI chains could contribute to the gradual structural disruption observed during tensile testing, potentially affecting parameters such as tensile strength, elongation at break, and overall mechanical behavior of the coatings. Mechanical test data revealed the highest maximum elongation at break for [TMA][OTf] and [BenzDMA][OTf] at 1.75 % and 1.49 %, respectively. Tensile strength was also highest for these two ionic liquids with values of 43 N/mm² for [TMA][OTf] and 41 N/mm² for [BenzDMA][OTf]. In addition, the crosslinking density was the highest among all the samples tested, with values of 92.89 % and 88.48 %, respectively. In contrast, the results for [TEA][OTf] were lower, with a maximum elongation at break of 0.94 %, a tensile strength of 37 N/mm², and a crosslinking density of 79.83 %. These results suggest that within the structure of the PANI:Epoxy coatings for the discussed AnILs, there are specific regions containing PANI

that contribute to the variations in the modulus of elasticity and cross-linking degree of the coatings. These properties are influenced by the structural complexity and distribution of reinforcing components within the material.

However, it is crucial to conduct a thorough analysis of the phenomenon, especially considering that the partial rupture phenomenon is rarely observed with the [TEA] cation, where complete rupture is favored under sufficient force. To this end, a thorough examination of the potential structures assumed by the aniline derivatives remaining within the epoxy matrix after resin polymerization was conducted. Clearly, both [TMA][OTf] and [BenzDMA][OTf] retain analogous radicals featuring solely methyl groups, whereas in the case of [TEA], diethylaniline molecules are evident. Ethyl radicals likely exhibit a comparatively restrained inclination toward polymerization, implying that [TEA][OTf] may not contain significant quantities of PANI chains in the final epoxy coating structure, or perhaps such chains are substantially diminished. Conversely, in the case of [TMA][OTf] and [BenzDMA][OTf], a notable abundance of methyl radicals is generated, which is predisposed to facile polymerization. Polymer chains can exist in both fully reduced (Fig. 6) and ionic forms, which are influenced by the trifluoromethanesulfonate anion. Determining the predominant form is complex, depending on the availability of a substantial quantity of trifluoromethanesulfonate anions within a designated area of the epoxy network and the nature of the aniline derivative, whether mono *N*-dealkylated or undergoing successive transformations, ultimately yielding the *N*-methylaniline molecule.

4. Conclusions

In this study, we successfully synthesized anilinium-based ionic liquids (AnILs) with dicyanamide and trifluoromethanesulfonate anions. Thermal analysis of the obtained AnILs revealed distinct transitions, with the size of the cation influencing the thermal behavior. Crucially, detailed thermal analysis measurements were conducted for the ionic liquids and epoxy resin systems. AnILs with [DCA] anion displayed lower enthalpy values, indicating slow polymerization with potential low energy efficiency. Conversely, [OTf] anion-containing AnILs exhibited high enthalpy values, suggesting rapid polymerization with the potential for significant crosslinking. The resulting coatings

underwent thorough mechanical analysis, revealing varied properties compared with a reference coating. Notably, ANILs with a dicyanamide anion exhibited a correlation between increased strength, crosslinking, and structural complexity. The observed behavior was attributed to the [DCA] anion's strong affinity for the cation, hindering *N*-dealkylation and influencing the initiation of the reaction. In contrast, ANILs with [OTf] anion demonstrated unique polymerization behavior even at lower temperatures. Further exploration into the curing mechanics highlighted that the polymerization process involves distinct pathways, influenced by factors such as anion strength, dealkylation initiation temperature, and structural branching. The tensile strength assessment of coatings with trifluoromethanesulfonate anion revealed interesting behavior, suggesting that additional reinforcement during curing, is crucial for structural integrity in impact-prone scenarios. This phenomenon was observed in both [TMA][OTf] and [BenzDMA][OTf] systems. Moreover, the study proposed a mechanism involving residual aniline molecules that influence structural outcomes, presenting areas within the coating with varied PANI chain distributions. This hypothesis suggests a gradual structural disruption rather than a complete fracture, emphasizing the importance of localized PANI configurations.

CRedit authorship contribution statement

Dawid Zielinski: Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Conceptualization. **Andrea Szepecht:** Writing – review & editing, Validation, Methodology, Investigation. **Paulina Nadobna:** Investigation. **Magdalena Palacz:** Investigation. **Marcin Smiglak:** Writing – review & editing, Validation, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

This work was supported by the National Science Centre (Poland) [grant number 2017/26/E/ST8/01059].

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.porgcoat.2024.108353>.

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Article

Multifunctional Modifying Systems Based on Ionic Liquids for Epoxy Resin Systems and Composites

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Abstract: The continuous development of the industry of composite materials and epoxy resins requires the development of components that modify these systems. It is extremely beneficial to modify functionality by using one or two substances instead of modifying only one system parameter. Typically, this end-use will determine the key parameters of the resin system that should be modified and the modification systems designed as such. In this study, we introduce novel systems utilizing ionic liquids, strategically designed to concurrently alter multiple system parameters, including: (i) flexibility, (ii) crosslinking density, and (iii) fire resistance. The following techniques were used in the research: (i) Differential Scanning Calorimetry (DSC), (ii) Thermogravimetric Analysis (TGA), (iii) Dynamic Mechanical Analysis (DMA) and (iv) fire performance tests (UL-94, Limiting Oxygen Index and Mass loss type cone calorimetry (MLC)) to show as much dependence of material parameters on the type of modifying additive as possible. Both the cured resin and the curing process as well as a single-layer composite reinforced with carbon fiber were tested. The results show that properly designed ionic liquids are able to perform many functions in the composite material and simultaneously affect several parameters, both by lowering and increasing them. In addition, they can exhibit activity in the field of flame-retardant composites.

Keywords: ionic liquids; epoxy composites; flame-retardancy; curing agents; bioepoxy resin



Citation: Zielinski, D.; Szepecht, A.; Pomázi, Á.; Kovács, Z.; Szolnoki, B.; Pinke, B.; Toldy, A.; Smiglak, M. Multifunctional Modifying Systems Based on Ionic Liquids for Epoxy Resin Systems and Composites. *Appl. Sci.* **2023**, *13*, 10661. <https://doi.org/10.3390/app131910661>

Received: 15 August 2023

Revised: 13 September 2023

Accepted: 22 September 2023

Published: 25 September 2023



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1. Introduction

Composite materials based on epoxy resins and reinforcing fibers are the backbone of polymer materials used widely around the world. It is a valuable construction material in areas such as electronics (equipment housings, electronic components) [1], paints and coatings [2], construction (construction material used both indoors and outdoors) [3], or transportation (construction materials in aviation, automotive, marine or railroad industries) [4]. It owes its popularity due to its high tensile strength, high adhesion to substrates, good corrosion resistance, chemical resistance, and moisture resistance [5,6].

The biggest disadvantage of this group of materials is their flammability, resulting in the generation of large amounts of heat and the formation of a number of combustion products that are harmful to human health, such as: (i) toxic gases (HBr, HCl), (ii) benzene derivatives and higher aromatic hydrocarbons (PAHs), (iii) non-flammable gases (CO₂,

NO_x, SO_x), (iv) flammable VOCs (methane, ethane) or (v) organic irritants, the composition of which is determined by the components of the resin and the overall composite [6–10].

Glass and carbon fibers are the most widely used fiber reinforcement in polymer composites. Although both reinforcements can be considered inert materials that significantly reduce the heat release rate compared to the polymer matrix, they often need additional flame retardancy to comply with the relevant fire safety standards. Flame retardant compounds containing halogens are known, but their use is not friendly to health and the environment as their combustion products are mainly toxic gases (HCl, HBr, HCN). Restrictive requirements for flame retardants and their effectiveness and properties (especially in terms of environmental and health impacts) are forcing the search for halogen-free solutions. Organophosphorus compounds used in composites to increase their thermal stability can be described as reactive (such as 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide, DOPO [9,11]) or non-reactive (such as triphenyl phosphate, TPP [12–15]). Their flame-retardant effect is directly related to the form in which phosphorus is present in them and can sometimes consist, for example, of generating large amounts of foam during combustion, which prevents further ignition (swelling when exposed to fire). Silicon-based flame retardants (e.g., borosilicates) are preferred to reduce flammability and suppress smoke, which is extremely beneficial in the case of epoxy resins [6]. These flame retardants are widely regarded as environmentally friendly and can be combined with each other: (i) synergy between silicon and phosphorus compounds, (ii) synergy between phosphorus and nitrogen compounds, and (iii) synergy of organophosphorus compounds with inorganic filler (metal oxides and hydroxides) [6,16–18]. Admittedly, inorganic fillers such as magnesium hydroxide and magnesium oxide can impart flame-retardant properties of epoxy resin, but to meet the flame-retardancy criterion they need to be used in high concentrations, which deteriorates the mechanical properties of the final material. The search for effective flame retardants, using synergistic interaction between elements that are biodegradable or environmentally friendly and easily scalable from the lab to industry, is currently a challenge in many research groups around the world [6].

Ionic liquids, denoted as ILs, constitute a unique category of chemical compounds defined by their distinctive ionic architecture. These compounds consist of a cation and an anion, each endowed with specific and remarkable attributes that set them apart from other chemicals. Typically, the cation component of ionic liquids originates from organic sources and manifests a wide array of structural variability. Of particular scientific interest is the fact that the positive charge of the cation may be localized on a variety of atoms, frequently encompassing nitrogen, phosphorus, or sulfur, and affording the potential for diverse functional groups within the cation's molecular framework. Additionally, ILs offer the flexibility to incorporate anions spanning the spectrum from organic to inorganic, and the choice of anionic species exerts a profound influence on the nuanced properties exhibited by the entire IL compound [5].

So, a small group of imidazolium ILs is known, which in their structure have organosilicon groups, mainly based on siloxanes [19,20]. Recent papers propose the use of this type of compound as electrolytes in lithium-ion batteries [19] and discuss their potential areas of application as surfactants with the ability to specific aggregation in aqueous solutions [21]. In addition, the ability to store hydrogen in this type of ionic liquid was also presented [22], but in most published works, attention is focused on the synthesis and properties of these quaternary salts, and the scope of structures is limited to the basic ones, i.e., imidazolium and ammonium ionic liquids.

On the other hand, ionic liquids containing a phosphorus atom in their structure can be divided into two groups: (i) phosphonium ionic liquids (PhILs) in which the positive charge of the cation is located on the phosphorus atom, and (ii) ionic liquids in which the phosphorus atom is located in the alkyl chain or the anion and is devoid of a direct charge. The precursors of PhILs are mostly various types of phosphines. However, the high sensitivity of phosphines to air requires advanced synthetic equipment that provides an appropriate environment for the process. This feature significantly limits the possibilities

of free design of this type of ILs, and only a small group of phosphines is known that show low sensitivity to air. Nevertheless, the applications of PhILs are diverse and in recent years the areas of their use have been presented as catalysts for the cycloaddition of carbon dioxide to epoxides [23], anticorrosive additives for pigments in epoxy coatings [24] or in the extraction of gold from thiosulfate solutions [25]. Moreover, many applications of this group of compounds in catalysis and carbon dioxide absorption are known [26,27]. In contrast, ionic liquids containing charge-free phosphorus in their structure are simpler to synthesize and, in most cases, do not require special conditions. This group of compounds has found use primarily in cellulose dissolution processes [28,29] and electrochemistry [30].

ILs have a number of advantages for use in composite materials and resin systems themselves. One of their most important properties is their ability to initiate the polymerization process of the epoxy resin [5,31,32]. ILs can be designed to predict their performance as cure initiators in a selected range of temperatures and intensities. The curing process can be either cationic or anionic, and the amount of ionic liquid required for the curing process is much smaller than for classical amine curing agents. Critical to the success of the process is the temperature reached by the resin system, as the system itself is inactive at room temperature, which also brings the advantages of a very long gelation time (up to 60 days) and the possibility of long-term storage at room temperature of the already finished resin/hardener mixture in the form of ionic liquid. Ionic liquids affect the properties of the final material through the reduction in the crosslinking density of the resin after curing, resulting in an increase in the stress intensity factor and tensile strength without significant loss of other mechanical properties [33]. In addition, ionic liquids have a scientifically proven effect on fibers of various types. Flax fibers functionalized using an ionic liquid—for example, didecyldimethylammonium nitrate—become resistant to the growth of microorganisms [34]. The antifungal efficacy is derived from a lengthy alkyl chain. However, the most important ability of ionic liquids with respect to different types of fibers is their ability to initiate and stimulate the fibrillation process of the fiber [35,36]. This phenomenon involves the splitting of the main structure of the fiber with the simultaneous formation of a network of microfibrils that diverge from the main stem. During fibrillation, the fibers additionally undergo twisting by which a layer of microfibrils is formed around the shaft. So far, the effect of ionic liquids in initiating fiber fibrillation has been successfully confirmed for both: natural [37] (silk, cellulose) and synthetic (aramid) fibers [38]. Recent studies show the potential of ionic liquids to impart fire-resistant material characteristics to composites. For this purpose, work is carried out with the use of PhILs, from which it is known to use, for example, ethyltributylphosphonium diethyl phosphate [39], 1-vinyl-3-(diethoxyphosphoryl)-propylimidazolium bromide [40] or imidazolium diphenylphosphinate [41], which can act as both a flame-retardant and an epoxy resin hardener. Sometimes, to increase these properties, admixtures of graphene suspended in an ionic liquid are used [16].

Research on flame retardants in recent years has focused on the search for new compounds with effective action and has largely consisted of organic synthesis of substances based on previously known flame retardants (structural improvements of substances, new derivatives) or synthesis of completely new molecules. The mechanism of flame retardancy is, in general, a set of physicochemical reactions and processes that can occur in the gaseous (flame) or condensed (plastic, decomposition products) phase [12,18]. Predicting and designing the mechanisms of flame retardancy is a difficult task [42], and studies show that even compounds containing the same amount of phosphorus, with very similar spatial structures, can flame retard the material in different ways. This is due to dependencies in the molecule such as (i) susceptibility to esterification reactions (hydroxyl groups, acid groups) or (ii) the ability of the flame retardant to migrate inside the resin network [18]. Typically, a flame retardant can simultaneously act in both the gaseous and condensed phases but maintain a preference for one or the other. The mechanism of flame retardancy focuses on the following effects: (i) reducing heat release during combustion, (ii) reducing the amount of smoke and gas released during combustion, and (iii) restricting oxygen, not

sustaining combustion [43,44]. However, research on flame retardants has centered around the use of additive-type flame retardants, such as cyclophosphazene derivatives [7], DOPO (9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide), or ammonium polyphosphates and resorcinol bis(diphenylphosphate) [15]. Although the synergistic effect between ionic liquids and inert compounds has been studied [13,14,16], it has not been considered in the context of using as flame retardants only ionic compounds such as ionic liquids, which, containing phosphorus, silicon, and nitrogen atoms, may also exhibit a synergistic effect.

The examples cited illustrate the extensive impact of ionic liquids on resin systems and composites, highlighting the multitude of factors that must be carefully considered to accurately evaluate their cumulative effects on specific materials. At the same time, the cited examples inspire and justify the study of ionic liquids in the context of the search for multifunctional compounds that can perform a function in the area of composite materials on many levels. The aim of the study was to explore the possibility of creating a multifunctional system that modifies both the properties of the epoxy resin and the composite itself on multiple levels. The key task was to identify the areas of influence of the modifications and to assess the intensity of their impact. As a result, a resin system based on an epoxy resin and three ionic liquids was developed: (i) an ionic liquid that is a curing agent, and (ii) a system of two ionic liquids containing silicon and phosphorus in their structure, affecting the parameters of the resin and the carbon composite produced on its basis.

2. Materials and Methods

2.1. Materials

All organic reagents were purchased from Merck, Germany (3-Chloropropyl)trimethoxysilane 97%, 1-methylimidazole 99%, organic solvents with a minimum HPLC grade). Ionic liquids were purchased from IoLiTec GmbH, Heilbron, Germany. Epoxy resin, EnviPox 525 (Bisphenol A (BPA) type resin with biocarbon content) was purchased from Spolchemie a.s., Usti nad Labem, Czech Republic. Twill (2 × 2) carbon fabric with a weight of 600 g/m² was purchased from G. Angeloni S.r.l., Venice, Italy. For all ionic liquids, both purchased and synthesized, Karl-Fisher water content titration was performed as a routine procedure. The water content value for purchased ILs did not exceed 100 ppm and for the synthesized IL the water content value did not exceed 150 ppm. Therefore, they were considered dry, and the water content was negligible during the evaluation of the results.

2.2. Ionic Liquids

A total of seven ionic liquids were selected for the study. Five of them are liquids containing phosphorus atoms in their structure, while the sixth is an ionic liquid containing silicon and the seventh is an ionic liquid curing agent. All the structures of the ionic liquids are shown in Figure 1.

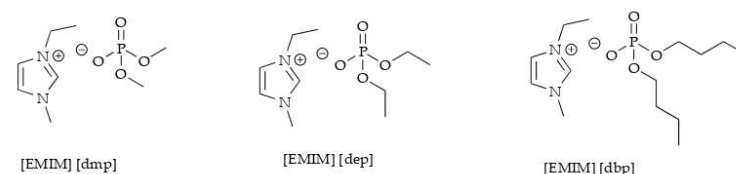


Figure 1. Cont.

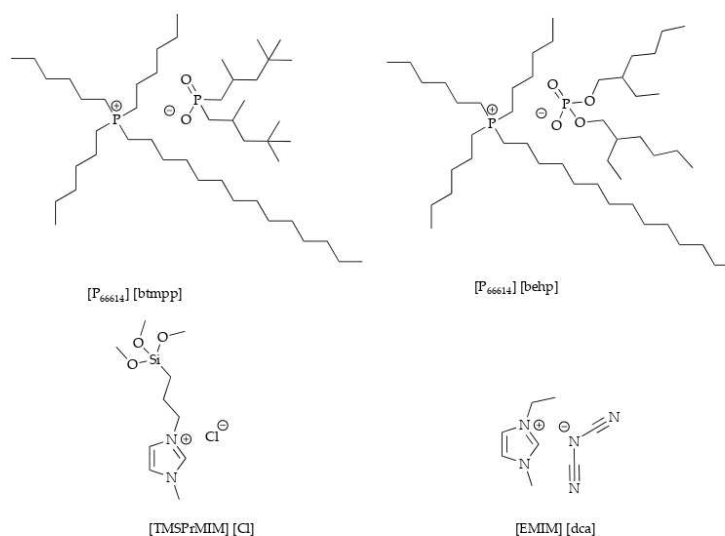


Figure 1. Structures of ionic liquids.

2.2.1. Synthesis and Analysis of 1-methyl-3-(3-(trimethoxysilyl)propyl)imidazolium Chloride

• Synthesis and analysis

A solution of 1-methylimidazole (10 g, 0.122 mol, 1.0 eq.) in acetonitrile (50 mL) was heated up to 65 °C and then (3-chloropropyl)trimethoxysilane (24.24 g, 0.122 mol, 1.0 eq., 27.6 mL) was added dropwise. The reaction scheme is shown on Figure 2. The reaction mixture was stirred under a reflux condenser for 72 h. Afterwards, the acetonitrile was evaporated, and the resultant liquid was dissolved in water and then washed three times with diethyl ether. The water solution was evaporated, resulting in a viscous, yellow liquid (25 g, 73.11%).

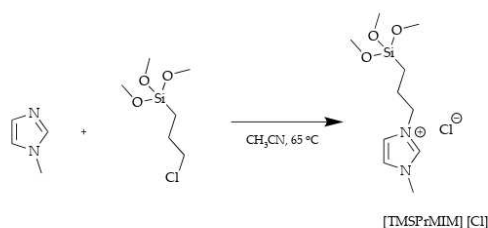


Figure 2. Reaction scheme of [TMSPPrMIM][Cl] synthesis.

¹H NMR (400 MHz, CDCl₃): δ = 9.67 (s, 1H), 7.32 (d, *J* = 1.8 Hz, 1H), 7.16 (d, *J* = 1.8 Hz, 1H), 3.75 (dt, *J* = 14.7 Hz, *J* = 7.0 Hz, 2H), 3.49 (s, 3H), 2.90 (s, 9H), 1.37 (dd, *J* = 9.7 Hz, *J* = 6.0 Hz, 2H), 0.01 (ddd, *J* = 16.7 Hz, *J* = 10.2 Hz, *J* = 6.6 Hz, 2H)

¹³C {¹H} NMR (100 MHz, CDCl₃): δ = 133.56, 122.39, 120.78, 48.95, 48.77, 34.71, 22.47, 4.25.

2.2.2. Preparation of Modification Formulations and Epoxy System

Six of the seven ionic liquids were used to prepare modification systems (Table 1, A–E) for the epoxy resin. For this purpose, each ionic liquid containing phosphorus in its

structure was used to create a mixture (at an elevated temperature around 50 °C) with an ionic liquid containing silicon in equimolar ratios.

Table 1. Parameters of modification systems based on ILs.

Modification System	IL 1—P Donor (1 eq.)	IL 2—Si Donor (1 eq.)	Total Molecular Weight [g/mol]	% P	% Si
A	[EMIM] [dmp]	[TMSPPrMIM] [Cl]	587	5.3	4.8
B	[EMIM] [dep]	[TMSPPrMIM] [Cl]	559	5.5	5.0
C	[EMIM] [dbp]	[TMSPPrMIM] [Cl]	643	4.8	4.4
D	[P ₆₆₆₁₄] [btmpp]	[TMSPPrMIM] [Cl]	1128	5.5	2.5
E	[P ₆₆₆₁₄] [behp]	[TMSPPrMIM] [Cl]	1096	5.7	2.6

2.3. Preparation of Carbon Fiber-Reinforced Epoxy Composites

A resin system consisting of: (i) an epoxy resin (ER), (ii) an ionic liquid acting as a curing agent (CA, 2 g/98 g of ER), and (iii) a modification system based on silicon- and phosphorus-containing ionic liquids (A–E, 10 g/90 g of ER with CA), has been used to prepare prototype structures of carbon composites, using hand lamination. The prepared composites were in the form of monolayers with dimensions of 30 × 30 cm and a thickness of about 1 to 2 mm. The ratio of fiber saturation with resin was 40 to 42% wt. Then, carbon preimpregnates were annealed at 120 °C for a period of 4 h. In addition, a reference (R) composite, devoid of modifying ionic liquids, was also produced.

2.4. Test Methods

2.4.1. Thermal Analysis

Both differential Scanning Calorimetry and thermogravimetric analysis were performed using a method described in previous papers by the authors. Detailed measurement parameters and curves are presented in the Supplementary Materials.

2.4.2. Dynamic Mechanical Analysis (DMA)

Dynamic Mechanical Analysis was performed using a method described in previous papers by the authors. Detailed measurement parameters and curves are presented in Supplementary Materials.

2.4.3. Fire Behavior

UL-94 flammability tests, limiting oxygen index (LOI) tests, and Mass loss type calorimetry (MLC) were performed according to: (i) ASTM D3081 and ASTM D635 (UL-94), (ii) ASTM D2863 (LOI), and (iii) ISO 13927 (MLC). Detailed measurement parameters are presented in Supplementary Materials.

3. Results and Discussion

3.1. Synthesis and Preparation of Modification Formulations Based on Ionic Liquids

In the first stage of the research, modification systems based on six ionic liquids were produced. The goal was to produce such systems that would differ in (i) the chemical structure of the components, (ii) the content of phosphorus and silicon and the ratio of the two to each other, and (iii) the form of phosphorus bonding in the ionic liquid molecule (tertiary phosphorus atom in the cation or phosphorus in the form of organic phosphate). This goal was achieved, and the mixtures produced remained stable throughout the research period.

Nevertheless, it should be noted that all the ionic liquids selected in the study were present at room temperature in the liquid state, which greatly facilitated their preparation. On the basis of the conducted studies, it was observed that the greater the similarity of the cation structure of the two components of the mixture, the more homogeneous it was

(mixtures A, B, and C). In contrast, when the ionic liquids differ significantly in their structure (D and E), the formation of emulsions, rather than homogeneous systems, was observed. The emulsion phenomenon is more pronounced, the longer a given mixture is stored and manifests itself in the gradual disintegration of the emulsion into individual phases. Despite the use of elevated temperatures during the preparation of mixtures, this effect could not be eliminated. The observed phenomenon seems to be typical for these types of systems and well understood, if only during studies considering formation of eutectic mixtures of ionic liquids. Two or more ionic liquids will therefore form more stable and homogeneous systems with each other if their structural similarity is greater and they can commonality the individual ions in their composition.

The process of formation of the final epoxy system is shown graphically in Figure 3. The total content of ionic liquids in the system varies at about 12% by weight, with about 2% by weight being [EMIM] [dca], which acts as a cure initiator (CA) in the epoxy system. The mode of action and properties of this liquid as a curing agent have been studied by numerous groups of scientists [32,45–48], and it is because this substance is so well known that it was chosen for this study. The polymerization of the epoxy resin initiated by [EMIM] [dca] starts around 80–100 °C, depending on the type of resin. The process is characterized by the presence of two thermal peaks on the DSC thermogram, which can indicate simultaneous cationic polymerization (initiated by IL cation) and anionic polymerization (initiated by [dca] anion). The polymerization peak occurs in the temperature range of 140–180 °C. After the epoxy resin system is properly prepared with CA, a previously prepared modifying system based on phosphorus- and silicon-donor ILs is added with an amount of 10% by weight. Therefore, five homogeneous epoxy systems were obtained that remained stable for the duration of the conducted tests and did not cure at room temperature for at least 30 days (the test period). The systems containing phosphonium ionic liquids were characterized by the presence of a light-yellow full color, which limited the transparency parameters of the system.

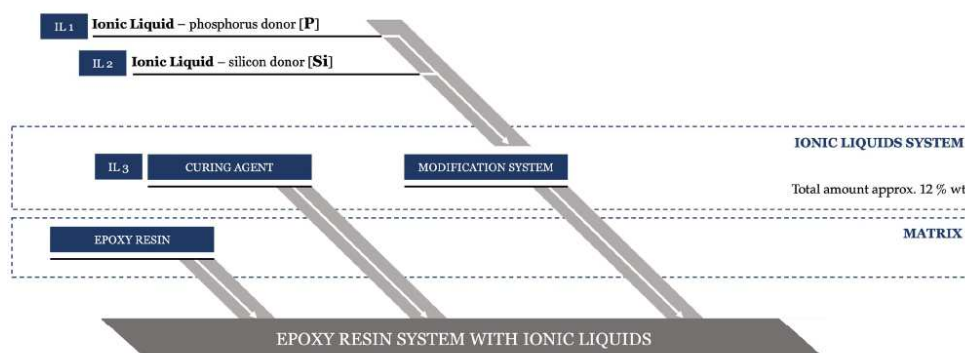


Figure 3. Schematic presentation of epoxy systems prepared with ionic liquids.

Table 2 summarizes the most important parameters of the obtained systems. The systems were characterized by a relatively equal mass content of phosphorus (0.5–0.6 g in terms of pure phosphorus for every 100 g of resin system). However, noticeable differences are observed in the case of silicon content, which varies between 0.2 and 0.5 g for every 100 g of the resin system. Such an assumption made it possible to thoroughly investigate the effect of the ratio of the various elements on the achieved modification effect of both the cured resin and the carbon fiber composite.

Table 2. Composition of the epoxy systems with ionic liquids.

Epoxy System	CA	Modification Formulation		Mass of P [g/100 g]	Mass of Si [g/100 g]
		[Si] IL (1 eq.)	[P] IL (1 eq.)		
		2 g/98 g of ER	10 g/90 g of ER with CA		
R	[EMIM] [dca]	0	0	0	0
A	[EMIM] [dca]	[TMSPrMIM] [Cl]	[EMIM] [dmp]	0.5	0.5
B	[EMIM] [dca]	[TMSPrMIM] [Cl]	[EMIM] [dep]	0.6	0.5
C	[EMIM] [dca]	[TMSPrMIM] [Cl]	[EMIM] [dbp]	0.5	0.4
D	[EMIM] [dca]	[TMSPrMIM] [Cl]	[P ₆₆₆₁₄] [btmpp]	0.5	0.2
E	[EMIM] [dca]	[TMSPrMIM] [Cl]	[P ₆₆₆₁₄] [behp]	0.6	0.3

3.2. Curing Properties of Modified Epoxy Resin Formulations

Thermal Analysis

DSC analysis was performed for all resin systems, the results of which are summarized in Table 3. All modified systems relative to the reference, containing only [EMIM] [dca] as a curing agent, showed a decrease in onset temperature values, even by 24–25% (C and E). At the same time, there was also a decrease in the temperature of the maximum thermal peak in all modified systems relative to the reference. A proposed explanation for this phenomenon is the aggregate increase in the concentration of 1-ethyl-3-methylimidazolium cation in the systems, thereby shifting the polymerization equilibrium toward cationic polymerization. This fact also seems to be confirmed by the decrease in intensity or even the almost complete disappearance of the second thermal peak observed in the case of thermograms for the modified systems, indicating the almost complete elimination of anionic polymerization (C and D, thermograms in Supplementary Materials). In addition, compounds with long alkyl chains introduced into the systems can also affect the reduction of the temperatures of thermal transformations occurring during the polymerization of the epoxy resin. In the case of the total enthalpy of the process, a decrease in its value was observed in all cases, with a marked change of 14% for system E.

Table 3. Characteristic of the curing process, determined with DSC.

Sample	Onset Temperature [°C]	Maximum Peak [°C]	Total Enthalpy [J/g]
R	147	162	520
A	117	150	508
B	133	151	507
C	111	124	486
D	127	169	484
E	110	121	446

Similarly, according to the results obtained, a decrease in the glass transition temperature values of the modified systems was observed. The average decrease in the T_g value was 41% with respect to the reference value, reaching the largest decrease for system B. At the same time, systems D and E, containing phosphonium ionic liquids, recorded the lowest decrease at 33 and 34%, respectively, regarding the reference. The results obtained allow us to conclude that, despite the generally observed plasticizing effect achieved by modifying the resin system with ILs, this phenomenon can be somewhat controlled and due to the long-chain alkyl compounds, be significantly reduced.

The effect of modifying the resin system with ionic liquids on thermal stability was investigated using thermogravimetric analysis (TGA), the results of which are presented in Table 4. The following parameters were used in the analysis of the results: (i) the temperature at which the mass of the sample is reduced by 5% ($T_{5\%}$), (ii) the temperature

when 50% of the sample decays ($T_{50\%}$), (iii) the maximum mass loss rate (dTG_{max}), and (iv) the maximum mass loss rate temperature ($T_{dT_{Gmax}}$). For all the tested systems, the thermal stability decreases, however, in the case of system E, these changes are practically imperceptible.

Table 4. Thermogravimetric analysis results of the reference and samples modified with ionic liquids.

Sample	$T_{5\%}$ [°C]	$T_{50\%}$ [°C]	dTG_{max} [%/°C]	$T_{dT_{Gmax}}$ [°C]
R	401	443	3.1	442
A	322	403	1.7	401
B	285	396	1.4	395
C	324	402	1.9	401
D	325	418	2.2	418
E	329	436	2.0	438

For system E, containing a PhIL and [TMSPrMIM] [Cl] and at the same time a two-fold excess of total phosphorus in relation to silicon, a decrease in the $T_{50\%}$ value by only 2% was observed, while a decrease in $T_{dT_{Gmax}}$ by 1%. In addition, $T_{5\%}$ decreased by 18% compared to the reference, and the maximum mass loss rate was reduced to 2%/°C. In all systems, the decrease in the value of $T_{5\%}$ was at the level of 18–20%. In turn, the results obtained for system B, which is characterized by the highest total content of phosphorus and silicon (with a predominance of phosphorus), significantly differ from the entire matrix. The $T_{5\%}$ and $T_{50\%}$ values, reduced by 29% and 11% respectively, indicate that this system can exhibit flame retardant activity in the gas phase, unlike the other systems where this activity is expected rather in the solid phase. For all systems, the maximum mass loss rate was reduced by an average of 41%.

3.3. Carbon Fiber Reinforced Composites' Properties

DMA

Dynamic Mechanical Analysis was used to investigate the properties of carbon fiber-reinforced epoxy composites produced using ionic liquid systems. Table 5 summarizes the results of the determined glass transition temperatures for the composites, using data on storage modulus (E'), tan delta values ($\tan \delta$), and loss modulus (E''). The value of the T_g , which actually represents a certain range of temperatures, was presented as a specific numerical value in order to evaluate the performance of the obtained materials. The results obtained in the DMA analysis were compared with the T_g result determined during the DSC analysis of the resin systems themselves without carbon fiber reinforcement. The results show how much influence the reinforcement has on the properties of the final material. Moreover, for all the systems modified with ionic liquids, a significant increase in the glass transition temperature value was recorded compared to the reference. Systems A, B, and C show an increase in T_g values of nearly 50%, while for system E the increase was 75%. To assess the effect of the modification on the polymer network inside the material, the crosslinking density was determined, the value of which for each system translates into an increase in the glass transition temperature, which is the expected result. Crosslinking density was determined by a mathematical equation presented in several other works [49,50]. A denser network inside the material reduces the potential of the polymer chain to stress and rotate by making the final material stiffer and stronger. An explanation for this phenomenon may be that ionic liquids supplied to the system build into the polymer structure, and the presence of long chains stabilizes bond rotation. Interestingly, in the case of resin systems without carbon fiber reinforcement, the trend in the change in glass transition temperature values is opposite to that observed for fabricated composite structures. This primarily demonstrates the influence of factors such as reinforcement, fibers, sample size, or, most importantly, the technique of determining the parameter, on the value of glass transition temperatures.

Table 5. Glass transition temperatures and crosslinking density of the reference and samples modified with ionic liquids. Glass transition for pure epoxy resin with ionic liquids determined with DSC. Glass transition temperatures and crosslinking density for carbon-reinforced composite samples determined with DMA.

Sample	T _g DSC * [°C]	T _g from E' ** [°C]	T _g from tan δ ** [°C]	T _g from E'' ** [°C]	Crosslinking Density [mol/cm ⁻³]
R	166	68	94	89	1.2
A	89	102	118	109	3.8
B	84	99	113	114	2.3
C	98	104	120	110	3.5
D	112	74	84	71	2.1
E	109	119	131	127	3.1

* pure epoxy resin, ** epoxy resin with carbon fiber reinforcement.

Complementing the T_g analysis is the effect of temperature on the E' value and the intensity of the shift of this value toward lower values depending on the modification system. The results presented in Table 6 indicate that the sample modified with the D system retains the most similar storage modulus parameters at 28 °C compared to the reference. In the case of the other systems, a shift towards more elastic rather than rigid materials is observed. On the other hand, the situation changes dramatically if we consider the rate at which the value of the parameter E' changes with increasing temperature. In this comparison, the most stable in relation to the reference is the E system, while the fastest change is observed in the D sample, which, as noted earlier, at a temperature of 28 °C retained the value of E' closest to the reference, while at temperature 75 °C this value decreased by almost half in relation to the reference. We suppose that the modifying system D influences the elasticity of the composite material the most among all those tested, however, systems A, C, and E also show noticeable activity in this direction.

Table 6. Storage modulus E' for carbon-reinforced composite samples of the reference and samples modified with ionic liquids.

Sample	E' at 28 °C [MPa]	E' at 75 °C [MPa]	ΔE' [MPa/°C]
R	14,971	12,285	9.8
A	6144	5699	15.2
B	8502	7817	55.4
C	7139	6639	10.9
D	11,677	7140	104.0
E	6721	6391	7.3

3.4. Fire Performance

3.4.1. UL-94 and LOI

The final stage of the research was to evaluate the ability of the produced ionic liquid-based modification systems to flame retard the epoxy resin. For this purpose, the UL-94 test was first performed and the LOI was determined, the results of which are summarized in Table 7. Tests were conducted for resin samples without reinforcement. The obtained results allow us to assume that at a concentration of 10% by weight in the epoxy material, the tested modifying systems do not show significant flame-retardant properties towards the resin, which, considering the actual amount of phosphorus and silicon introduced into the system, was an expected result. Nevertheless, some dependencies are observed between the modifying system and the flame-retardant properties. Although, according to the classification, all materials received the HB rating, the LOI value increased to 30 V/V%

for the E system. The result is also interesting because it is the E system that contains the smallest total amount of phosphorus and silicon. It is assumed that in the case of the tested systems, the oxygen index was influenced not so much by the content or presence of silicon and phosphorus, but by the extensive structure of the phosphonium ionic liquid molecule with numerous long alkyl chains.

Table 7. Limiting oxygen index and UL-94 results of the reference and samples modified with ionic liquids.

Sample	LOI [V/V%]	UL-94
R	25	HB
A	26	HB
B	29	HB
C	27	HB
D	27	HB
E	30	HB

3.4.2. MLC

For samples of composites reinforced with carbon fiber, a test was carried out using mass loss type cone calorimetry, the results of which are presented in Table 8. In this case, System E showed a 34% increase in pHRR relative to the reference value (143 vs. 107 kW/m²) with a simultaneous shift in time of pHRR from 32 to 36 s, while System A showed a 24% increase (133 vs. 107 kW/m²). A slight decrease of this value was observed for systems B and D and amounted to 7 and 3%, respectively. THR values have been reduced the most in the case of system B (4.8 MJ/m²), however, this difference (16%), compared to the reference (5.7 MJ/m²), proves that the flame-retardant properties are insufficient. No significant effect of modifying systems on the amount of residues was observed. We suppose that, despite the changes in individual values during the analysis, the amount of the modifying system used in the composite and the amounts of silicon and phosphorus related to it were not enough to significantly delay the development of the fire.

Table 8. Mass loss calorimetry results of the reference and samples modified with ionic liquids.

Sample	TTI [s]	pHRR [kW/m ²]	Time of pHRR [s]	THR [MJ/m ²]	Residue [Mass%]
R	17	107	32	5.7	68%
A	15	133	28	7.4	66%
B	20	100	33	4.8	69%
C	15	127	28	6.5	65%
D	16	104	30	5.4	67%
E	21	143	36	7.2	64%

TTI—time to ignition, pHRR—peak of heat release rate, THR—total heat release.

4. Conclusions

This study presented multifunctional modifying systems based on ionic liquids for epoxy resin. The proposed modifying systems introduced into the epoxy composite in an amount of 10% by weight: (i) increase the degree of crosslinking of the polymer matrix, (ii) increase the glass transition temperature, and (iii) improve the fire resistance of the material. Moreover, the produced systems showed a significant effect on the value of storage modulus, allowing for control of this parameter depending on the modifying system used. The studied systems showed an effect on increasing the flexibility of the fabricated structures. The paper pointed out the determining effect of the structure of the ionic liquids included in the modifying system, and in particular, the influence of long

alkyl chains on individual material parameters such as crosslinking density. In addition, all modifying systems contained silicon and phosphorus atoms in various ratios, but due to the limiting content of the modifying system in the resin, it was not possible to thoroughly investigate the effect of the presence of these elements on individual parameters, in particular, on fire resistance. This aspect will be more thoroughly studied in future work. To summarize, the most important result of the present work is the confirmation, that ionic liquids can simultaneously modify many parameters both in the epoxy resin itself and in the composite, and each time the use of these substances and their effect on the final material should be studied in a multifaceted manner. Properly selected ionic liquids can be great alternatives as functional additives in composite materials with more than one functionality, but sometimes the wrong liquid can result in improving some values at the expense of worsening others.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/app131910661/s1>, 1. NMR spectrum, 2. DSC curves, 3. TGA curves, 4. DMA curves and 5. MLC curve.

Author Contributions: Conceptualization, D.Z., A.T. and A.S.; Formal analysis, D.Z.; Funding acquisition, M.S.; Investigation, D.Z., A.S., Á.P., Z.K., B.P. and B.S.; Methodology, D.Z., A.T. and M.S.; Software, D.Z., B.S., B.P. and A.S.; Supervision, A.T. and M.S.; Validation, D.Z., A.T. and M.S.; Visualization, D.Z.; Writing—original draft, D.Z.; Writing—review & editing, D.Z., A.T., Á.P., A.S. and M.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by National Science Centre, grant number 2017/26/E/ST8/01059 and grant number 2019/35/B/ST8/03736. This research was funded by the National Research, Development and Innovation Office (NKFIH K142517).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Dicyanamide ionic liquid mixtures for curing and modifying flax-fiber reinforced epoxy resin composites

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ARTICLE INFO

Keywords:
Ionic liquids
Epoxy resin
Polymerization
Crosslinking

ABSTRACT

Epoxy composites reinforced with natural fibers are a research area that has been growing tremendously in recent years, with increasing reports providing a better understanding of the interactions within such structures, resulting in newer and more specialized applications. This article presents a comprehensive study on the design and application of ionic liquids (ILs) in the development of flax fiber-reinforced epoxy composites with tailored mechanical properties. Three distinct ILs, namely 1-hexyl-3-methylimidazolium dicyanamide [HMIM][DCA], 1-hexyl-1,4-diazabicyclo[2.2.2]octan-1-ium dicyanamide [DABCO-C₆][DCA], and trimethyloctadecylammonium dicyanamide [N₁₁₁₁][DCA], were strategically engineered to incorporate longer carbon chains, with the primary objective of influencing the mechanical parameters of the resulting composites, specifically aiming for enhanced flexibility and resistance to bending and stretching. Using these designed ILs, two mixtures were developed and crafted to facilitate the effective curing of epoxy resin, which was examined using Differential Scanning Calorimetry (DSC). Investigation of the resin crosslinking process revealed that the mixtures of ILs exhibited a lower total enthalpy of thermal conversion than single-IL systems. Moreover, shifts in the polymerization onset temperatures were observed for the mixtures, with some systems displaying dual temperature peaks during crosslinking, indicative of potential parallel polymerization reactions.

1. Introduction

In recent years, there has been a remarkable surge in the exploration and development of epoxy composites reinforced with natural fibers. This burgeoning interest stems from the increasing demand for sustainable and eco-friendly materials in various industries, ranging from automotive to construction. Natural fibers, such as flax, hemp, and jute, offer several advantages over traditional synthetic reinforcements, including their renewable nature, low cost, lightweight nature, and biodegradability.

Of particular note is the use of ILs in composite materials. In this case, the range of applications is very wide and includes (i) modifying epoxy resins with ILs [1], (ii) flame retarding epoxy systems [2,3], (iii) improving the mechanical performance of composites [4,5], (iv) fibrillating reinforcing fibers in composites [6], and (v) initiating resin curing [7,8]. The latter is the most important application area for ILs. In 2009, the first reports described the use of 1-ethyl-3-methylimidazolium dicyanamide ([EMIM][DCA]) as a latent initiator of resin polymerization [9]. In the following years, the research progressed and brought

knowledge about, among other things, the mechanism of such initiated polymerization [10,11], ways to prolong the life of the resin blend [12,13], optimal concentrations of ILs [5,11], and challenges and predictions for the future [5]. However, most studies focus on the addition of a single IL and evaluate its effect on the resin and composite. The use of multiple IL systems that are capable of affecting more than one parameter of composites while maintaining their curing ability is still underexplored. There are known reports of studies on deep eutectic mixtures (DES), which include ILs supported by, for example, glycerol, glycols, or organic acids. In this context, DESs containing 1-butyl-3-methylimidazolium thiocyanate [14] or choline chloride [15] have been studied, proving their effectiveness as crosslinking agents. Another approach is bifunctional ILs, the results of which were published in 2020 [16]. In this study, it was shown that properly designed dual-functional ILs have crosslinking properties against epoxy resin and at the same time the material has better heat resistance with a glass transition temperature of 187–212 °C and the decomposition temperature at 10 % weight loss of 282–357 °C. Still, this remains a study that focuses on a single IL, which is only supported by the right choice of additives. In the 2023

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<https://doi.org/10.1016/j.molliq.2024.125340>

Received 1 February 2024; Received in revised form 20 June 2024; Accepted 21 June 2024

Available online 22 June 2024

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study, the use of two IL mixtures was shown as an example of systems that modify a composite material in terms of, for example, flame retardance while maintaining resin polymerization initiation properties [17]. Such research remains limited and needs to be continued. Although ILs can be freely designed, certain modifications require complex synthetic processes and complicated reactions or multistep syntheses of components that are intermediates on the way to obtaining the assumed structure. It seems reasonable to assume that certain functionalities can be achieved much more easily using mixtures of several liquids that incorporate the desired features.

Controlling the rheology of ILs is essential for their successful incorporation into materials. Certain ILs, particularly those with longer chain lengths, exhibit high viscosity, which can impede their processing. To overcome this challenge, the addition of another liquid can be employed to facilitate processing by altering the rheological properties of the mixture. This approach not only enhances the processability of the ILs but also enables the manipulation of their state of aggregation, particularly for solid ILs.

Longer alkyl chains in ILs enhance the overall chain mobility within the material matrix. This increased mobility allows for greater flexibility and deformability of the material, leading to enhanced elastic properties. For example, long-chain alkyl groups in ILs can facilitate polymer chain sliding and relaxation, resulting in improved elasticity [18]. Furthermore, such ILs can promote stronger interfacial adhesion between the additive and the matrix material. This improved adhesion helps prevent delamination and improves load transfer between the components, resulting in enhanced elastic properties. For instance, in composite materials, long-chain ILs can improve the bonding between the reinforcing fibers and the matrix, leading to increased elasticity [19].

The addition of long alkyl chain ILs to elastomeric polymer matrices, such as silicone rubber or polyurethane, can improve the material's elasticity, tear strength, and resilience [20]. One study evaluated the impact of ILs with different alkyl chains (butyl and octyl) on the mechanical properties of soft denture lining material. They found that the addition of ILs to Molloplast-B decreased the bond strength. Because ILs that have long alkyl chains (typically C8 and more) exhibit surfactant properties, the authors postulated that the decrease in bond strength may be attributed to the surfactant properties of the pyridinium-based ILs used. However, it is worth noting that the materials obtained using octylpyridinium chloride displayed either lower or similar Shore A test values compared with the control sample, which directly correlates with their enhanced elastic properties with regards to the materials with butylpyridinium chloride [21]. In a separate study, the effectiveness of two different charged ions, hexadecyltrimethylammonium and 1-methyl-3-octylimidazolium, as organophilization agents for sodium montmorillonite was recognized. The treated clay minerals exhibited improved compatibility with the rubber matrix composed of nitrile butadiene, along with enhanced thermal stability. These findings suggest that these clays can serve as effective reinforcing fillers, thereby facilitating a more practical vulcanization approach and consequently improving the mechanical and physical properties of the elastomer [22]. Incorporating long alkyl chain ILs into hydrogel networks can increase the flexibility and stretchability of the hydrogel, leading to improved elastic properties. This is particularly relevant in applications such as soft robotics and biomedical devices. In the study of polyacrylamide/Ca-alginate hydrogels prepared, it was presented that hydrogel with 1-hexyl-3-vinylimidazolium bromide showed 645 % improvement in tensile strength, 177 % in elongation at break, and 617 % in Young's modulus, compared to the hydrogel without any IL. However, it should be noted that the hydrogel based on 1-octyl-3-vinylimidazolium bromide had worse mechanical properties, which can be attributed to the hydrophobic nature of the cation, which in turn decreased the solubility of the hydrogel in water [23]. In addition, there have been studies on conjugated polymers with long 2-octyldodecyl side units, in which the mechanical properties were significantly improved compared with those

of polymers short 2-ethylhexyl units.

The first stage of the research focused on the synthesis of ILs with DCA anions. Literary sources describing the synthesis of comparable compounds suggest conducting a metathesis reaction using a silver salt of DCA, which is prepared just before the metathesis reaction itself, using a halide quaternary ammonium salt. This approach involves restricting light exposure because light triggers salt decomposition. In addition, it incurs high costs due to the necessity of using the silver salt [24,25]. On the other hand, conducting the metathesis reaction with the sodium salt of DCA under mild process conditions does not yield the expected results, and even if the desired product is obtained, the yield of the reaction is unsatisfactory (between 30 – 50 %) [26,27]. In contrast, few reports in the literature propose conducting the metathesis reaction between a quaternary halide and NaDCA without solvent [28] at a temperature at which the halide melts and can participate in the reaction. This method is limited to quaternary salts with relatively attainable melting points. This is precisely the route of synthesis adapted in the present study, and it allowed us to obtain the compounds assumed in the research plan in yields above 80 %, with the reaction temperatures varying from salt to salt and directly correlated with the melting point of the substrate in question.

The design of the structures of the ILs focused on incorporating longer carbon chains, at least six carbon atoms, into their structure. Such action was aimed at acquiring the ability of the ILs to affect the fundamental mechanical parameters of the composites, such as bending and stretching. In our opinion, these two parameters are usually limiting in terms of the application of a composite structure in an area that requires the material to be flexible. In addition, increasing the flexibility and bending resistance of the material also affects the safety of the application of the material in question. When damaged, it does not undergo a complete rupture, which can be accompanied by the exposure of the reinforcement and, consequently, the formation of places in the composite structure where fragments of the structural skeleton saturated with the cured resin appear. Such fibers are very small, and their shape and hardness resemble needles, which pose a risk of serious injury to the user. Given this fact, two tasks were set for the selected ILs: (i) to effectively initiate the curing of the epoxy resin and, (ii) to influence the enhancement of bending and tensile resistance parameters and protect the structure by potentially only partially rupturing and preventing the material from fully rupturing with the release of reinforcement.

The research presented in this paper was influenced and inspired by our previous studies. Using the knowledge we had already gained [17,29], a research plan was developed to demonstrate that appropriately designed systems consisting of two or three ILs, both having a dicyanamide anion, would be capable of significantly affecting the mechanical performance of flax fiber-reinforced epoxy composites while retaining the ability to effectively initiate resin crosslinking. To this end, two IL systems were developed and thoroughly tested, both under laboratory conditions and by preparing biocomposite structures from them. Based on our own experiments, long-chain ILs, at least containing a chain of six carbon atoms correlated with a DCA anion, were selected as the most promising modification-curing systems.

2. Materials and methods

2.1. Materials

All chemicals and synthesized compounds are shown in the Table 1. Synthesis procedures and analytical data are presented in Supplementary Material. Flax fabric was purchased from TC3 sp. z o.o. (Szczecin, Poland).

2.2. Mixture preparation

To prepare mixtures of ILs, appropriate amounts of each compound were weighed on an analytical balance, placed in a round-bottom flask,

Table 1
Chemicals.

Chemical compound	CAS No	Purity	Supplier	Other information
1-Chlorohexane	544-10-5	≥ 99.0 %	Merck GmbH Darmstadt, Germany	n/a
1,4-Diazabicyclo[2.2.2]octane	280-57-9	≥ 99.0 %	Merck GmbH Darmstadt, Germany	water content (KF): 0.2 %
Sodium dicyanamide	1934-75-4	≥ 97.0 %	Merck GmbH Darmstadt, Germany	water content (KF): 0.3 %
Trimethyloctadecylammonium chloride	112-03-8	≥ 98.0 %	Ambeed Inc. Arlington Heights, USA	water content (KF): 0.5 % pH: 5.8
1-hexyl-3-methylimidazolium chloride	171058-17-6	≥ 98.0 %	Ambeed Inc. Arlington Heights, USA	water content (KF): 0.4 %
1-Hexyl-1,4-diazabicyclo[2.2.2]octan-1-ium chloride	n/a	[IC]: 99.0 %	own synthesis	water content (KF): ≥ 0.5 %
1-Hexyl-3-methylimidazolium dicyanamide	927902-57-6	[IC]: 98.0 %	own synthesis	water content (KF): ≥ 0.5 % halogen content (IC): ≥ 2.0 %
1-Hexyl-1,4-diazabicyclo[2.2.2]octan-1-ium dicyanamide	n/a	[IC]: 96.0 %	own synthesis	water content (KF): ≥ 0.5 % halogen content (IC): ≥ 4.0 %
Trimethyloctadecylammonium dicyanamide	n/a	[IC]: 98.0 %	own synthesis	water content (KF): ≥ 0.5 % halogen content (IC): ≥ 2.0 %
epoxy resin LH 289	n/a	n/a	Havel Composites CZ s.r.o. Práslavice, Czechia	epoxy index [mol/1000]: 0.51 – 0.56 Viscosity [mPa]: 500 – 900 Density [g/cm ³]: 1.12 – 1.16
<i>Organic solvents</i>		HPLC grade,	Merck GmbH	
Acetonitrile	75-05-8	≥ 99.9 %	Darmstadt, Germany	water content (KF): < 0.01 %
Diethyl ether	60-29-7			water content (KF): 0.01 %
Dichloromethane	75-09-2			water content (KF): < 0.01 %
Isopropanol	67-63-0			water content (KF): 0.01 %

and stirred at 70 °C for one hour. After this time, the mixture was dried under vacuum overnight.

2.3. Thermal analysis

Thermal analyses of ILs and their mixtures, as well as mixtures of ILs with epoxy resin using Differential Scanning Calorimetry, were performed on a DSC 3 instrument (Mettler Toledo, Greifensee, Switzerland) according to the procedure described in our earlier papers [17,29,30].

2.4. Ion chromatography analysis

IL purity analyses using ion chromatography were performed on an ECO IC (Metrohm, Herisau, Switzerland) according to the procedure described in our earlier works [29].

2.5. NMR spectroscopy

NMR Spectroscopic analyses were performed on a Bruker Ascend™ (USA) instrument. ¹H spectra were recorded with a resolution of 400 MHz, whereas ¹³C spectra were recorded with a resolution of 100 MHz. The deuterated solvent used in each analysis was indicated when describing the synthesis of each compound. The value of the standard measurement uncertainty did not exceed ± 0.02 ppm. NMR spectra for [HMIM][DCA], [DABCO-C₆][DCA] and [N₁₁₁₁₈][DCA] can be found in [Supplementary Material](#).

2.6. Composite structure preparation

The vacuum bag method was used to produce composite structures, which is an improvement over the manual lamination method. The epoxy resin and the IL system (4 % wt.) were heated to 32 °C before saturating the fabric. The first step was to make a given element using the contact method, and then apply auxiliary materials to its surface and cover the whole thing with a flexible bag attached to the edges of the mold with an adhesive gasket. Then, the air with the excess resin mixture was sucked out through the vacuum pump stub placed in the mold. The auxiliary materials used to produce the composite were as follows: (i) Peel ply, which guaranteed the cleanliness of the surface and the required texture, (ii) perforated release film, which isolated the

composite from other surfaces, and (iii) a venting and draining fabric made of needle-punched non-woven fabric, which was intended to facilitate even distribution of the vacuum over the surface of the entire element and to remove excess resin mixture. Composite structures reinforced with flax fiber with a weight of 200 g/m² and a 2x2 weave were made. The composite structures from which appropriate measurement shapes for individual tests were prepared (by cutting strips from composite boards using a table saw with water cooling) were 4.0 or 2.0 mm thick (depending on the type of further study) and cured at 160 °C for 3 h with a temperature ramp 1 °C/min. Because the flax fabric is hydrophilic, which directly influences the hardening process of the composite, before its production, the fabric was dried at a temperature of 70 °C for 3 h. Perfectly dry fabric was used for the preparation of the composite structures.

2.7. Bending strength test

Bending strength tests were performed at room temperature according to EN ISO 178 using an Instron 5982 testing machine (Instron Inc., Norwood, USA) equipped with a 10 kN head and 3-point bending fixture. Specimens approximately 10.0 mm in width and 4.0 mm in thickness were used. The bending rate was 2.0 mm/min, and the support spacing was 64.0 mm. For this test, 6 or 8 samples of a given composite were used. Graphical representations of the results obtained for the mixture HMIM/ DABCO-C₆ DCA and HMIM/ DABCO-C₆/ N₁₁₁₁₈ DCA can be found in the [Supplementary Material](#).

2.8. Tensile strength test

Composite static tensile tests were performed at room temperature according to EN ISO 527-4 using an Instron 5982 testing machine (Instron Inc., Norwood, USA) equipped with a 10 kN head and pneumatic jaws. Specimens approximately 25.0 mm in width and 2.0 mm in thickness (type 2) were used. The tensile rate was 2.0 mm/min. For this test, 7 or 8 samples of the given composite were used. Graphical representations of the results obtained for the mixture HMIM/ DABCO-C₆ DCA and HMIM/ DABCO-C₆/ N₁₁₁₁₈ DCA can be found in the [Supplementary Material](#).

2.9. Heat deflection temperature (HDT)

HDT tests were performed using the D-VICAT/HDT-2-300/SA apparatus (Donserv, Warsaw, Poland) according to the PN-EN ISO 75-2 standard, using a nominal surface stress of 1.8 MPa for flat samples (method A, variant f, width approx. 10.0 mm). The tests were conducted at temperatures of 25–250 °C in silicone oil (heating rate 120 °C/h, counting after 5.0 min from the moment of applying the load) using 3 samples of a given composite.

2.10. Dynamic mechanical thermal analysis (DMTA)

DMTA measurements were performed using a DMTA Q800 device (TA Instruments Inc., New Castle, USA) with the three-point bending mode in the range of 25–250 °C (heating rate 3 °C/min, amplitude 1 Hz, strain 20.0 μm).

3. Results and discussion

3.1. Synthesis and mixture preparation

Given the need to achieve effective curing of epoxy resin while simultaneously enhancing the bending and tensile resistance parameters, two mixtures of ILs were developed. The structures of the ILs used are presented in Fig. 1.

The first mixture, comprised of two ILs sharing a DCA anion and featuring a six-carbon alkyl chain, aims to leverage the superior cross-linking properties associated with imidazolium liquids along with the mechanical enhancement potential demonstrated by [DABCO-C₆][DCA]. The second mixture, incorporating three ILs including [N₁₁₁₁₈][DCA] with its elongated eighteen-carbon alkyl chain, sought to further influence the bending and stretching parameters. These selections were made to address the dual objectives of crosslinking and mechanical reinforcement. Detailed description of the composition of each system is presented in Table 2. Two mixtures were obtained using the method employed in the DES preparation[54,55].

3.2. Thermal properties of ILs and their mixtures

Both individual ILs and their mixtures have been studied using DSC to determine their thermal properties, and in particular, how the interactions between the ILs in the mixtures affect their change in thermal properties with respect to single-component systems. All collected data are shown in Table 3.

For ILs alone, a glass transition temperature, T_g, of −60.7 °C was recorded for [DABCO-C₆][DCA], which is consistent with previously reported data for this compound [29]. On the other hand, [N₁₁₁₁₈][DCA] shows a melting point, T_m, at 80.3 °C and crystallizes, T_c, at 54.4 °C. However, for [HMIM][DCA], no phase transitions were observed under the analysis conditions. Furthermore, for the mixtures numbered 4 and 5 in the table, a glass transition temperature of

Table 2

Molar composition of the IL mixtures.

Ionic liquid	Mixture	
	HMIM/ DABCO-C ₆ DCA	HMIM/ DABCO-C ₆ /N ₁₁₁₁₈ DCA
[HMIM][DCA]	2 mol	3 mol
[DABCO-C ₆][DCA]	1 mol	2 mol
[N ₁₁₁₁₈][DCA]	–	1 mol

Table 3

Thermal properties of the ILs and their mixtures.

No	IL / Mixture	Thermal analysis		
		T _g [°C]	T _m [°C]	T _c [°C]
1	[HMIM][DCA]	–	–	–
2	[DABCO-C ₆][DCA]	–60.7	–	–
3	[N ₁₁₁₁₈][DCA]	–	80.3	54.4
4	HMIM/ DABCO-C ₆ DCA	–70.6	–	–
5	HMIM/ DABCO-C ₆ /N ₁₁₁₁₈ DCA	–	54.7 / 59.9	23.8 / 30.8

* no phase transition, T_g – glass transition temperature, T_m – melting point, T_c – temperature of crystallization, [HMIM][DCA] – 1-Hexyl-3-methylimidazolium dicyanamide, [DABCO-C₆][DCA] – 1-Hexyl-1,4-diazabicyclo[2.2.2]octan-1-ium dicyanamide, [N₁₁₁₁₈][DCA] – Trimethyloctadecylammonium dicyanamide.

–70.6 °C was observed for mixture 4, which indicates that it decreased with respect to the pure IL exhibiting analogous parameters – [DABCO-C₆][DCA]. In contrast, for the second mixture labeled 5, the analysis indicated the presence of two melting points (54.7 °C and 59.9 °C) and two crystallization temperatures (23.8 °C and 30.8 °C). Both values are significantly lower than those for the IL itself ([N₁₁₁₁₈][DCA]). The presence of two temperatures may indicate the mixture's complex molecular structure and inhomogeneity in terms of structure.

3.3. Curing properties

A key element of the research was the evaluation of the resin crosslinking process initiated by ILs as single-component systems as well as by their mixtures. DSC analysis was used for this purpose, and the results are shown in Table 4. The ideal concentration of IL was determined through screening tests across a concentration range of 2–8 % wt., using the DSC analysis. Optimal concentrations were identified as those where the process enthalpy value remained relatively unchanged. Following this, the best concentration was established for each individual IL and subsequently standardized, to ensure effective crosslinking. Similarly, this standardized concentration was applied when using mixtures of ILs.

The results summarized in the table show the following parameters: the temperature at the beginning of polymerization (T_{onset}), the temperature at the peak of polymerization (T_{max}) and the temperature at the end of polymerization (T_{offset}). The range between T_{onset} and T_{offset} can



Fig. 1. Structures of the selected ILs.

Table 4
Thermal analysis of the curing process initiated using ILs and their mixtures.

No	IL / Mixture	Thermal analysis			
		T _{onset} [°C]	T _{max} [°C]	T _{offset} [°C]	ΔH [J/g]
1	[HMIM][DCA]	144.3	154.3	167.1	31.4
		171.9	192.5	213.3	57.3
2	[DABCO-C ₆][DCA]	152.3	189.0	218.0	67.8
3	[N ₁₁₁₁₀][DCA]	146.7	174.9	223.5	64.2
4	HMIM/ DABCO-C ₆ DCA	160.9	171.7	180.8	12.2
		184.1	197.9	213.6	7.6
5	HMIM/ DABCO-C ₆ /N ₁₁₁₁₀ DCA	162.9	173.8	183.0	7.3

T_{onset} – temperature of polymerization start, T_{max} – temperature of the peak of polymerization, T_{offset} – temperature of the end of polymerization, ΔH – enthalpy.

be considered to be the temperature range in which epoxy resin polymerization initiated by ILs occurs. Peak polymerization, on the other hand, refers to the temperature at which the amount of energy released in the process in the form of heat is greatest. For each of the processes studied, the value of the enthalpy of the transformation is also given, which indicates the total energy released from the system during the reaction. The first important observation noted during the study is that the total enthalpy of thermal conversion is significantly lower for mixtures of ILs than for single ILs. For single-IL systems, the value ranges from 31.4 to 67.8 J/g, whereas for mixtures, the value ranges from 7.3 to 12.2 J/g. In our opinion, this may indicate that a process involving more than one IL is inherently less exothermic in terms of heat released, and that a greater amount of starting energy in the form of heat is required to initiate the process. The kinetics of polymerization reactions play a pivotal role in determining the total enthalpy of the process, which is particularly evident in systems involving two or three ILs compared with single systems. Variances in the rates of reaction between different hardeners can impact the energy released, with lower energy evolution suggesting a slower, more controlled reaction – a desirable trait in applications requiring precise process management. Moreover, systems comprising multiple ILs may exhibit enhanced thermal stability, contributing to lower enthalpy during the hardening process. This increased stability can prolong product lifespan, which is crucial for applications necessitating long-term property retention. This can also be seen in the polymerization onset temperatures, which in the case of mixtures is typically shifted by approximately 20.0 °C with respect to analogous systems containing only one IL. It is also worth noting that for some of the tested systems, numbered 1 ([HMIM][DCA]) and 4 (HMIM/ DABCO-C₆ DCA) in the table, two temperature peaks were observed during crosslinking, which may indicate the occurrence of two parallel polymerization reactions initiated by the anion or cation of the IL. This phenomenon is observed for ILs containing DCA anion and has been previously reported in the literature [5,11,29].

3.4. Mechanical properties

3.4.1. Glass transition and heat deflection temperature

To study the properties of the fabricated composite structures, the glass transition temperatures were measured by DMTA and HDT. The results of the tests were collected and are shown in Table 5. Analysis of

Table 5
Glass transition temperatures and HDT for the composite structures.

Mixture	Glass transition [°C]		HDT [°C]
	Loss modulus G''	Tan δ	
HMIM/ DABCO-C ₆ DCA	51.3 / 114.1	58.8 / 109.3	44.7
HMIM/ DABCO-C ₆ /N ₁₁₁₁₀ DCA	–	39.7	<RT*

* The sample reached the assumed deformation at room temperature.

the results for the first mixture (4) provides important information regarding its thermal properties. Glass transition temperatures determined by different methods present some variation, suggesting the complex structural nature of the material. The first pair of glass transition temperatures, obtained from the Loss Modulus, were 51.3 °C and 114.1 °C. This indicates that the first material transitions from a glassy to a rubbery phase over this extensive temperature range. This discrepancy may suggest the existence of heterogeneous areas or a differentiated structure of the material. In contrast, the second pair of glass transition temperatures, determined from Tan δ (58.8 °C and 109.3 °C), also presents a range in which the material changes elasticity in response to varying temperatures. The differences between the results of the two methods are due to differences in the sensitivity and specific characteristics of each method. In contrast, the HDT value is 44.7 °C, indicating that the material maintains its stiffness under thermal loading up to this temperature. The lower HDT values compared with the glass transition temperatures suggest that beyond this temperature, the material becomes more flexible and begins to enter the glassy state. Ultimately, the differences in the results indicate potential heterogeneity or structural complexity of HMIM/ DABCO-C₆ DCA. On the other hand, the glass transition temperature value for the second mixture (5), determined from Tan δ, is 39.7 °C. In this case, the value suggests that the second system is already more flexible at a relatively low temperature. It is noteworthy that the HDT for this mixture is below room temperature, and the sample has already reached the assumed load at room temperature. This means that the material maintains its stiffness under thermal loading under ambient conditions. Such characteristics are advantageous in applications where the stiffness of the material is required under normal operating conditions. The results obtained suggest that the HMIM/DABCO-C₆/N₁₁₁₁₀ DCA system exhibits a relatively low glass transition temperature, which means that it becomes more flexible even with small temperature changes. Simultaneously, it maintains its stiffness under room conditions, which could be crucial in practical applications of this composite material.

3.4.2. Bending strength tests

Based on the obtained results, the research was continued by conducting flexural strength tests on composite structures made with mixtures of ILs. The results of the bending strength tests on the two different composite blends show significant differences in their mechanical properties. The biocomposite prepared with the mixture HMIM/DABCO-C₆ DCA has a moderately high bending strength, reaching 28.6 MPa ± 7.2. This suggests that the material is relatively strong under flexural loading. The deflection at maximum strength is 5.7 % ± 0.6, indicating that the material has moderate deformation capacity. The deflection arrow value at strength is 9.4 mm ± 0.9, indicating that the material undergoes significant bending under bending forces, and the modulus at bending in the range of 0.05 % to 0.25 % strain is 1900.0 MPa ± 422.0, indicating that the material is relatively stiff in a small range of deformation. All the results of the measurements were collected and are

Table 6
Bending strength prosperities of the composite structures.

Mixture	Bending strength [MPa]	Deformation at strength [%]	Deflection arrow at strength [mm]	Modulus at bending (0.05–0.25 %) [MPa]
HMIM/ DABCO-C ₆ DCA*	28.6 ± 7.2	5.7 ± 0.6	9.4 ± 0.9	1900.0 ± 422.0
HMIM/ DABCO-C ₆ /N ₁₁₁₁₀ DCA**	3.2 ± 0.3	6.2 ± 1.5	9.4 ± 2.3	138.0 ± 28.0

* number of samples: 8.

** number of samples: 6.

presented in Table 6.

In the case of the HMIM/DABCO-C₆/N₁₁₁₁₈ DCA mixture, we observed a significantly lower flexural strength, reaching 3.2 MPa ± 0.3. This material exhibits low bending strength, which may affect its ability to maintain its structure during flexural loading. The deflection at strength is 6.2 % ± 1.5, suggesting a higher deformation capacity compared with the first mixture. Thus, the deflection arrow value at strength is similar at 9.4 mm ± 2.3. The modulus at bending in the range of 0.05 % to 0.25 % strain is much lower, at 138.0 MPa ± 28.0, indicating that the material has lower stiffness compared with the first mixture. However, this may indicate that the material is more flexible because of its low stiffness. In summary, the first mixture (HMIM/DABCO-C₆ DCA) showed significantly better bending strength and stiffness than the second blend (HMIM/DABCO-C₆/N₁₁₁₁₈ DCA), which had lower flexural strength and stiffness. These differences are important for the potential applications of these materials which depend on their structural and mechanical requirements.

3.4.3. Tensile strength tests

At the same time, tensile tests were performed for all fabricated structures, the results of which are shown in Table 7.

The results of the tensile strength measurements for the two epoxy composite blends show significant differences in their mechanical properties. The HMIM/DABCO-C₆ DCA blend has a high tensile strength, reaching 55.0 MPa ± 1.3, demonstrating the material's ability to withstand high tensile stresses before fracture. The tensile strength at break is maintained at 54.9 MPa ± 1.3, confirming that the material maintains high stresses even at rupture. Despite the low elongation at break (1.6 % ± 0.1), which suggests relative stiffness, it is worth noting that the full structural break that occurred in these specimens is usually characteristic of more brittle materials. In addition, the value of Young's modulus in the range of 0.05 % to 0.25 % strain is 5.9 GPa ± 0.3, confirming the high stiffness of the material in the region of small deformations. Fig. 2 shows the appearance of the tested samples after the tensile tests.

For the HMIM/DABCO-C₆/N₁₁₁₁₈ DCA blend, the tensile strength is 40.4 MPa ± 5.0, indicating a lower resistance to tensile forces than the first blend. Nevertheless, the important aspect here is that the specimens did not completely crack or break the structure, indicating that the composite structure remains partially cohesive even after rupture. The tensile strength at break is maintained at 39.2 MPa ± 5.7, which suggests that stresses persist even at rupture, while the structure remains continuous. Elongation at break is 2.4 % ± 0.1, indicating some flexibility of the material before rupture, and this can certainly be beneficial in applications where there is a risk of tensile stress. The value of Young's modulus in the range of 0.05 % to 0.25 % strain is 1.7 GPa ± 0.1, which translates into a lower stiffness of the material compared to the first blend.

The obtained results provide valuable insights into the mechanical properties of the composite structures fabricated using mixtures of ILs. The HDT values correlated with the material's stiffness under thermal loading. For instance, the composite made with HMIM/DABCO-C₆ DCA

demonstrates a relatively high HDT value of 44.7 °C, whereas the HMIM/DABCO-C₆/N₁₁₁₁₈ DCA mixture exhibits a much lower HDT value, even below room temperature. This difference in HDT values aligns with the observations from the bending strength tests, where the HMIM/DABCO-C₆ DCA composite shows significantly higher bending strength (28.6 MPa ± 7.2) than the HMIM/DABCO-C₆/N₁₁₁₁₈ DCA blend (3.2 MPa ± 0.3). The higher HDT value of the former composite corresponds to its superior bending strength, indicating that it can withstand greater flexural loads without deformation. Similarly, when considering the tensile strength, the HMIM/DABCO-C₆ DCA composite presented a higher value (55.0 ± 1.3 MPa) than the HMIM/DABCO-C₆/N₁₁₁₁₈ DCA (40.4 ± 5.0 MPa). This difference corresponds with the HDT values of the respective composites. The HMIM/DABCO-C₆ DCA composite, characterized by a higher HDT range, demonstrates greater tensile strength than its counterpart with a lower HDT range. Furthermore, the tensile strength tests revealed similar trends. The HMIM/DABCO-C₆ DCA composite exhibits a high tensile strength of 55.0 MPa ± 1.3, along with a high Young's modulus (5.9 GPa ± 0.3), indicating its ability to withstand high tensile stresses and maintain stiffness under tension. In contrast, the HMIM/DABCO-C₆/N₁₁₁₁₈ DCA blend shows lower tensile strength (40.4 MPa ± 5.0) and a lower Young's modulus (1.7 GPa ± 0.1), suggesting reduced resistance to tensile forces and lower stiffness compared with the former composite. Materials with higher HDT values possess enhanced mechanical properties and exhibit greater resistance to deformation under both bending and tensile stresses. This correlation underscores the importance of HDT as a predictive indicator for assessing the mechanical performance of composite materials, particularly in applications where exposure to elevated temperatures is a concern. Therefore, the two blends show differences in tensile strength, but the structure of the samples produced using the second blend remains partially consistent after rupture, and this can be seen as a significant advantage from the perspective of the safety of use of the composite material.

4. Conclusions

In our study, we focused on the design and characterization of ILs ([HMIM][DCA], [DABCO-C₆][DCA], and [N₁₁₁₁₈][DCA]) tailored to influence the mechanical properties of composite materials. These ILs were incorporated into mixtures with specific molar ratios to enhance the flexibility and resistance to bending and stretching of the epoxy resin composites. Thermal analysis of the ILs and their mixtures revealed variations in key parameters such as glass transition temperatures, melting points, and crystallization temperatures, indicating the intricate interplay within the mixtures. Notably, the evaluation of resin cross-linking revealed that the mixtures exhibited distinct thermal conversion behavior compared with single-IL systems, with shifted polymerization onset temperatures and evidence of parallel polymerization reactions. HDT values demonstrate a strong correlation with the material's stiffness under thermal loading. Specifically, the composite made with HMIM/DABCO-C₆ DCA exhibits a notably higher HDT value than the HMIM/DABCO-C₆/N₁₁₁₁₈ DCA mixture. This disparity aligns consistently with observations from bending strength tests, where the HMIM/DABCO-C₆ DCA composite displays significantly superior bending strength, in contrast to the HMIM/DABCO-C₆/N₁₁₁₁₈ DCA blend. Moreover, the trend extends to tensile strength, with the HMIM/DABCO-C₆ DCA composite demonstrating a higher value compared to the HMIM/DABCO-C₆/N₁₁₁₁₈ DCA blend. This difference directly corresponds to the HDT values of the respective composites. Materials with higher HDT values possess enhanced mechanical properties and exhibit greater resistance to deformation under both bending and tensile stresses. In conclusion, while the two blends exhibit differences in tensile strength, it's notable that the structure of the samples produced using the HMIM/DABCO-C₆/N₁₁₁₁₈ DCA blend remains partially consistent after rupture. This attribute can be interpreted as a significant advantage from the perspective of the safety of use of the composite

Table 7
Tensile strength parameters for composite structures.

Mixture	Tensile strength [MPa]	Tensile at break [MPa]	Elongation at break [%]	Young modulus (0.05–0.25 %) [GPa]
HMIM/DABCO-C ₆ DCA [*]	55.0 ± 1.3	54.9 ± 1.3	1.6 ± 0.1	5.9 ± 0.3
HMIM/DABCO-C ₆ /N ₁₁₁₁₈ DCA ^{**}	40.4 ± 5.0	39.2 ± 5.7	2.4 ± 0.1	1.7 ± 0.1

^{*} number of samples: 7, type of failure: brittle resolution breakthrough.

^{**} number of samples: 8, type of failure: brittle and slip breakthrough.

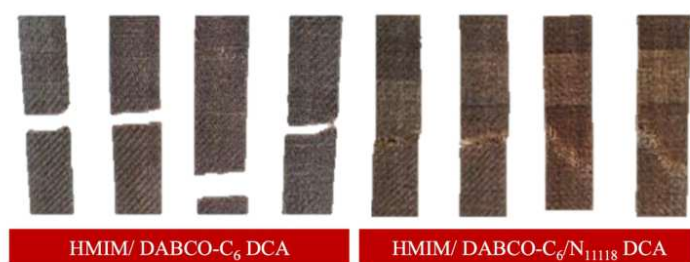


Fig. 2. Images of composite samples after tensile strength tests.

material, underscoring the importance of considering both mechanical properties and structural integrity when evaluating composite materials for practical applications.

CRedit authorship contribution statement

Dawid Zielinski: Writing – original draft, Validation, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Andrea Szecht:** Writing – review & editing, Methodology, Investigation. **Marcin Smiglak:** Writing – review & editing, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgment

The authors acknowledge financial support from the National Science Centre (Poland), project SONATA BIS (No. 2017/26/E/ST8/01059) entitled “Multifunctional composite systems based on epoxy resins with ionic liquids as a crosslinking initiators” and project PRELUDIUM (No. 2023/49/N/ST11/04057) entitled “ILFLAME - Synergistic interaction of phosphorus, silicon, and nitrogen in the flame retardancy of epoxy composites using ionic liquids and SILP materials with additional activity as a curing agent”.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.molliq.2024.125340>.

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Supported Ionic Liquid-Phase Materials (SILP) as a Multifunctional Group of Highly Stable Modifiers and Hardeners for Carbon and Flax Epoxy Composites

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This paper introduces a novel approach to enhance epoxy resin formulations by using SILP materials as multifunctional hardeners and fillers in composite structures reinforced with carbon and flax fibers. This study explores the integration of ionic liquids (ILs) onto a silica support structure, presenting various permutations involving silica selection, ionic liquid choice, and concentration. The focus of this study was to elucidate the influence of SILP on resin curing ability and the mechanical properties of the resulting composites. Detailed research was conducted, including Brunauer-Emmett-Teller analysis (BET) for SILP materials and curing characterization for epoxy resin formulations with different SILP materials. Furthermore, the mechanical properties of the obtained composites were

determined by Scanning Electron Microscopy analysis (SEM) (the force at break, the maximum elongation at break, tensile strength, and modulus of elasticity). Through SILP incorporation, the mechanical properties of composites, including the modulus of elasticity and tensile strength, are substantially improved, a phenomenon akin to traditional filler effects. The findings highlight SILP materials as prospective candidates for concurrent hardening and filling roles within composites (through a single-step procedure, with prolonged storage stability and controlled processing conditions), particularly pertinent as the composite industry veers toward epoxy bioresins necessitating liquefaction via temperature application.

Introduction

More than 80 years have passed since the first European patent on epoxy resins was granted, which has led to the worldwide expansion of this type of substance around the world.^[1] Despite many years of research, epoxy resin technologies are still undergoing new modifications and improvements, which are not only a response to the emerging new areas of application of this type of material but also, above all, result from the need to improve technologies in terms of reducing their negative impact on the environment.^[2–4] The use of materials based on epoxy resins is so extensive today that, the complete elimination of this type of raw materials is practically impossible. Therefore, the key is to strive to achieve the greatest possible environmental neutrality, both in the process of producing resins and components necessary for their final use and in implementing recycling methods and advanced modifications that change the properties of these types of materials. These efforts extend the life cycle of products made from them.

The epoxy resin itself is practically useless, and the most important process that makes it acquire the desired properties is the cross-linking process, which can be initiated by many substances belonging to various chemical groups.^[5] The use of an appropriate curing system is crucial for achieving the assumed parameters, both in terms of the resin polymerization process itself and the final properties of the cross-linked material.^[6–8] The most classic approach to initiating the epoxy resin polymerization process is the use of an amine or acid anhydride.^[9,10] Over the years, numerous studies have been conducted on the optimal structures of amine-curing agents^[3,11] and the selection of acid anhydrides.^[10,12] High availability and low price have contributed to the widespread use of these two groups of substances as universal hardeners. However, their use entails numerous limitations, such as the short lifetime of the resin:hardener mixture, in which the polymerization process begins practically immediately after mixing the components, sometimes making it impossible to properly process the system to achieve the assumed goals of the final product.^[3,5,9] Moreover, both amines and acid anhydrides are compounds that do not provide the cured resin with any unique functional properties that could not be replaced.^[3,13] In addition, their use poses potential dangers to both human health and the environment, as they can increase the risk of resin contamination or affect the health of those who come into contact with them.

In addition, many effective biohardeners are currently known,^[3,6,13–16] and have been tested in terms of their mechanism of action or impact on the cured resin. The most significant groups of biohardeners are terpenes,^[3,13] amino

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Supporting information for this article is available on the WWW under
<https://doi.org/10.1002/cplu.202400193>

acids,^[17–20] and porphyrins,^[21] which seem to be well-thought-out choices in the design of advanced epoxy biomaterials. However, considering several unique features that the hardener can impart to the resin mixture and the extent to which its cross-linking activity can be controlled, ionic liquids (ILs) seem to be the most valuable group of compounds that combine, apart from the resin cross-linking ability, many advantages for resin systems. Ionic liquids are substances with an ionic structure, which are characterized by being in a liquid state below 100 degrees Celsius and maintaining this state over a wide range of temperatures, while being very thermally and chemically stable.^[22,23] The properties of ILs include, above all, low vapor pressure and the possibility of their design based on any selected structures of cations and anions (organic or inorganic), obtaining millions of combinations and matching them to the assumed expectations.^[24] One of the areas of application of ILs is their use as latent initiators of epoxy resin crosslinking, which are activated only after energy is supplied to the system in the form of temperature.^[25–27] Moreover, at low temperatures, they usually remain inactive toward the epoxy resin molecule. The mechanism of resin curing by ionic liquid is complex but, relatively well understood, and the relationships between the temperature of the crosslinking process (necessary to start curing) and the decomposition temperature of the IL are not directly correlated.^[8] Moreover, the chemical structure of the IL remains crucial and has a decisive influence on its activity as a cross-linking initiator.^[27]

Furthermore, the application of hyperbranched polymers originating from itaconic anhydride has resulted in notable enhancements in the durability and fire resistance of epoxy resins containing minimal phosphorus amount.^[28] Similarly, the attainment of superior mechanical strength, recyclability, and preservation of thermal characteristics was achieved by employing ferulic acid-based hyperbranched epoxy resin (FEHBP) in crafting catalyst-free epoxy vitrimers.^[29] In the context of ionic liquids used with epoxy resins, the comparison of various ILs as epoxy hardeners demonstrated, that certain ILs effectively cure epoxy resins, producing similar or superior mechanical properties and lap shear strength compared to conventional amine-based curing agents, thus advancing sustainability due to the non-volatility and reduced usage of ILs.^[30] Thus, the reported tetra-epoxidized imidazolium ionic liquid monomer with ester-cleavable groups, which, when incorporated into conventional epoxy-amine networks, significantly reduce gel time, improve thermal stability, enhance homogeneity, and facilitate degradability under mild conditions, thereby demonstrating the potential of IL-based comonomers to tailor the physical properties and sustainability of high-performance thermosets and composites.^[31] Chemically modified silica with halide ionic liquid deposited on its surface was first presented in 2017. This study reported the enhancement of mechanical and thermal properties of epoxy composites through the incorporation of SILP, which not only improves interfacial interaction and reinforcement but also acts as a cure agent, leading to superior performance compared to composites containing unfunctionalized silica by significantly increasing storage modulus, tensile strength, toughness, and thermal stability. However, the low

curing efficiency of the chloride anion compared with other anions available in ILs (such as dicyanamide or acetate), as well as the rather complicated method used for obtaining SILP material, inspired us to adopt a different strategy and look more broadly at designing suitable SILP-type materials.^[32]

Among the solid hardeners, the most popular is sodium dicyandiamide, whose properties initiate the polymerization of resins are well known.^[33–36] However, it is a universal hardener that does not provide many additional benefits to the final product. Therefore, the search for new groups of loose hardeners is important for the development of bioresin technologies. In addition, an appropriate loose hardener may ultimately enable the sale of single-component loose epoxy resins, which will be properly mixed with the hardener, thus, the method of their use to produce composite structures will be devoid of the process of preparing the resin-hardener mixture, increasing the repeatability of the parameters of these systems. Here, ILs may be useful, which, if properly designed, will melt at the melting point of the epoxy resin, leading to the formation of a ready-made resin mixture. Another interesting approach may be SILP materials. In this group of materials, the ionic liquid is physically deposited on the surface of the support, which can be, depending on the application, silica, activated carbon, or other loose minerals.^[37–39] The most popular carriers include silica, the porosity of which enables a high degree of packing of the ionic liquid while maintaining high flowability. SILP materials have found application primarily in catalysis, where, apart from the ionic liquid, the appropriate catalyst is dissolved in it, and then the mixture is placed on the support in appropriate concentrations.^[37,38,40–42] However, this is an interesting solution because in the case of epoxy resin, by introducing the SILP material with the ionic liquid applied to it, we simultaneously introduce a latent cross-linking initiator and a filling element, e.g., silica. The range of packing possibilities of the ionic liquid on the silica depends on the porosity of the silica and may be optimized in the context of the final application.^[37]

From year to year, in the era of high awareness of end users and producers, the attractiveness of this type of solution decreases. Consequently, the need to search for both new epoxy bioresins and biohardeners was initiated,^[3] which will not only be a substitute for classic raw materials but also provide at least analogous process and utility properties.^[6,43] The last decade has seen a significant acceleration in research on new methods of initiating epoxy resin polymerization, which, apart from the polymer cross-linking, will have an additional function, such as the stability of the resin:hardener system,^[44] flame retardant,^[45,46] increasing mechanical properties^[8] or natural origin.^[13,14] There are known reports of the possibility of curing the epoxy resin by Ultraviolet radiation (UV), which allows not only a very short time needed for complete cross-linking, but also due to the lack of activity of the photoinitiator toward the resin in the absence of sufficiently intense radiation, it significantly extends the life of the prepared mixture, increasing the possibility of more efficient processing resin before it is fully cured.^[47] In addition, the curing process, which proceeds via radical-induced cationic frontal polymerization (RICFP), was thoroughly characterized, providing important information in

the context of manufacturing specific products using this method.^[47,48]

On the other hand, in recent research on the development of new resin molecules, mainly derived from bioavailable raw materials or waste raw materials, we observe that new resins are often in the form of solids with melting points around 100 degrees Celsius.^[3,16,49] Commonly used epoxy resins are liquid raw materials that, in addition to the resin molecule, contain numerous auxiliary substances, such as rheology modifiers or solvents. Their task is to match the resin system to the application requirements. Similarly, hardeners were developed, which, remaining at room temperature in the liquid phase, enable precise connection with the liquid resin and facilitate the entire process of preparing the resin mixture. However, in the case of new types of bioresins that occur as solids, it seems crucial to search for new groups of cross-linking initiators that will be in solid form at room temperature. Combining liquid hardeners with solid resin, which will only become liquid when heated, prevents full mixing of the system and may result in defects in the structure of the final product or uneven cross-linking.

In addition, the use of silica as a filler increases the viscosity of the resin mixture, increases the value of Young's modulus, and elasticity increases the strength of the hardened material in the static tensile test.^[50–53] Resin mixtures enriched with silica can be further used to produce composite structures reinforced with carbon or other fibers,^[54] leading to the development of advanced materials characterized, depending on the type of reinforcement, by increased tensile strength, increased elasticity, or higher hardness.

The aim of this work is to design and manufacture SILP materials based on three silica materials differing in terms of pore size and degree of fragmentation, and three ionic liquids, which are known to have cross-linking properties for epoxy resins: 1-ethyl-3-methylimidazolium acetate ([EMIM][OAc]), 1-butyl-3-methylimidazolium dicyandiamide ([BMIM][DCA]), and 1-benzyl-3-methylimidazolium dicyandiamide ([BenzMIM][DCA]). To date, such planned, extensive, and comprehensive research on the use of SILP materials in resin systems and their impact on these systems has not been conducted. In the next stage, the use of SILP materials as components of a resin mixture in a system with a commercial epoxy resin was investigated, and the production of composite structures based on carbon and flax fibers and reinforcement was investigated. The cross-linking process was tested using differential scanning calorimetry (DSC), referring the obtained parameters to systems without silica, and Shore hardness was selected as a parameter for quick assessment of cured structures. Furthermore, the obtained composite structures were characterized using a scanning electron microscope (SEM) equipped with an attachment for testing the static tensile strength. In addition, the effect of silica filling introduced into the system in the form of SILP material was also examined, referring to the composite produced by introducing the IL and silica separately into the system, but without prior preparation of the SILP material. This study also presents a research model that specifies the exclusion conditions for individual prototypes. This is important

because as part of the research, numerous prototype combinations were generated, for which the boundary conditions of the process were assumed, including: curing temperature up to 150 degrees Celsius, compatibility with the resin and no sedimentation, concentration in terms of ionic liquid up to a maximum of 5% by weight, maximum curing time of 4 hours in isothermal simulation conditions using a vacuum oven, and minimum hardness range of 75 D on the Shore hardness scale.

Results and Discussion

The study began with the preparation of a research plan that will consider not only all the boundary conditions that have been assumed but also allow the development of a method for screening the results obtained at each of the research stages. Thanks to this approach, the research process was conducted on the basis of a clear and legible methodology, and as a consequence, it was possible to test 45 samples of SILP materials. The research process, consisting of 4 steps containing individual examination and test packages, is presented in Figure 1. Thus, starting with 45 samples of SILP materials, the screening process resulted in 3 best combinations that were subjected to a full study.

SILP Materials

In the first stage of research, 45 SILP materials based on three different types of silica, 3 ionic liquids, and 5 concentrations of ionic liquid deposited on a silica support were prepared. The selected silica differed in pore size, ranging from 22 to 150 Å. At the same time, they were selected in such a way as to maintain a fairly consistent mesh range for all of them. This action was primarily aimed at investigating the effect of pore size on the properties of SILP in the context of the ability to cure epoxy resin and, to demonstrate the relationship between this parameter and the possibility of depositing a specific amount of IL on the surface of the support.

On the other hand, the choice of ionic liquids was primarily dictated by their proven ability to initiate epoxy resin polymerization. Among the three ILs, for two of them: 1-ethyl-3-methylimidazolium acetate and 1-butyl-3-methylimidazolium dicyanamide, literature reports on their activity as resin polymerization initiators are known.^[25,44,55–58] The third ionic liquid, 1-benzyl-3-methylimidazolium dicyanamide, was proposed by us and complements the IL portfolio as a compound with a slightly different chemical structure. In addition, it allows the expectation that it will show activity in the field of the tested application, based on the knowledge generally known in the literature about the use of ionic liquids as latent hardeners. The selected ILs not only present a different structure, but also have certain features that may affect their use in the context of SILP materials and their further use as hardeners. These features include the following: (i) highly hygroscopic properties ([EMIM][OAc]), (ii) a longer alkyl chain in the cation structure with potential effect on the elasticity of the material ([BMIM][DCA]),

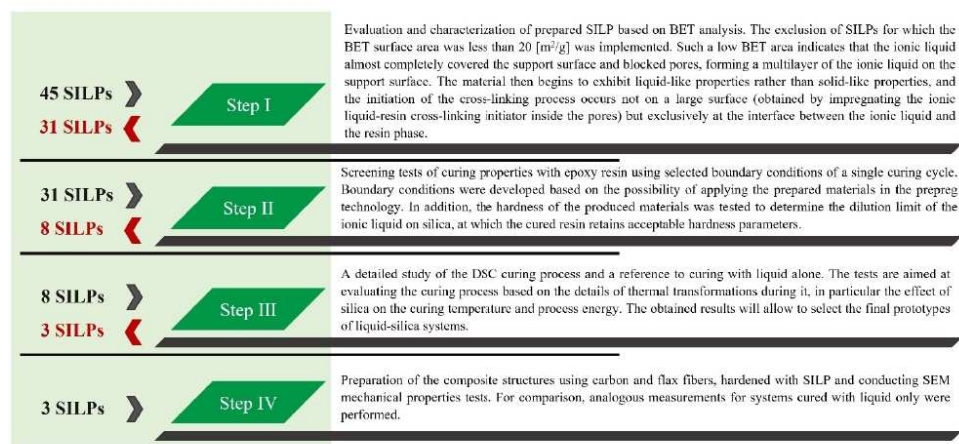


Figure 1. Iterative representation of the research process.

and (iii) the presence of an aromatic ring with potential effect on the stiffening of the final material ([BenzMIM][DCA]). Moreover, each of the selected ionic liquids exhibits curing activity in a different temperature range from 60 °C (depending on the epoxy resin), whereas dicyandiamides effectively cure the resin only at temperatures above 120 °C. Finally, a concentration range of 10–50% of the ionic liquid deposited on a silica support was selected. Such a scope made it possible to examine two key features in the context of the presented research. First, it allowed us to assess the ability of the maximum packing of the ionic liquid on the silica surface, which enables us to maintain the features of the monolayer and does not lead to full coverage of all the pores of the supporting phase. This is of key importance in the design of this type of material and in the selection of appropriate components: silica support and ionic liquid. On the other hand, such a range of concentrations allowed us to assess the effect of the amount of IL on the silica and the ability to initiate the polymerization of the epoxy resin (in the context of the activity itself and the impact on the thermal parameters of the process). Moreover, as the concentration of the ionic liquid on the silica decreased, it was necessary to provide more and more SILP material into the epoxy resin (the amount of IL curing agent was always constant relative to the resin), which consequently increased the content of silica filler. This aspect has notable implications for the materials' properties and fundamental characteristics, including hardness.

All SILP materials were prepared in an analogous manner, and the BET method was used for their characterization, leading to the determination of the number of parameters, as presented in Table 1. Davisil Grade 62 silica (DG62), characterized by the largest pore size, allowed the preparation of SILP materials in the full range of concentrations for almost all three ionic liquids. The singular exception was the 50% concentration of [BMIM][DCA]. For the other two ILs, a concentration of 50%

led to a silica surface with no available area for interaction with [BenzMIM][DCA] (BET surface area 23.2 m²/g) and for [EMIM][OAc] (BET surface area 86.9 m²/g). This means that for [BenzMIM][DCA], the concentration of 50% seems to be the upper limit in the case of DG62 silica, whereas in the case of the second IL, this concentration may still be slightly increased. In turn, the value of the pore-filling degree (α) for all SILP materials obtained with the use of DG62 silica maintained a downward trend with the decrease in concentration, which is the expected effect and proves the correct deposition of ILs on the surface of the support. However, DG62 silica promotes the formation of a thick layer of ionic liquid on its surface (2.55 up to 3.44 nm for 50% of [BenzMIM][DCA]), which is not a beneficial effect. This means that only a certain part of the IL molecules is stabilized by interacting with the silica carrier, whereas the remaining part is less stabilized, which increases the likelihood of leaching or excessive migration within the entire layer. We suppose that such a large silica pore size may favor full pore filling with the formation of lake-like areas in the continuity of the ionic liquid layer, which affects the overall layer thickness parameter. Regrettably, it bears negative implications within the proposed application because the material prepared in this way will not be able to effectively use all the ionic liquid deposited on the silica in the curing process. Primarily, the process will occur mainly on the surface of lake-like areas, blocking access to the IL-hardener trapped in the deeper part of the silica support. Therefore, this may affect the formation of uncured spaces inside the composite, particularly in the zones close to the silica filler, thereby reducing its mechanical parameters and stimulating the process of structural defects by increasing the heterogeneity of the cured material.

Medium pore size silica, Davisil Grade 635 silica (DG635), also allowed us to obtain SILP materials in virtually the full range of concentrations, excluding only 50% concentration for each of the tested ILs. The results of the BET surface analysis

Table 1. SILP characterization.

No	Ionic liquid	Silica	Concentration [%]	BET [m ² /g]	Total Pore Volume [cm ³ /g]	Average Pore Diameter [nm]	α^{st}	Layer thickness ^{b)} [nm]
S1		DG62		290.6	1.10			
S2		DG635		550.9	0.78			
S3		DG12		716.1	0.39			
1	[BenzMIM] [DCA]	DG62	50	23.2	0.10	16.8	0.91	3.44
2			40	72.4	0.29	16.7	0.74	2.79
3			30	130.6	0.50	15.4	0.55	2.06
4			20	189.5	0.70	14.7	0.36	1.38
5			10	234.4	0.84	14.3	0.24	0.89
6		DG635	50	1.0	n/a	n/a	n/a	n/a
7			40	40.2	0.08	8.1	0.90	1.27
8			30	129.4	0.25	7.7	0.68	0.96
9			20	274.4	0.42	6.1	0.46	0.65
10			10	390.2	0.66	6.7	0.15	0.22
11		DG12	50	0.7	n/a	n/a	n/a	n/a
12			40	0.8	n/a	n/a	n/a	n/a
13			30	0.9	n/a	n/a	n/a	n/a
14			20	20.3	0.02	3.2	0.95	0.52
15			10	352.0	0.20	2.4	0.49	0.27
16	[BMIM] [DCA]	DG62	50	13.0	n/a	n/a	n/a	n/a
17			40	58.2	0.26	10.9	0.76	2.89
18			30	116.0	0.49	10.5	0.55	2.10
19			20	181.9	0.72	9.9	0.35	1.31
20			10	266.8	0.99	9.6	0.10	0.38
21		DG635	50	1.0	n/a	n/a	n/a	n/a
22			40	26.8	0.06	9.4	0.92	1.31
23			30	112.2	0.26	9.4	0.67	0.94
24			20	206.5	0.39	7.6	0.50	0.71
25			10	370.0	0.57	6.1	0.27	0.38
26		DG12	50	0.9	n/a	n/a	n/a	n/a
27			40	0.0	n/a	n/a	n/a	n/a
28			30	0.7	n/a	n/a	n/a	n/a
29			20	0.9	n/a	n/a	n/a	n/a
30			10	336.0	0.18	2.2	0.54	0.29
31	[EMIM] [OAc]	DG62	50	86.9	0.36	16.6	0.67	2.55
32			40	157.8	0.58	14.7	0.47	1.79
33			30	185.9	0.69	14.9	0.37	1.41
34			20	209.0	0.79	15.1	0.28	1.07
35			10	249.5	0.92	14.8	0.16	0.62
36		DG635	50	0.7	n/a	n/a	n/a	n/a
37			40	38.8	0.10	10.3	0.87	1.23
38			30	111.6	0.23	8.3	0.71	1.00
39			20	289.6	0.44	6.1	0.44	0.62
40			10	380.7	0.57	6.0	0.27	0.38
41		DG12	50	0.0	n/a	n/a	n/a	n/a
42			40	0.0	n/a	n/a	n/a	n/a
43			30	1.7	n/a	n/a	n/a	n/a

Table 1. continued

No	Ionic liquid	Silica	Concentration [%]	BET [m ² /g]	Total Pore Volume [cm ³ /g]	Average Pore Diameter [nm]	$\alpha^{[a]}$	Layer thickness ^[b] [nm]
44			20	160.8	0.09	2.2	0.77	0.42
45			10	426.0	0.24	2.2	0.38	0.21

^[a] Pore-filling degree of support as the ratio IL volume/support pore volume. ^[b] Ratio of the IL volume used for coating and the initial surface area. n/a – not available.

showed that at the concentration level of 40%, the entire surface of the silica is practically used, leaving a free part at the level of the BET surface area: 40.2 m²/g for [BenzMIM][DCA], 26.8 m²/g for [BMIM][DCA], and only 38.8 m²/g for [EMIM][OAc]. All obtained SILP materials retained the value of total pore volume at a very low level in the range of 0.06 to 0.10 cm³/g. In addition, the α degree retained the expected trend of decreasing value with decreasing ionic liquid concentration. Nevertheless, for SILPs obtained with the use of DG635 silica, the formation of much thinner IL layers was noted, 49% thinner (for 40% concentration of IL) compared with DG62 silica. This proves the even distribution of the ionic liquid on the surface of the support and, above all, allows us to assume that silica with a pore size of 60 Å seems to be the most optimal for the preparation of SILP materials, based on the tested ILs. It allows not only to obtain various concentrations of the deposited phase, but also guarantees even distribution on the surface of the silica and to obtain a thin layer with the same intensity of interaction with the supporting phase.

The last silica used for the preparation of SILP materials was Davisil Grade 12 silica (DG12), which was characterized by the smallest pore size, approximately 7 times smaller than DG62 silica and almost 3 times smaller than DG635 silica. Such a small pore size translated into a huge silica surface determined by the BET method with a very small total pore volume of only 0.39 cm³/g, 2 times smaller than that for DG635 and almost 3 times smaller than that for DG62. Therefore, only the lowest concentrations of the ionic liquid deposited on its surface were obtained, respectively 10% and 20% for [BenzMIM][DCA] and [EMIM][OAc] and 10% for [BMIM][DCA]. For these SILP materials, the smallest average pore diameter of 2–3 nm was determined among all the tested materials, as well as a low thickness of the deposited layer. This type of silica can be useful when very low concentrations of IL on the support and very thin layers are required. In this study, it should be noted that in the case of SILP materials based on DG12 silica, massive amounts of silica filler will always be introduced into the system, and the small pore size will certainly affect the ability to interact between the ionic liquid curing agent and the epoxy resin matrix, which in turn will result in low curing activity of this type of SILP.

Based on the BET surface analysis of the obtained SILP materials, out of 45 combinations, 31 passed to the next stage of research and 14 were eliminated.

Curing Properties of SILP Materials

The subsequent phase of the investigation involved the evaluation of the ability of SILPs to initiate curing of the epoxy resin. For this purpose, initial screening tests were performed in a vacuum oven. This test encompassed an assessment of not only the curing properties of newly prepared materials but also the resulting Shore hardness of the cured resin. Of the 31 tested SILPs, only 8 met the predefined boundary parameters, such as hardening in one temperature cycle or reaching a specific hardness value (75 D). For these top 8 combinations, representing all types of silica and ILs, a detailed study of the curing process using DSC was performed in relation to the reference systems cured with ILs not deposited on silica. This comparison was intended to show the effect of silica deposition on curing temperatures and energy efficiency. The ILs were deposited on microporous silicas, which generally provided an excellent degree of dispersion in the epoxy matrix. During the 30-day stability study of these combinations, no significant sedimentation or loss of uniformity of the silica distribution in the resin was observed. We assume that the determining factors could be the physicochemistry of the epoxy resin itself, its viscosity and density, and the method of preparation, which reduces aeration of the systems during mixing by degassing the samples.

The results of the screening test are shown in Table 2. For resin systems cured with SILPs based on DG62 silica, full curing was usually observed in the second temperature cycle, with the exception being the highest (40%) concentration of [BMIM][DCA], which showed full curing in the first temperature cycle. In addition, concentrations of 10% and 20% proved to be effective in initiating the polymerization of the epoxy resin, in which full curing was also visible after the second temperature cycle. However, it should be noted that as the concentration of the liquid decreased, the increasing content of silica in the material significantly lowered the hardness of the obtained samples, making them much more brittle. This is the most justified effect because the amount of silica, which is definitely a weakening filling, has been introduced into the resin, exceeding 10% and 20%. The average hardness of the [BenzMIM][DCA] SILP cured samples was 75 D. On the other hand, the average decrease in hardness with a decrease in IL concentration and an increase in silica content was 6%, whereas the decrease in hardness of samples with 10% IL content compared with the sample with 50% concentration was 22%. It has been

No	Ionic Liquid	Silica	Conc. of IL on silica [%]	Conc. of silica filling [%]	Curing parameters Temperature and Time/cycle [°C/min]	No. of cycles ^[a]	Result	Hardness [Shore D]
1	[BenzMIM] [DCA]	DG62	50	5.7	170.0/240.0	2	c	86
2			40	7.0		2	c	80
3			30	9.1		2	c	72
4			20	13.0		2	c	69
5			10	23.1		2	c	67
7		DG635	40	7.0		1	c	89
8			30	9.1		1	c	74
9			20	13.0		2	c	70
10			10	23.1		2	c	62
14			DG12	20		13.0	3	n/c
15		10	23.1	3	n/c	n/a		
17	[BMIM] [DCA]	DG62	40	7.0	1	c	79	
18			30	9.1	2	c	74	
19			20	13.0	2	c	72	
20			10	23.1	2	c	71	
22			DG635	40	7.0	1	c	87
23		30		9.1	1	c	78	
24		20		13.0	2	c	72	
25		10		23.1	2	c	63	
30		DG12		10	23.1	2	c	61
31		[EMIM] [OAc]	DG62	50	5.7	2	c	76
32	40			7.0	2	c	68	
33	30			9.1	2	c	62	
34	20			13.0	2	c	59	
35	10			23.1	2	c	55	
37	DG635		40	7.0	1	c	86	
38			30	9.1	1	c	75	
39			20	13.0	2	c	68	
40			10	23.1	2	c	63	
44			DG12	20	13.0	2	c	67
45			10	23.1	2	c	60	

^[a] Number of heating cycles necessary to obtain a cured material or the number of maximum heating cycles carried out to verify the ability of the SILP material to initiate resin polymerization. n/c – not cured, c – cured.

observed that the decrease in hardness is most intense at the transition between the concentration of 50%–40%–30%, whereas at the concentrations of 20% and 10%, it stabilizes and fluctuates less. This phenomenon is observed not only for samples cured with DG62-based SILP, but also for other types of silica. The average hardness values for the remaining ionic liquids were 74 and 64 D, respectively. The lower value obtained for [EMIM][OAc] probably results from the presence of a certain amount of moisture in the IL itself, which is natural for this type of hygroscopic ionic liquid, and significant moisture reduction is practically unattainable, even by long-term desiccation on a vacuum pump. In turn, the lowest value of the change in hardness with the increase in silica content and

decrease in the concentration of ionic liquid was recorded for SILP materials prepared using [BMIM][DCA]. The change between the hardness of the sample containing 10% IL concentration in relation to the sample with 40% was only 10%, whereas for analogous samples with [EMIM][OAc], it was as much as 28%. This may indicate the influence of this ionic liquid on the stiffening of the cured resin structure.

The second group of SILP materials incorporates DG635 silica. Samples with ionic liquid concentrations of both 30% and 40%, regardless of their specific type, exhibited successful curing in the first temperature cycle.

Lower concentrations of ILs required two cycles to achieve complete curing, thereby highlighting the effect of a substantial

increase in silica content within the resin. This heightened content of silica slows down the curing process and requires the supply of energy necessary to continue the polymerization process for a longer time. For all the highest concentrations of the ILs (40%), the highest hardness was recorded among all the analogous samples tested for other types of silicas, which can be explained by the fact that the distribution of the ionic liquid on the surface of the DG635 silica favors the effective occurrence of the polymerization reaction of the resin in the close vicinity of the silica filler. This phenomenon causes the formation of a dense network of cured polymer in the immediate vicinity of the fill, creating a compact structure without defects that could arise from inefficient processes or partial leaching of the IL from the silica surface. As in the case of DG62 silica, the greatest discrepancy in hardness between the lowest and highest concentrations of ionic liquid on the silica was observed for [EMIM][OAc]. In turn, the lowest change in hardness was shown by samples based on [BMIM][DCA]. This result shows that regardless of the type of silica, the structure of the ionic liquid and its nature, e.g., hygroscopicity, are also factors determining the basic mechanical parameters of the cured resin, such as its hardness.

The lowest curing efficiency, visible both in the long curing time (at least two temperature cycles) and in the achieved hardness parameter, was shown by SILPs based on DG12 silica. Such results are understandable considering the low concentration of the ionic liquid, which directly affects the curing time and has already been confirmed for other types of silica. In addition, at low concentrations, a large amount of silica introduced into the system resulted in low hardness of the materials, which was the lowest for [EMIM][OAc]. On the other hand, even after three temperature cycles, the samples containing [BenzMIM][DCA] were still not fully cured. This suggests that this type of silica does not work well when used as an IL-hardener support, degrading the overall IL properties responsible for initiating resin polymerization because of its small pore size and limiting the possibility of contact between the ionic liquid and the resin. This undoubtedly also affects the

formation of defects in the structure and uncured holes in the immediate vicinity of the filling, which influences the hardness results.

Based on the evaluation of the results from the screening tests, 8 combinations were selected that represented all types of silica and ionic liquids, considering the best results obtained for each group. These 8 combinations were tested using differential scanning calorimetry, the results of which are summarized and presented in Table 3. The characteristic of ionic liquids with dicyandiamide anion, is the appearance of two thermal peaks during the analysis on the chromatographs. This is an expected effect, indicating that cationic polymerization (the main initiator of hardening is the IL cation) and anionic polymerization (the main hardener is the IL anion) occur independently of each other. The peak with a lower thermal peak temperature represents anion polymerization, which occurs when, under the influence of the temperature supplied to the system, the anion moves further away from the cation, becomes more mobile, starts reacting with the epoxy groups of the epoxy resin. The peak at higher temperatures corresponds to cationic polymerization, which occurs only when the cation of the ionic liquid is dealkylated with the simultaneous release of a highly reactive imidazolium radical. The details of this process are discussed in the section on the curing mechanism. However, for the two SILP samples (17 and 30), there was a significant reduction in the occurrence of two thermal peaks at the expense of only one thermal peak with various thermal transitions between polymerization start (T_{onset}) and end (T_{offset}) temperatures. We suppose that in the case of these SILPs, there was such a high interaction between the silica and the ionic liquid that a significant reduction in the cationic polymerization occurred, and the time of only anionic polymerization was extended. This thesis is confirmed by the significantly low total enthalpy of the process (ΔH). Perhaps this is a phenomenon characteristic of a particular ionic liquid that is highly stable.

Generally, in all the tested samples, the phenomenon of shifting the polymerization process to higher temperatures occurred in relation to the relevant references (R1, R2 and R3),

Table 3. Thermal behavior of epoxy resin with SILP material measured by DSC.

No	Ionic Liquid	Silica	Conc. of IL on silica [%]	Thermal analysis		T_{offset} [°C]	ΔH [J/g]	T_g [°C]
				T_{onset} [°C]	T_{max} [°C]			
R1	[BenzMIM] [DCA]			136.36	146.12	181.29	442.24	127.66
1		DG62	50	148.15	152.87	186.87	205.38	130.00
7		DG635	40	144.07	150.16	183.15	200.91	96.41
R2	[BMIM]			134.81	145.23	179.56	186.93	113.43
17	[DCA]	DG62	50	156.51	190.17		213.46	154.54
22		DG635	40	142.59	148.94	181.36	193.37	161.13
30		DG12	10	162.37	182.09		205.95	52.76
R3	[EMIM]			88.5	110.37		122.03	483.48
31	[OAc]	DG62	50	116.01	132.85		157.23	111.9
37		DG635	40	107.28	125.25		143.03	340.20
44		DG12	20	145.39	166.34		186.71	26.74
								5.65

which were devoid of silica, and the ionic liquid was freely dispersed throughout the epoxy matrix. The type of silica and the concentration of the ionic liquid have a significant impact on the magnitude of this shift. It can be observed that the silica with the largest pore size (DG62) increases the T_{onset} which corresponds to the temperature of the start of polymerization of the epoxy resin, compared to the reference by 12 degrees for [BenzMIM][DCA], 22 degrees for [BMIM][DCA], and 28 degrees for [EMIM][OAc]. At the same time, it shifts the polymerization peak temperature (T_{max}) by 6, 11 and 22 degrees for [BenzMIM][DCA], [BMIM][DCA], and [EMIM][OAc], respectively. Similarly, the T_{offset} correlating with the signal at the end of the resin polymerization process is also shifted. This value increases by 12, 27, and 35 degrees in the same order as IL. However, the most important result recorded is the significant reduction in the total enthalpy of the curing process for SILP materials compared with curing with ionic liquid alone. This is because with SILP materials, the crosslinking process is slower and more controlled because silica stabilizing the ionic liquid causes a gradual release of active molecules that initiate polymerization. It takes slightly more energy to be supplied to the system for the process of beginning. Depending on the intended use of such systems, this phenomenon can be advantageous, especially in situations where there is a need to transport the previously mixed epoxy resin/hardener system to provide cooling, or in situations where ambient conditions are not conducive to maintaining low temperatures. In addition, in certain advanced applications, such as systems dedicated to nanomaterials, a higher cross-linking temperature may be desirable. The difference in relation to the reference system in the case of DG62-based SILP is 258, 290, and 372 J/g, respectively, for individual ionic liquids, with the smallest difference for [BenzMIM][DCA] and the largest difference for [EMIM][OAc]. Moreover, for DG62-SILP with [EMIM][OAc], the range of temperature changes during curing was as much as 41 degrees between the beginning and the end of polymerization, whereas for the reference, it was 34 degrees. For the other combinations, no noticeable changes in this temperature range were noted. This observation confirms the slowdown of the curing process and the reduction of its energy when silica interacts too strongly with the ionic liquid and affects its activity.

In contrast, DG635-based SILPs exhibited the least effect on the temperature shift to higher values for all individual thermal peaks of the polymerization start, peak, and end. Moreover, they demonstrated a marginal reduction of the enthalpy of the process. Small changes between the SILP material and the reference material were most expected and are obvious if we consider the presence of silica in the system and its effect on the ionic liquid and the resin system itself. However, for DG635 silica, these changes are the smallest, regardless of the tested IL. This once again confirms that this type of silica stands out from the others, as the one with the best properties on many levels of parameters. In turn, DG12-based SILPs are a group of hardeners with the worst parameters. However, they cannot be directly related to the other SILPs because they do not represent the analogous concentration range of the ionic liquid,

which affects the obtained results. However, it should be noted that this group of hardeners had the greatest impact on the increase in process temperatures and a significant reduction in process enthalpy. The results obtained support the observations from the screening tests, where curing of the resin with DG12 silica-based samples at 10% and 20% liquid concentration is long-lasting and requires long-term temperature delivery. By correlating the value of the maximum temperature of the thermal peak from the DSC analysis (182.09 °C) for sample 30 with the value of the constant temperature in the vacuum oven during the screening tests (170.0 °C) and the low enthalpy of thermal transformation, it can be concluded that the process was below the effective curing temperature for these samples. In addition, this may also be the reason for the lack of curing of the samples in the case of other DG12-based samples, for which presumably the process temperatures were higher and the conditions prevailing in the vacuum oven were insufficient for curing.

In this study of epoxy resins cured with different SILP materials, the influence of the employed silica and ILs on the T_g values was examined. The choice of silica had a notable impact on the T_g values observed. In particular, SILP materials based on DG635 silica exhibited the highest T_g values among the tested combinations. For instance, [BMIM][DCA] and [EMIM][OAc] combinations displayed T_g values of 161.13 °C and 104.17 °C, respectively. Furthermore, the influence of ILs used alongside silica was evident in the T_g values obtained. Despite the superior performance of DG635 silica, intriguing variations were observed. Notably, although the T_g for SILP materials based on [BenzMIM][DCA] exhibited the highest value with DG62 silica, surpassing that of DG365 silica, the latter still showcased a commendable T_g value of 96.41 °C. Conversely, SILP materials incorporating DG12 silica demonstrated the lowest T_g values among the tested combinations. Particularly noteworthy was the substantial decrease in T_g values observed for samples 30 and 44, amounting to 96% and 93% decreases, respectively, compared with the reference. This emphasizes the significant role of silica morphology and structure in influencing the thermal behavior of epoxy resin systems, thereby underscoring the importance of careful selection and optimization of SILP components for the desired thermal properties.

Mechanism of Curing with SILP Material

The results obtained during this research led to a discussion on the mechanism of curing that occurs when SILP is used as a hardener. To start this discussion, it is necessary to locate the polymerization process initiated by the ionic liquids in the epoxy matrix. When such a system consists only of epoxy resin and IL, we are dealing with a situation in which the hardener is freely distributed throughout the resin matrix and is not subject to any additional stimuli during the polymerization process. Then, the energy supplied to the system in the form of heat, which is necessary to start the process (the ionic liquid alone is incapable of curing the resin at room temperature, it needs temperature to be ready for such action), causes two phenom-

ena. The first is to increase the mobility of ions in the IL so, that the anion, gradually moving away from the cation, reacts with the epoxy groups of the resin, forming 1:1, 1:2 adducts,^[59] etc., finally leading to the closure of the polymer chain. The ionic liquid cation, on the other hand, needs the energy input first to conduct the dealkylation process leading to the formation of the imidazolium molecule, which is highly reactive to the epoxide group in the resin because of its lone pair of electrons. In this way, the corresponding adducts 1:1, 1:2^[8] etc. are formed, which also leads to the closure of the polymer network. The mechanism of this transformation is identical to that of resin hardening by amine hardeners.

However, it is important to understand the functioning of this mechanism when the ionic liquid is deposited on silica. For this purpose, a diagram illustrating this phenomenon is proposed and presented in Figure 2. The ionic liquid deposited on the silica support directs the cation toward the surface of the silica, because of the nature of this material, the surfaces of which are made of silicon oxide blocks. However, no chemical bonding is formed between the silica surface and the ionic liquid; only physisorption occurs. This means that this interaction is weaker as the ionic liquid is farther from the surface of the silica. Consequently, the formation of a thick layer of ionic liquid on the surface is an undesired effect. Each cation of the ionic liquid forms a connection with an anion through ionic interactions between these molecules. In practice, this means a certain freedom of these molecules in terms of their ability to move and rotate freely. SILP distributed in the epoxy matrix causes resin particles (DGEBA) to appear on the surface of the silica. However, they are too large to penetrate deep into the pores; therefore, the curing process occurs at the surface of the silica rather than inside it. As mentioned, even in the case of the ionic liquid itself, the anion is ready to react with the epoxide group faster than the cation. It can be assumed that in the case of the SILP material, the supplied energy necessary to start anionic polymerization is lower than that in the case of the

liquid itself because, the cation also interacts with the carrier surface, which partially weakens its attachment to the anion. In fact, it appears that because the anions are close to the cation, largely inside the pores of the silica, the final energy required to activate them is greater because they need to get out of the pores of the support, not just far enough away from the cation. On the other hand, in the case of SILP, the cation has an additional difficulty in the form of interaction with silica and requires more energy supplied to the system to be able to freely move away from the carrier, undergo dealkylation, and start the reaction with DGEBA. After both molecules are ready to react with the resin, the polymerization mechanism is the same as that of the ionic liquid itself.

There is one major difference between the two processes. In the case of the SILP material, the polymerization chain reaction of the resin occurs directly at the surface of the silica as soon as the cation or anion is ready to react. This brings the cross-linked material as close as possible to the silica filler, which is not possible with the introduction of the silica filler. Externally introduced silica is usually insufficiently calcined, so there are air or moisture bubbles in its pores, which prevent the polymer chain from reaching its surface. Consequently, microbubbles of air and water are trapped in the material, which weakens the structure of the cured resin. The SILP material cannot absorb water or air because its surface is coated with an ionic liquid, which, when properly selected, can be hydrophobic. We assume that the solution proposed by us, in which SILP is a hardener and a composite filler at the same time, is the best possible way of introducing the filler into the composite because it guarantees the proximity of the filler and the composite matrix, eliminates the problem of moisture and air, and additionally effectively hardens the material, requiring a small increase in energy input to start its operation in relation to the system based on the IL alone.

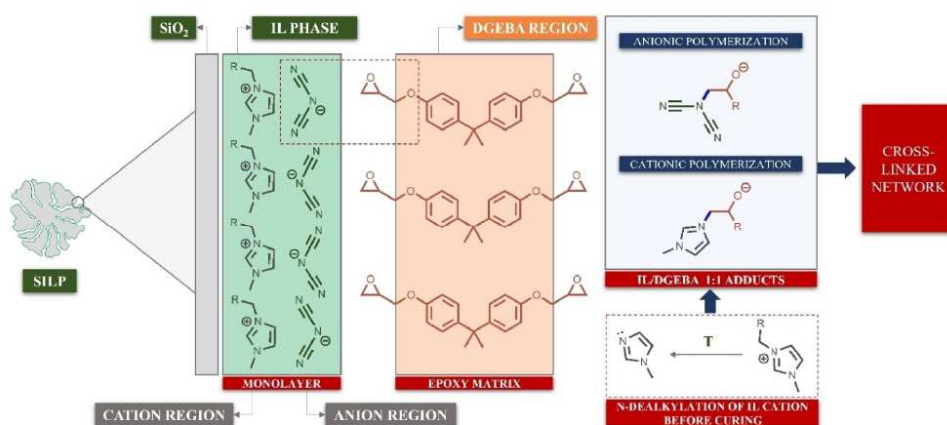


Figure 2. Proposed scheme for epoxy resin curing with SILP.

Mechanical Properties of the Cured Materials

During the research, it was found that in terms of application as an epoxy resin hardener, the most promising results were achieved for SILP based on silica DG635. For these samples, which contained different ILs at a concentration of 40 %, composite structures reinforced with carbon fiber and flax fiber were fabricated. The aim of this study was to evaluate the effect of fiber-based reinforcement on the resin curing ability of SILPs and how the presence of silica affects the mechanical performance of these fabricated structures. For these tests, a Scanning Electron Microscope equipped with an appropriate attachment for measuring the tensile strength of the samples was used. The results of these measurements are presented in Tables 4 and 5.

In the case of composites reinforced with carbon fiber, a decrease in tensile strength was observed, which was correlated with a simultaneous increase in the modulus of elasticity. Concurrent with the decrease of tensile strength, a decrease of tensile toughness was also observed with regard to the reference samples. Materials with lower tensile strength tend to exhibit reduced resistance to fracture and may absorb less

energy before failure, which can lead to lower tensile toughness. In such cases, the material is more prone to breaking under applied stress, and it may fail more easily or with less deformation compared with materials with higher tensile strength. This is expected when a silica filler is introduced into the system. At the same time, all samples showed a decrease in the maximum elongation at break for samples with SILP material compared to references without silica. The largest decrease in the maximum elongation at break was recorded for [EMIM][OAc], and its value decreased by 0.47 %. The smallest in turn was presented by the sample hardened with [BMIM][DCA], for which the value compared to the reference decreased by 0.29 %. Similarly, the greatest change in tensile strength and tensile toughness was also noted for [EMIM][OAc], which was lower by as much as 38 % and 69 %, respectively, compared to the reference. Once again, a significant effect of the presence of silica on the behavior of this IL and its action as a hardener was observed. We assume that this liquid has the greatest affinity for silica, which can also be confirmed by a small change in the modulus of elasticity (4 % compared to the reference), which proves the compact structure of the composite with the filling and the fact that the curing process occurred extremely close to

Table 4. Mechanical properties of the carbon composites.

No	Resin saturation [%]	Thickness [mm]	Mechanical analysis				
			Max elongation at break [%]	Tensile strength [N/mm ²]	Force [N]	Modulus of Elasticity [GPa]	Tensile toughness [MJ/m ³]
R1	45	0.59	1.42	130.85	1544	9.23	12.13
7	48	0.53	1.01	121.04	1283	11.93	8.45
R2	46	0.53	0.93	123.87	1313	13.26	7.19
22	45	0.61	0.64	96.97	1183	15.15	4.30
R3	47	0.50	1.17	142.80	1428	12.16	11.06
37	48	0.68	0.70	88.53	1204	12.65	3.40

R1,7 – [BenzMIM] [DCA], without and with silica, respectively, R2,22 – [BMIM] [DCA], without and with silica, respectively, R3, 37 – [EMIM] [OAc], without and with silica, respectively.

Table 5. Mechanical properties of flax composites.

No	Resin saturation [%]	Thickness [mm]	Mechanical analysis				
			Max elongation at break [%]	Tensile strength [N/mm ²]	Force [N]	Modulus of Elasticity [GPa]	Tensile toughness [MJ/m ³]
R1	56	0.63	1.53	42.94	541	2.81	4.22
7	58	0.68	0.65	36.25	493	5.54	1.49
R2	55	0.58	1.65	47.93	556	2.91	5.28
22	57	0.66	0.94	42.20	557	4.50	2.60
R3	58	0.63	1.59	38.73	488	2.43	4.61
37	59	0.69	0.72	35.51	490	4.91	1.71

R1,7 – [BenzMIM] [DCA], without and with silica, respectively, R2,22 – [BMIM] [DCA], without and with silica, respectively, R3, 37 – [EMIM] [OAc], without and with silica, respectively.

the silica surface. As it was for the carbon structures, a decrease in tensile toughness was also observed with regard to the reference samples, and the highest decrease was recorded for [BenzMIM][DCA] and [EMIM][OAc] (65 % and 67 % respectively).

Composites made with reinforcement based on flax fiber also showed changes depending on the type of hardener (ionic liquid or SILP) in analogous mechanical parameters. Their values remained at a different level because the flax fiber itself is more flexible than the carbon fiber. The modulus of elasticity for the ionic liquids [BenzMIM][DCA] and [EMIM][OAc] increased by approximately 100 % compared with the reference, which is a huge increase and indicates a significant stiffening of the sample under the influence of the presence of silica. However, for [BMIM][DCA], this parameter increased by 55 %, which is also a high value. In contrast, the maximum elongation at break was reduced by approximately 50 % for all tests, without any significant differences depending on the IL. The prepared structures also had a lower tensile strength, with the difference being 16, 12 and 8 %, respectively, for [BenzMIM][DCA], [BMIM][DCA], and [EMIM][OAc].

Figure 3 presents the tensile strength measurement graphs, in which the shift of the reference value (black line) in relation to the SILP cured composite (orange line) can be observed. In some samples, gradual tearing of the sample with increasing force is visible; however, no significant correlations were observed between this phenomenon and the type of SILP or ionic liquid. It is assumed that this was an individual phenomenon for a given composite structure, and the moment of the

first break in the continuity of the composite structure was used to determine the mechanical parameters.

To visualize the surface of the composites, SEM images were taken, which are presented in Figure 4. The magnified surface of the composite structure under the microscope indicates that the distribution of SILP particles on the surface of the material is randomized but retains fineness. The formation of silica agglomerates, which could significantly affect the heterogeneity of the composite coatings, was not observed. Moreover, the silica on the surface of the composite structures appears to be covered with resin and permanently bonded with this coating. It should be noted that the random distribution of silica particles may not always be the desired effect in the composite and must be considered each time. We suppose that in the case of the studied composite structures, the phenomenon of random distribution may be related to the method of fiber hand lamination. This method is mainly intended for coating fibers with a homogeneous resin system without filling, and it may affect the distribution of SILP in the composite because the silica will not be able to penetrate the interior of the composite and fibers. However, as mentioned earlier, the deposition of the ionic liquid curing agent on the surface of the silica requires the resin to adhere directly to the silica to polymerize, thus the bond between the reinforcing fiber, resin, and silica is extremely strong.

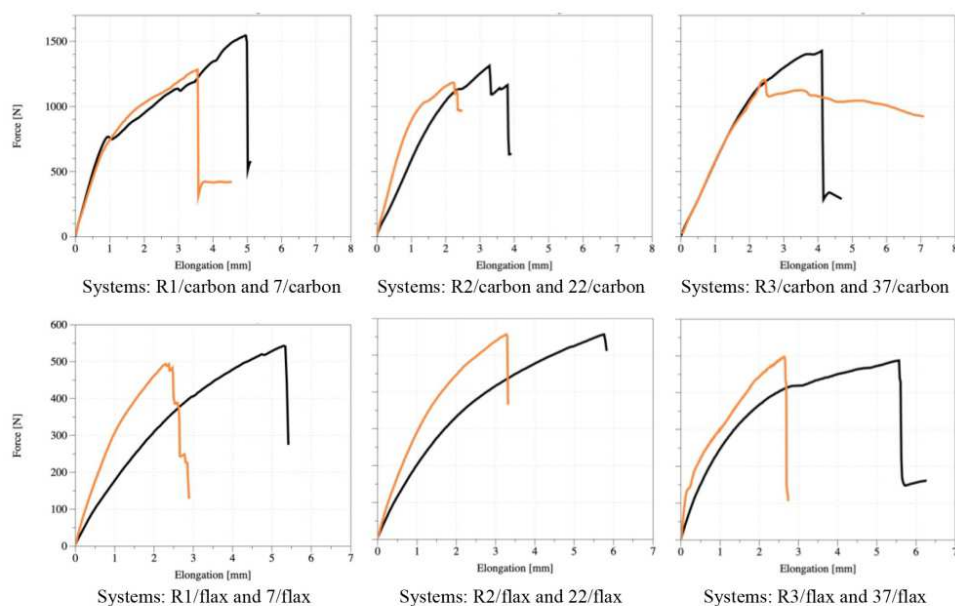


Figure 3. Tensile strength measurement graphs. The black line represents the reference sample, and the orange line represents composites cured with SILPs.

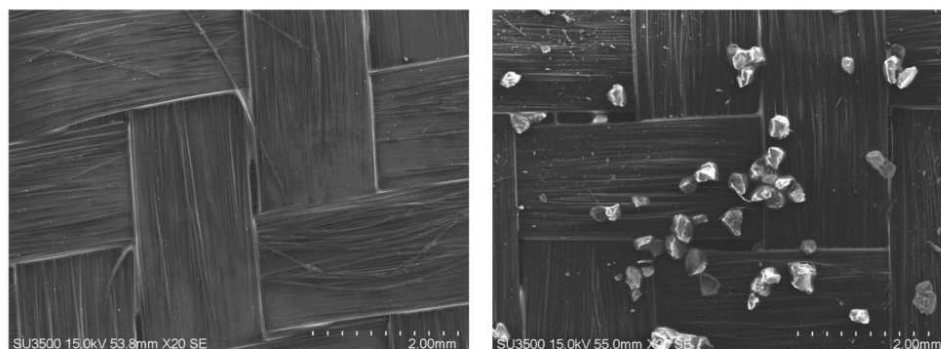


Figure 4. SEM pictures (20x) of the composite structures. On the left side, R1/carbon, on the right side 7/carbon.

Conclusions

In conclusion, this study presents a new approach to the search for multifunctional hardeners for epoxy resins: SILP materials in which an ionic liquid is deposited on a silica support. Various variants of this solution were presented, both in the context of the selection of silica and ionic liquid and its concentration. In addition, several parameters and properties influenced by the SILP material are presented.

Matching the appropriate curing system to the resin and then adapting this system to a specific application is an extremely complex process, and there is no perfect solution for all final applications of a given composite structure. This paper describes universal silica, DG635, and presents its operation along with various ionic liquids. It has been shown that due to the influence of SILP, the composite changes its mechanical properties, such as modulus of elasticity or tensile strength. This phenomenon is characteristic of the presence of a filler such as silica. However, in the case of SILP, the way and strength with which the silica filler is bonded to the composite matrix is much stronger because the polymerization of the resin occurs in a forced manner, directly at the surface of the silica. Moreover, it has been shown that the effect of SILP, compared with the use of IL alone, on the thermal transformations and temperatures of the curing process itself is insignificant. This shifts these values to higher process temperatures in the case of SILP.

SILP materials as simultaneous hardeners and fillers in the composite seem to be a good direction of research, especially in the context of the shift of the composite industry toward epoxy bioresins, which are usually in the solid state and require temperature to liquefy. Solutions such as SILP will allow for the preparation of resin recipes with a hardener and filler using the one-pot method, and then their long storage due to the stability of SILP itself and the lack of activity toward the resin in a system devoid of energy supplied in the form of temperature. SILP-type materials are a new group of epoxy resin hardeners, the understanding of which may be

crucial in the future design of epoxy systems based on biosubstances. Performing dual functions in the system, they can not only contribute several additional properties to the final material, but when properly designed, they can meet even the most complex crosslinking temperature requirements, maintaining controlled process conditions and preventing the possibility of exceeding the polymerization peak temperature by stabilizing the hardener with silica. Finally, various types of ionic liquids can be deposited on the silica surface, the properties of which with respect to composite materials, such as flame retardancy, stiffening, or increasing electrical conductivity, are widely described in the literature. Thus, SILP materials will in the future serve as a platform for the design of modern, multifunctional resin systems based on environmentally friendly substances that meet numerous technical and technological requirements.

Experimental Section

Materials

The ionic liquids: (i) 1-ethyl-3-methylimidazolium acetate, (ii) 1-butyl-3-methylimidazolium dicyanamide and (iii) 1-benzyl-3-methylimidazolium dicyanamide were purchased from IOLiTec-Ionic Liquids Technologies GmbH (Germany). Their structure is presented on Figure 1 in Supplementary Information.

Silica gel: (i) high-purity grade silica gel (Davisil Grade 635), (ii) high-purity grade silica gel (Davisil Grade 62), and (iii) high-purity grade silica gel (Davisil Grade 12) were purchased from Merck GmbH (Germany). The parameters of the selected silica are summarized in Table 6. All organic solvents used in the study were of at least HPLC grade and were purchased from Merck GmbH (Germany).

Reinforcement fabrics: (i) PrimeTex® carbon fabric (twill, spread) 200 g/m² based on Tenax® HTA 40/200 tex (3k) fibers and (ii) FLAXDRY-UD180 cross-stitched unidirectional flax fabric 180 g/m² were purchased from Hexcel Corporation (USA) and Eco-Technilin (France), respectively. Epoxy resin: EPD certified EnviPOXY 530, based on Bisphenol A diglycidyl ether (DGEBA), was purchased from Spolchemia a.s. (Czech Republic).

Table 6. Parameters of the silica gels.

Silica	Pore size [Å]	Mesh
DG62	150	60–200
DG635	60	60–100
DG12	22	28–200

SILP Preparation and Characterization

Preparation of the SILP

All SILP materials with different IL concentrations from 10% to 50% were prepared based on the methodology previously described in the literature,^[37] and a graphical diagram is presented on Figure 2 in Supplementary Information. The previously calcined silica and ionic liquid were placed in a flask containing dichloromethane. The prepared system was stirred at room temperature (rt) for approximately 30 minutes, and then the solvent was very slowly evaporated on a vacuum evaporator, leaving a thin layer of ionic liquid on the surface of the silica. The SILP material, after evaporation of dichloromethane, was dried on a vacuum pump for at least 24 hours.

BET Measurement

The surface area was determined by the BET method for all obtained SILP materials, according to the methodology described earlier.^[37] Measurements were made using nitrogen adsorption at 77 K and a sorptometer. Then, using the Barrett-Joyner-Halenda (BJH) method for the isotherm desorption branch, the following parameters were determined: (i) total pore volume and (ii) average pore diameter. All samples were previously degassed at 393 K for 20 hours.

Curing Screening

Screening tests using a vacuum oven were used to examine the ability of the obtained SILP materials to initiate the epoxy resin curing process. Each SILP/Epoxy resin system was prepared by physically mixing SILP and epoxy resin, each time maintaining a constant amount of ionic liquid initiator (3% by weight, based on ionic liquid deposited on silica). The mixed system was degassed on a vacuum pump and then placed in a vacuum oven set to a constant temperature of 170 °C for 240 minutes. Such a one-time temperature treatment of the system in the oven was a single curing cycle, which was repeated up to a maximum of 3 test cycles if the sample failed to cure. Samples that did not cure during the 3 cycles were considered to have no epoxy cross-linking properties.

Curing Characterization

The properties of SILP materials to initiate curing of the epoxy resin were also tested using Differential Scanning Calorimetry (DSC) based on the methodology previously described in the literature.^[18,60]

Composite Preparation

Systems of epoxy resins with SILP materials were used to produce monolayer composite structures reinforced with (i) carbon and (ii) flax fibers. For this purpose, the technique of hand lamination of fabric fibers using a previously degassed resin system was used. During the wetting of the fibers with resin, the degree of wetting was controlled and maintained at the following levels: (i) 45–48% for carbon-reinforced composites and (ii) 55–59% for flax-reinforced composites. The preimpregnates were cured in a vacuum oven at 170 °C, in the form of composite sheets with dimensions of 30×30 cm.

Mechanical Testing

Hardness

The selection of Shore hardness measurement as the fundamental parameter for assessing cured silica-containing resin stems from the recognition that materials incorporating fillers such as silica often face challenges related to excessive brittleness and low hardness. In this context, Shore hardness measurement seems to be a simple, repeatable, and universal way to control this parameter. For this measurement, the methodology described previously in the literature^[8] was used, in which, on the basis of SILP/epoxy resin systems, 1×1 cm cubes were prepared and tested using a Shore D hardness tester.

SEM Mechanical Analysis

The mechanical properties of the composite structures were tested using a Scanning Electron Microscope (SEM, Hitachi SU3500, Japan) equipped with a measuring table for mechanical testing of the materials. For this purpose, measuring samples with dimensions of 2×3.5 cm and a thickness of 0.5–0.7 mm were prepared. Then, the samples were placed in the measuring jaws with a jaw extension rate of 1.5 mm/min. During the measurement, a 2KN single lead-screw tensile with 415:1 gearbox and 512-line encoder was used. The apparatus was calibrated at 2000 N, and the trip was set to 2000 N. The measurement was performed until the continuity of the composite structure was broken, observing a visible decrease in the force value. On the basis of the measurements carried out, the following were determined: (i) the force at break and (ii) the maximum elongation of the sample at break. The measurement data obtained were used to determine the following: (iii) tensile strength, defined as the stress corresponding to the highest tensile force *F* obtained during the static tensile test, related to the original cross-sectional area of the sample;^[61,62] (iv) modulus of elasticity, which quantifies the relationship between tensile stress (force per unit area) and axial strain (proportional deformation),^[63–65] and, (v) tensile toughness as a correlation between energy absorbed and volume. SEM was also used to take pictures of the surfaces of the composite structures.

Supporting Information

Structures of ionic liquids, SILP preparation method and Differential Scanning Calorimetry (DSC) curves of epoxy resin systems with ionic liquids and SILP materials.

Author Contributions

Dawid Zielinski: Funding acquisition, Investigation, Methodology, Writing – original draft, Writing – review and editing. **Andrea Szecht:** Investigation, Writing – review and editing. **Rafal Kukawka:** Investigation, Methodology. **Joanna Dzialkowska:** Investigation. **Mariusz Pietrowski:** Investigation, Methodology. **Michal Zielinski:** Investigation, Methodology. **Magdalena Palacz:** Investigation. **Paulina Nadobna:** Investigation. **Marcin Smiglak:** Supervision, Funding acquisition, Project administration, Writing – review and editing.

Acknowledgements

The authors acknowledge financial support from the National Science Centre (Poland), project SONATA BIS (No. 2017/26/E/ST8/01059), and project PRELUDIUM (No. 2023/49/N/ST11/04057).

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

Data will be made available on request.

Keywords: composite materials · epoxy resins · filler effects · ionic liquids · supported ionic liquid-phase (SILP)

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Manuscript received: March 12, 2024
Revised manuscript received: April 10, 2024
Accepted manuscript online: April 15, 2024
Version of record online: May 23, 2024

Cellulose (2024) 31:6747–6760
<https://doi.org/10.1007/s10570-024-05988-5>

ORIGINAL RESEARCH



Cellulose dissolved in ionic liquids as in situ generated filler in epoxy biocomposites with simultaneous curing initiated by ionic liquids

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Received: 18 January 2024 / Accepted: 25 May 2024 / Published online: 25 June 2024
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Abstract Cellulose, a ubiquitous natural biopolymer, has diverse applications in industries such as paper manufacturing, textiles, and food. A pivotal breakthrough emerged with the discovery that ionic liquids (ILs) can dissolve cellulose, initiating comprehensive studies over the past two decades. This study explores the effectiveness of a selected system comprising [EMIM][OAc], [EMIM][DCA], and DMSO in cellulose dissolution, validated through a 5% cellulose solution, and the use of such systems as initiators of epoxy resin curing. In epoxy resin systems, the cellulose fibers formed in situ affect the mechanical properties of the final

materials, which in the work presented here were flax fiber-reinforced epoxy composites. Differential Scanning Calorimetry (DSC) showed that cellulose inclusion minimally affected curing temperatures but reduced enthalpy. Scanning Electron Microscopy (SEM) demonstrated in situ cellulose fiber generation during mixing, ensuring high compatibility with the resin matrix. Mechanical testing revealed promising outcomes, including increased glass transition temperature (T_g) and enhanced Heat Deflection Temperature (HDT). However, a 50% reduction in impact strength indicated increased brittleness.

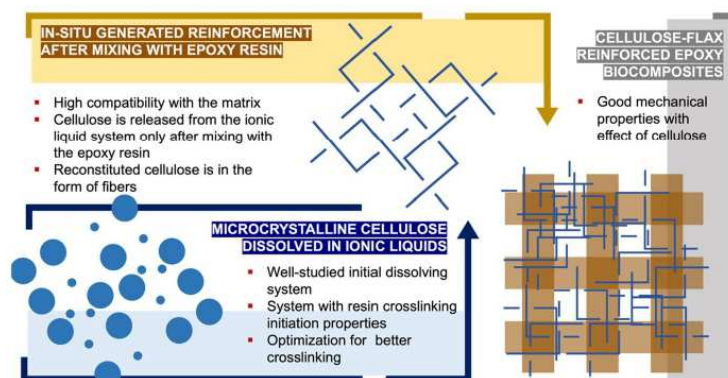
Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s10570-024-05988-5>.

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Graphical Abstract



Keywords Ionic liquids · Cellulose · Epoxy resin · Composites · Biocomposites · Flax-fiber reinforced composites

Introduction

Cellulose is one of nature's most widely distributed natural biopolymers, which has proven itself for many years in a variety of applications such as the manufacture of paper, textiles, and fibers. It is used as a thickener in the food industry or as an important stabilizing component in pharmaceutical preparations. In addition, because of its high natural availability, it is used in the production of biofuels or building materials with insulating properties.

However, all these applications are due to the elaborate structure of this polymer, which is characterized by high chemical and physical resistance. The priority task in the search for new areas of application and exploitation of the potential of cellulose is to study in depth the degradation of this biopolymer to obtain monomers and simpler chemicals, which will enable advanced modification of its structure. This is not an easy task, mainly because of the challenge of bringing cellulose into a liquid state, enabling further modification or mild degradation processes. It seems that the breakthrough moment in cellulose research was the discovery of the ability of ionic liquids (ILs)

to dissolve this biopolymer. The first reports on the dissolution of cellulose in ionic liquids appeared in 2002, thanks to a group of scientists led by Professor Robin D. Rogers (Swatloski et al. 2002). This article launched the research of scientists around the world, which, after a little more than 20 years, made it possible not only to thoroughly study the process of dissolving cellulose in ILs, but also to optimize the process and propose further steps involving, for example, the recovery of cellulose in an altered structural form.

Ionic liquids are a group of chemical compounds with different structures that retain ionic properties and exist at room temperature or temperatures below 100 degrees Celsius in the liquid state. In addition, they can be polar or non-polar in nature, exhibit very high thermal stability, and thanks to the multitude of potential cation and anion structures, both organic and inorganic, are compounds with almost unlimited design possibilities to suit a specific application (Zajac et al. 2019; de Jesus and Maciel Filho 2022). Currently, many ionic liquids are known to dissolve cellulose. In particular, research has focused on 1-ethyl-3-methylimidazolium and 1-butyl-3-methylimidazolium cations along with halide anions, formate, or phosphate (Isik et al. 2014). At the beginning of the studies, it was believed that the selection of the appropriate anion was of key importance in the ability of an ionic liquid to dissolve cellulose, and therefore acetates, in particular 1-butyl-3-methylimidazolium acetate and

1-ethyl-3-methylimidazolium acetate. However, further studies have shown that the cation structure is of no less importance in the effective dissolution of cellulose (Lu et al. 2014). Furthermore, not only the IL itself is important in terms of process efficiency, but also the presence and selection of the co-solvent (Andanson et al. 2014; Zhang et al. 2021). In addition to dissolving biomass, ionic liquids have numerous other applications. They can be used as alternative solvents in chemical reactions (Welton 2018), catalysts (Haumann 2020; Seitkalieva et al. 2021), electrolytes (Kazemiabnavi et al. 2016; Liu et al. 2022), and energy storage (Miao et al. 2021; Stettner and Balducci 2021). In the context of this work, their use as latent initiators of the hardening of epoxy resins, which are the building material of composite materials, is important (Rahmathullah et al. 2009). Under the influence of the supplied temperature, ILs decompose, leading to the release of compounds (derivatives of cations, e.g., amines or anions, e.g., dicyanamides), which actively initiate the resin cross-linking process, leading to the formation of dense polymer networks (Livi et al. 2022).

The ionic liquid 1-ethyl-3-methylimidazolium dicyanamide ([EMIM][DCA]) was investigated as a curing agent for epoxy resins in a study by Binks et al. (Binks et al. 2018a). They found that polymerization initiated by [EMIM][DCA] begins at 122 °C, with peak activity at 142 °C and 180 °C, and concludes at 198 °C. This contrasts with the known decomposition temperature of [EMIM][DCA] (275 °C) reported by Forsyth et al. (Forsyth et al. 2004), indicating that the curing process of epoxies by ionic liquids is not solely dependent on thermal stability. This suggests a more intricate relationship between thermal stability and curing activity. Additionally, the study highlights the complexity of the polymerization process, which involves both cations and anions. Therefore, although ionic liquids demonstrate thermal stability, they can still effectively initiate curing at lower temperatures, emphasizing the multifaceted nature of the curing process initiated by ionic liquids.

The use of cellulose in widely understood materials relies heavily on the use of cellulose fibers as composite reinforcement or for biomedical applications. Numerous reports using ionic liquids in the preparation of such fibers are known in the literature (Liu et al. 2021; Azimi et al. 2022). However, what is important from the point of view of materials science is the possibility of forming hybrid materials with

dissolved cellulose as a strategy for obtaining highly specialized materials with tunable properties. Some ionic liquids may have groups in their structure capable of creating a polymer network under the influence of various types of stimuli, such as: a radiation beam of a specific length (Minamimoto et al. 2015; Zajac et al. 2019), or the presence of an exterior initiator (Salminen et al. 2022). The research proved that polymerization carried out in a solution of a polymerizable ionic liquid in which cellulose was previously dissolved allows for obtaining a material containing cellulose embedded in the polymerized ionic liquid network, and it was proven that this biopolymer is highly compatible with such a matrix (Murakami et al. 2007; Isik et al. 2014). In turn, a slightly more simplified approach for forming cellulose-conventional polymer networks is achieved by co-dissolving cellulose and the polymer in IL and then precipitating the copolymer by, for example, adding water to the system. Numerous studies have proven such connections, and the method for producing such materials is simple (Isik et al. 2014). Another example of cellulose processing for its use in a composite is the fibrillation of biopolymer fibers by ionic liquids (Berglund et al. 2017). It has been proven that the production of cellulose nanofibers by treating them with ionic liquids is a more effective process than traditional ones, as it saves energy during production and bleaching.

The use of ionic liquids (ILs) in cellulose processing presents several potential challenges and negative aspects, as highlighted in various studies. These issues include reactivity with cellulose leading to chemical modifications, potential impurities catalyzing side reactions, and the risk of losing IL moieties over time, which is particularly problematic in medical applications. Furthermore, the incompatibility of certain ILs with oxidized cellulose limits their applicability in certain derivatives. The reversibility of reactions and the need for complex analytical techniques add layers of complexity. Lack of inertness of ILs with cellulose can lead to unexpected reactions, and anion reactivity may interfere with derivatization processes. Caution is advised in biological applications because of the risk of unwanted reactions. In addition, concerns about impurities impacting recyclability and the environmental impact of disposal highlight sustainability challenges. Finally, cost and scalability issues may hinder widespread industrial adoption. In conclusion, while ILs offer unique properties, their usage in cellulose

processing necessitates careful consideration of these challenges to maximize their potential benefits in sustainable applications (Ebner et al. 2008; Schrems et al. 2010; Zweckmair et al. 2015, p. 1).

In our opinion, research conducted on cellulose dissolved in ionic liquids is strongly focused on the following: (i) biomass processing and recycling toward the recovery of high-quality cellulose, (ii) modification of dissolved cellulose to valorize it after re-precipitation from the system with ionic liquids, and (iii) cellulose degradation processes in ionic liquids, leading to the production of valuable monomers and chemical compounds. It should be noted that research on the use of cellulose solutions in ILs is limited, and it is this step that has limited the widespread use of cellulose for decades. Hence, it is necessary to look broadly at the potential of dissolved cellulose and to find applications in areas that today require new solutions, especially those that are environmentally friendly. One such area is biocomposites and their modifications to increase their competitiveness and attractiveness in relation to epoxy composites, whose negative impact (both, epoxy resins itself, hardeners and modifiers) on the environment has been repeatedly emphasized in numerous works (den Braver-Sewradj et al. 2020). The aim of this study was to examine the influence of incorporating cellulose, previously dissolved in an ionic liquid system ([EMIM][OAc] and [EMIM][DCA]) along with DMSO as a co-solvent, on the curing process of epoxy resin. This system was strategically designed to initiate the *in situ* generation of cellulose nanofibers within an epoxy resin matrix when combined, serving as a latent initiator for resin hardening. We used this system to fabricate epoxy biocomposites reinforced with flax fibers and *in situ* generated cellulose nanofibers. This study involves comprehensive evaluation of the thermal and mechanical properties of the obtained materials. The main idea was to understand how the inclusion of dissolved cellulose in an ionic liquid system would impact both the curing process and the mechanical performance of the composites.

Experimental

Materials

1-Ethyl-3-methylimidazolium	chloride > 99.0%,
1-ethyl-3-methylimidazolium	acetate > 98.0%,

and 1-ethyl-3-methylimidazolium dicyanamide > 98.0% were purchased from IoLiTec GmbH (Heilbronn, Germany), Dimethyl sulfoxide $\geq 99.9\%$ (DMSO) and microcrystalline cellulose (20 μm) were purchased from Merck GmbH (Darmstadt, Germany), epoxy resin LH 301 was purchased from Havel Composites CZ s.r.o. (Přáslavice, Czechia), and flax fabric was purchased from TC3 sp. z o.o. (Szczecin, Poland). All organic solvents used in this study were of HPLC grade and were purchased from Merck GmbH (Darmstadt, Germany).

Cellulose dissolution

Ionic liquids mixed with the co-solvent in appropriate molar ratios (discussed later in the article) were thoroughly dried on a vacuum pump and then used to dissolve microcrystalline cellulose. The mixture of ILs and co-solvent was first heated to 100 °C, and then microcrystalline cellulose was added in portions to the constantly stirred system (each portion was added after the previous one was completely dissolved) until the cellulose content in the system was 5% wt. The prepared systems were additionally dried on a vacuum pump overnight before further experiments.

Preparation of composites

The vacuum bag method was used to produce composite structures, which is an improvement over the manual lamination method. The epoxy resin and the ionic liquid system with or without cellulose (4.0% wt.) were heated to 32 °C before saturating the fabric. The first step was to make a given items using the contact method, and then apply auxiliary materials to its surface and cover the entire thing with a flexible bag attached to the edges of the mold with an adhesive gasket. Then, the air with the excess resin mixture was sucked out through the vacuum pump stub placed in the mold. The auxiliary materials used to produce the composite were as follows: (i) Peel ply, which guaranteed the cleanliness of the surface and the required texture; (ii) perforated release film, which isolated the composite from other surfaces; and (iii) a venting and draining fabric made of needle-punched non-woven fabric, which was intended to facilitate even distribution of the vacuum over the surface of the entire item and to remove excess resin mixture. Composite structures reinforced with flax

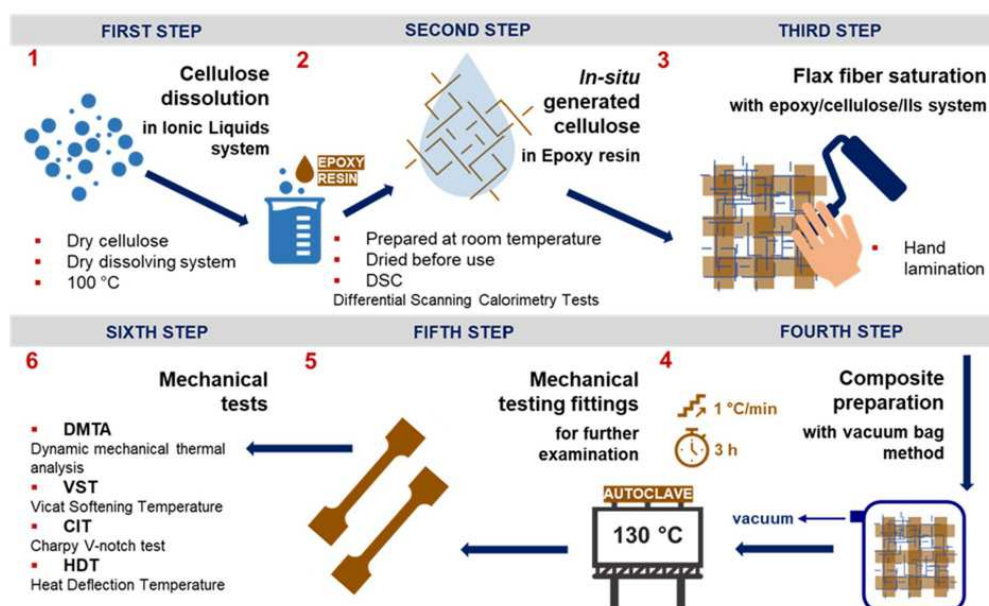


Fig. 1 Schematic diagram presenting the composite preparation process

fiber with a weight of 200 g/m² and a 2×2 weave were prepared. The composite structures from which appropriate measurement shapes for individual tests were prepared (by cutting strips from prepared composites using a table saw with water cooling) were 4 mm thick (7 layers) and cured at temperature 130 °C for 3 h with temperature ramp 1 °C/min. Because the flax fabric is hydrophilic, and this directly influenced the hardening process of the composite, before its production, the fabric was dried at a temperature of 70 °C for 3 h. Perfectly dry fabric was used for the preparation of composite structures. A schematic of the preparation of composite structures is shown in Fig. 1, while supplementary information includes photos of the various stages of fabrication of composite structures.

Thermal analysis

Differential Scanning Calorimetry (DSC)

All experiments using DSC, both involving the study of the ionic liquid system with or without cellulose, as well as the study of the epoxy resin

hardening process, were carried out on the DSC 3 device (Mettler-Toledo GmbH, Greifensee, Switzerland) according to the procedure described in detail in previous works of the authors (Zajac et al. 2019; Zielinski et al. 2021). In brief, the heating and cooling rate was 10 °C/min, and the analysis was performed in 50 mL/min nitrogen flow.

Scanning electron microscopy (SEM)

Images using a scanning electron microscope were taken on a SU3500 instrument. (Hitachi Ltd., Tokyo, Japan).

Mechanical properties

Dynamic Mechanical Thermal Analysis (DMTA)

Tests using DMTA were performed using a DMTA Q800 device (TA Instruments Inc., New Castle, USA)

with the three-point bending mode in the range of 25–250 °C (heating rate 3 °C/min, amplitude 1 Hz, strain 20 µm).

Heat Deflection Temperature (HDT)

HDT tests were performed using the D-VICAT/HDT-2–300/SA apparatus (Donserv, Warsaw, Poland) according to the PN-EN ISO 75–2 standard, using a nominal surface stress of 1.8 MPa for flat samples (method A, variant f, width approx. 10 mm). The tests were conducted at temperatures of 25–250 °C in silicone oil (heating rate 120 °C/h, counting after 5 min from the moment of applying the load) using 3 samples of a given composite.

Vicat softening temperature

Softening temperature tests using the Vicat method were performed using the D-VICAT/HDT-2–300/SA apparatus (Donserv, Warsaw, Poland) according to the PN-EN ISO 306 standard (A120 method) using a needle load equivalent to a pressure force of 10 N for flat samples (width approx. 10 mm). The tests were conducted in silicone oil (heating rate 120 °C/h) using 4 samples of a given composite.

Charpy V-notch test

Impact strength tests were performed with a Charpy hammer (Kögel Werkstoff- und Materialprüfssysteme GmbH, Leipzig, Germany) with an energy of 3.922 J (0.4 kpm) according to the PN-EN ISO 179–1 standard (notchless method) using samples with a width of approximately 10 mm (type 1, impact perpendicular to reinforcement layers (fU)). The tests were conducted at room temperature using 3 samples of a given composite.

Results and discussion

Cellulose dissolution

To dissolve the cellulose, a system consisting of two ionic liquids (1-ethyl-3-methylimidazolium chloride, [EMIM][Cl] and 1-ethyl-3-methylimidazolium acetate [EMIM][OAc]) and a co-solvent in the form of DMSO was selected first. The optimal ratios of the individual components and the ability to dissolve cellulose for such a system have been studied in depth and described in the literature (Stolarska et al. 2017). The well-established understanding of the functioning of this system in dissolving cellulose led to its selection for preliminary testing. Moreover, [EMIM][OAc], which is a component of this mixture, also has epoxy resin curing properties, as confirmed in literature reports (Carvalho et al. 2020).

The results of preliminary tests, in which a solution of dissolved cellulose (5% wt.) was used along with epoxy resin, effectively curing it, were used to optimize the composition of the mixture. The decision to replace [EMIM][Cl] with [EMIM][DCA] was made on the basis of the inefficiency of [EMIM][Cl] in dissolving cellulose and its ineffectiveness in initiating resin polymerization. [EMIM][DCA] was chosen for its excellent crosslinking properties toward the resin, and numerous research groups have studied its associated curing process (Rahmathullah et al. 2009; Binks et al. 2018b; Carvalho et al. 2020). The structures of the ionic liquids are presented in Fig. 2.

Table 1 Chemical composition of the prepared mixture based on ILs for cellulose dissolution

Ingredient	Molar ratio
[EMIM][OAc]	35
[EMIM][DCA]	15
Dimethyl sulfoxide [DMSO]	50

Fig. 2 Structures of the selected ionic liquids

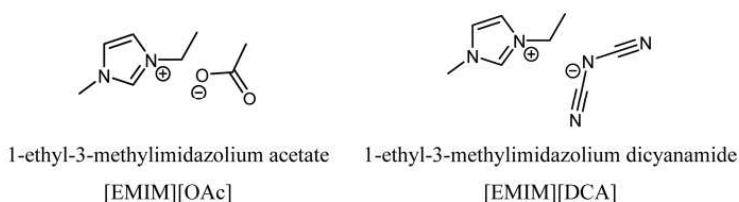


Table 2 Curing process parameters determined based on DSC analysis

	T_{onset} [°C]	T_{max} [°C]	T_{endset} [°C]	ΔH [J/g]
A – without cellulose	88.3	107.6	128.6	80.1
B – with cellulose	89.6	105.2	119.5	55.8

The system thus developed was used for further testing, and the composition of the final blend is presented in Table 1. Cellulose was dissolved in this formulation at 5% wt. and used in further tests. Moreover, for the mixture itself as well as for the cellulose-containing mixture, tests were performed using differential scanning calorimetry to identify phase transformations; however, no transformations were observed in the range of -80 to 250 °C.

Curing process

The next step of the study was to use DSC to characterize the curing process. The greatest emphasis when analyzing the results was to evaluate how the presence of cellulose in the resin mixture would affect the start (T_{onset}) and end (T_{endset}) temperatures of polymerization, as well as the temperature peak (T_{max}) of the curing process and its energy efficiency (ΔH). It was shown that cellulose does not affect significant changes in the curing process, and therefore does not cause a shift in temperature values compared with a reference in which there was no cellulose. Table 2 summarizes the experimental data for the tested systems, where System A is a mixture of ionic liquids and DMSO, and System B is a mixture containing an additional 5% wt. of dissolved cellulose.

It should be noted that the presence of cellulose reduces the enthalpy of the process from 80.1 J/g to a 55.8 J/g for the system containing cellulose. Lowered enthalpy during the polymerization process has significant implications for thermal efficiency (Ghanbari et al. 2023). It affects various aspects of the reaction, from heat transfer properties to energy requirements and final material properties. Studies indicate that reducing the enthalpy can influence non-bonding interactions within the polymer system, thereby impacting thermal conductivity and heat transfer efficiency (Huo et al. 2020). Moreover, lower enthalpy can lead to faster

reaction rates and improved control over the polymerization process, potentially resulting in higher yields of the desired polymer product (Huang et al. 2022). This reduction in enthalpy also influences the heat release during the curing reaction, affecting factors such as reaction kinetics, curing time, and final material properties. In certain cases, such as in epoxy-talc composites, increased filler content correlates with decreased curing enthalpy, suggesting less exothermic reactions and lower heat generation during polymerization (Shnawa 2022). Furthermore, the transition from one stage to another in the polymerization process, as seen in the shift from A-stage to B-stage resins, indicates significant network formation, reducing the energy required for subsequent curing steps (Gupta et al. 2024). This optimized reaction range is crucial for industrial applications where energy costs are critical. Molecular dynamics simulations have also shown promise in optimizing crosslinking network structures with minimum energy input, further enhancing thermal efficiency (Du et al. 2023). In essence, controlling the enthalpy during polymerization processes is key to achieving efficient and cost-effective manufacturing processes. The graph presented in Fig. 3 shows

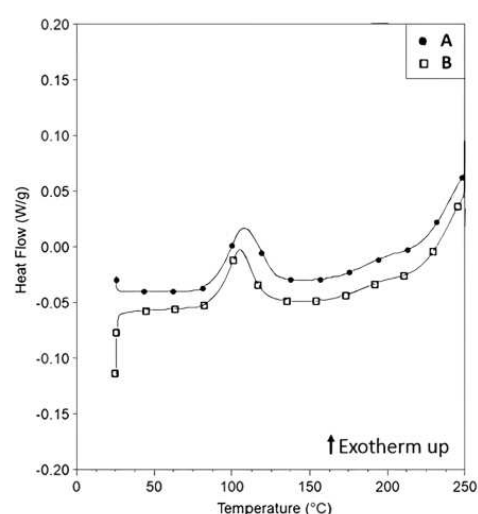


Fig. 3 DSC thermogram for the curing process of epoxy resin with IL and cellulose. A – ILs/DMSO, B – ILs/DMSO/Cellulose

the thermal curve during the curing process and the overlap of the thermal conversion values during the curing of the two systems. In conclusion, the systems containing 5% by weight of cellulose give off less thermal energy during crosslinking compared to systems without the biopolymer, while at the same time a reduction in the temperature of the end of polymerization of about 10 °C is observed. The slight reduction in the energy released in the process may be a direct result of the presence of cellulose and the absorption of some of the process energy in favor of its own structure in the cured material.

Properties of composites

A key element of the ongoing work was to conduct a series of tests on the mechanical parameters of the fabricated composite structures. Biocomposite structures were constructed based on epoxy resin, flax fabric serving as reinforcement, and a system of ionic liquids with DMSO and dissolved cellulose (**B**). As a reference, analogous cellulose-free structures were prepared (**A**). It is worth noting that when preparing resin mixtures with the IL/DMSO/Cellulose system, serving as a hardener and in situ generated filling/reinforcing the composite, when the ingredients are mixed, cellulose dissolved in ionic liquids is precipitated under the influence of the epoxy resin, in the form of microfibrils/cotton wool, of which the amount increases with time and intensity of mixing until all dissolved cellulose is reconstituted in the resin matrix. The process of mixing the system evenly at a constant speed throughout the volume is crucial for maintaining the proper homogeneity of the mixture and the distribution of cellulose fibers throughout the resin. An inadequately mixed system promotes the formation of large clusters of reconstituted cellulose and biopolymer clumps, increasing inhomogeneity. Proper distribution of the generated fibers ensures that the desired mechanical parameters of the final structure are maintained. The resin mixture prepared in this manner was used to laminate flax fabric fibers and then to create composite structures. Nevertheless, before evaluating the composite structure from a mechanical point of view, the focus was on the morphological evaluation of the cellulose.

Scanning electron microscopy

To evaluate the morphology of cellulose reconstituted from the ionic liquid system during mixing with epoxy resin, the fibers were isolated, dried, and examined using SEM and compared with samples of microcrystalline cellulose used for dissolution in ILs. Images obtained using the microscope are shown in Fig. 4. It can be seen that the in situ generated cellulose has a completely different form from its initial state. The magnifications clearly show the loosening of bonds in the structure of the biopolymer and the formation of fibers of considerable length, which are present throughout the composite. In addition, because the fibers are formed only at the time of mixing with the epoxy resin, moisture or air does not have the opportunity to appear in the system; thus the compatibility of the fiber and the resin matrix is very high and free of defects in the form of air bubbles or water molecules.

Mechanical properties

The following measurement parameters were selected: (i) DMTA analysis, which made it possible to determine the glass transition temperature for the composite structures; (ii) HDT measurement, which made it possible to determine the temperature at which the structure undergoes the assumed deformations; (iii) measurement of the softening temperature using the Vicat method (VST) and (iv) determination of impact strength using the Charpy method (CIT). The obtained mechanical properties are summarized in Table 3. All results were collected not only for the previously mentioned Systems **A** ([EMIM][OAc]:[EMIM][DCA]:DMSO) and **B** ([EMIM][OAc]:[EMIM][DCA]:DMSO + 5% wt. of cellulose) but also, performed for the system containing [EMIM][OAc]:[EMIM][Cl]:DMSO and 5% wt. of dissolved cellulose, in order to confirm the validity of replacing the ionic liquid [EMIM][Cl] with [EMIM][DCA] in terms of the mechanical parameters obtained. This system is marked in the table with the symbol "0—preliminary".

Depending on the parameters that were used to determine the glass transition temperature, or rather, the temperature range at which the composite structure exhibits glass transition characteristics, it was noted that the addition of cellulose

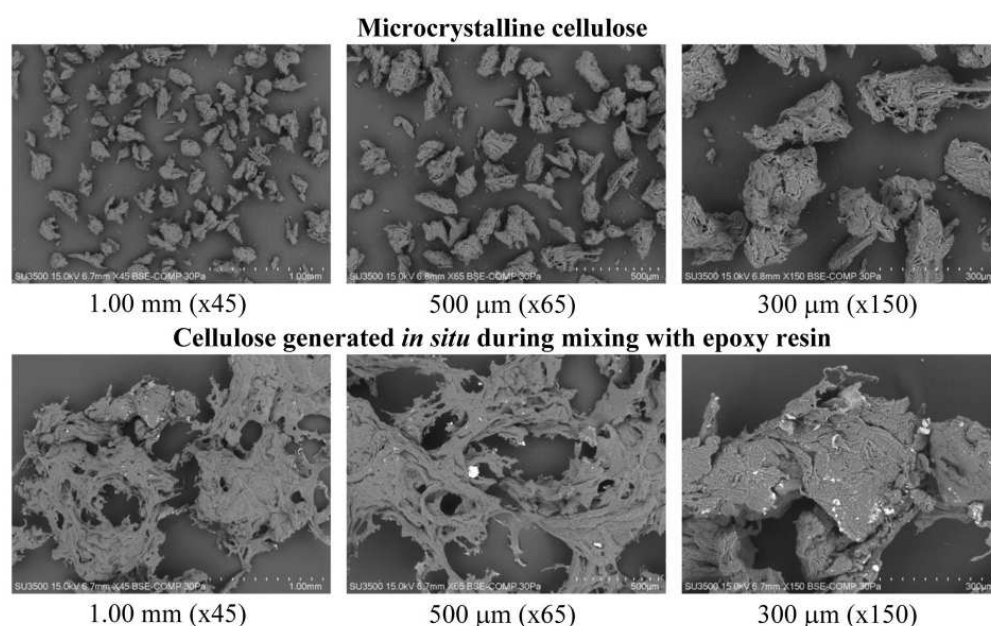


Fig. 4 SEM images of microcrystalline cellulose and cellulose present in the epoxy resin matrix. The degree of magnification is indicated in parentheses

significantly increases the value of this parameter, which in the case of System **B** reaches an upper value of almost 100 °C, based on storage modulus G' . Graphs showing the course of the DMTA analysis are shown in Fig. 5. A significant increase in the glass transition temperature caused by the presence of cellulose is also reflected in the resistance of the produced structures to deformation

under the influence of temperature (Laresser et al. 2024). The HDT values for composites containing cellulose were 60.9 °C for System **B**, containing [EMIM][DCA], and 44.0 °C for system **0**, containing [EMIM][Cl], which shows that the exchange of this compound with [EMIM][DCA] favorably influenced the deformation temperature. Moreover, for the composite structure without cellulose, the

Table 3 Mechanical properties of the obtained biocomposite structures

	Glass transition [°C]			HDT [°C]	VST [°C]	CIT			
	Loss modulus G''	Tan δ	Storage modulus G'			[kJ/m ²]	SN	P	N
A – without cellulose	50.5	41.6	57.5	< RT	59.7 ± 1.6	40.4 ± 3.6	13	5	8
B – with cellulose	61.3	79.4	99.2	60.9 ± 1.7	219.7 ± 1.4	20.5 ± 3.2	10	10	-
0 —preliminary	47.2	58.3	69.7	44.0 ± 1.6	227.6 ± 1.9	24.5 ± 3.8	11	11	-

HDT—Heat deflection temperature, VST—Vicat softening temperature, CIT—Charpy impact test, P – partial fracture, N – No fracture, SN – number of samples, A – ILs/DMSO system, B – ILs/DMSO/Cellulose system, 0 – [EMIM][OAc]/[EMIM][Cl]/DMSO/Cellulose.

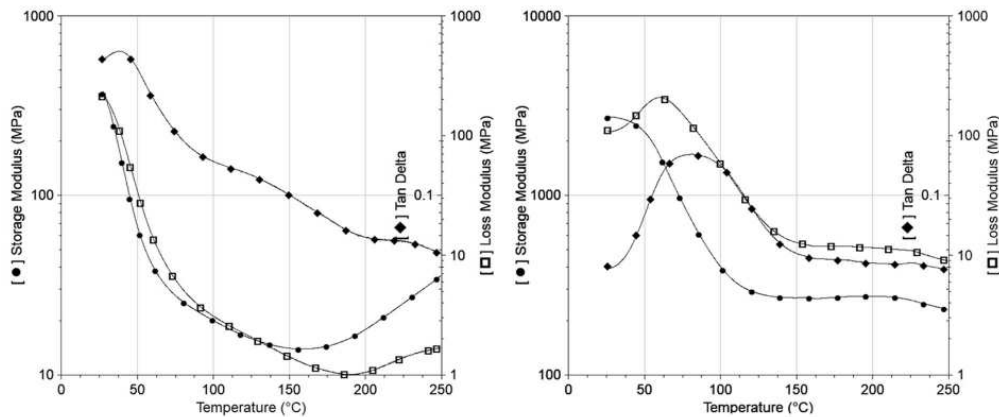


Fig. 5 DMTA curves for the obtained biocomposite structures. On the left side is a graph for System A (ILs/DMSO), and on the right side for System B (ILs/DMSO/Cellulose)

sample underwent all given deformations at room temperature.

The loss modulus values for the obtained composite structures, reinforced with flax fiber, were determined using DMTA analysis and likewise designated as System A, System B, and a reference system (0). The results obtained at various temperatures and temperature differentials provide insights into the viscoelastic properties of these composites. All results are presented in Table 4. The loss modulus is a measure of the energy dissipated as heat in a material when subjected to oscillatory stress. It is a key parameter in the study of viscoelastic materials, which exhibit both viscous (fluid-like) and elastic (solid-like) characteristics. In the context of testing composite materials, the loss modulus is important as it provides information about the damping properties of the material, i.e., its ability to dissipate vibrational energy. This is particularly relevant in applications

where vibration or noise control is crucial(Feng and Guo 2016; Essmeister et al. 2021).

At the glass transition temperature (T_g), System A exhibited a loss modulus of 32.5 MPa, whereas System B and the reference displayed higher values of 207.1 MPa and 278.6 MPa, respectively. This indicates that System A demonstrated increased viscoelastic behavior at T_g compared with the other systems(Chen and Lakes 1993; Wei and Li 2021). Upon reaching $T_g + 30$ °C, System A experienced a substantial decrease in the loss modulus to 5.1 MPa, signaling a pronounced transition in the viscoelastic properties(Ionita et al. 2015; Avila Torrado et al. 2022; Vizcaíno-Vergara et al. 2023). In contrast, System B and the reference system demonstrated values of 82.9 and 35.3 MPa, respectively, suggesting a less abrupt change in this temperature range. Continuing, at 28 °C, System A exhibited the highest loss modulus at 213.2 MPa, indicating greater

Table 4 Loss modulus parameters for the obtained composite structures

System	Loss modulus [MPa]				
	at T_g	at $T_g + 30$ °C	at 28 °C	at 75 °C	Δ 28 – 75 °C
A – without cellulose	32.5	5.1	213.2	6.3	206.9
B – with cellulose	207.1	82.9	108.1	150.9	42.8
0 – preliminary	278.6	35.3	156.9	40.9	116.0

A – ILs/DMSO, B – ILs/DMSO/Cellulose, 0 – [EMIM][OAc]/[EMIM][Cl]/DMSO/Cellulose

viscoelasticity compared with System **B** (108.1 MPa) and **0** (156.9 MPa). At 75 °C, System **B** displayed the highest loss modulus of 150.9 MPa, suggesting superior stiffness or resistance to deformation at this temperature. System **A** and the reference system showed values of 6.3 and 40.9 MPa, respectively. The temperature differential ($\Delta 28 - 75$ °C), representing the change in loss modulus over this temperature range, was highest for System **A** (206.9 MPa), followed by the reference system (116.0 MPa) and System **B** (42.8 MPa). This indicates that System **A** undergoes a substantial change in the viscoelastic properties over the tested temperature range. Considering the presence of cellulose in System **B**, the results suggest that the addition of cellulose contributes to enhanced stiffness and a more gradual change in viscoelastic properties compared with System **A**. System **B**, with the combined influence of ILs/DMSO and cellulose, exhibited notable stiffness at both 28 °C and 75 °C. The reference system, with [EMIM][OAc]/[EMIM][Cl]/DMSO/Cellulose, demonstrates intermediate behavior between **A** and **B** in terms of loss modulus values at different temperatures.

The presence of cellulose in the composite structure significantly increased the softening point value determined by the Vicat method. Vicat softening temperature serves as a pivotal measure in materials testing, specifically for plastics, revealing the temperature at which a material softens under a specified load. This parameter plays a crucial role in evaluating the heat resistance, quality, and overall performance of composite materials. Its significance lies in determining material compatibility, assessing the potential for blending with other polymers at lower processing temperatures, and understanding the impact of additives on material behavior. Furthermore, the VST, in conjunction with HDT, provides essential insights into the quality and performance of both emerging composite materials and established polymers in the realm of materials science and engineering (Arndt and Lechner 2014; Zhang et al. 2015). The increase in this parameter compared with the system without cellulose was as much as 160 °C. The biopolymer present in the composite structure causes the temperature of transition to the plastic mass state to be significantly increased, which is extremely important in the case of flax-reinforced biocomposites. In fiber-reinforced biocomposites, elevating the glass transition temperature is crucial. These biocomposites often use natural

plant fibers, which may have a lower T_g than synthetic fibers. Increasing T_g improves the thermal stability and mechanical properties of the composite. Above the glass transition temperature, the polymer becomes more flexible, enhancing the adhesion between fibers and the matrix. Elevating the T_g also improves the composite's processability, facilitating molding processes and leading to more efficient production. For biocomposites used in high-temperature environments, such as automotive or aerospace industries, a higher T_g is paramount. Thus, raising the glass transition temperature is crucial for achieving superior thermal and mechanical properties, and processability in biocomposites (Asim et al. 2020; Mahmud et al. 2021; Madyaratri et al. 2022; Ruiz de Azúa et al. 2023). On the other hand, impact tests of the produced materials showed that cellulose reduces this value by half compared with an analogous structure without cellulose. Based on all the tested parameters, it can be concluded that the cellulose present in the biocomposite in the form we propose has a positive effect on most of the tested properties, and these changes are desirable. However, cellulose also makes the composite more brittle. In our opinion, such a broad look at the properties of the obtained structures allows for better profiling of further application areas of this type of biocomposites (Bharath and Basavarajappa 2016; Hasan et al. 2021; Mudoi et al. 2022).

Conclusions

Our study introduces a novel methodology for leveraging cellulose dissolved in ionic liquids. The goal of this study was to investigate the impact of cellulose addition (previously dissolved and used as a solution) on the curing process of epoxy resin and subsequently analyze the mechanical properties of the resulting biocomposite structures. The chosen system involving [EMIM][OAc], [EMIM][DCA], and DMSO exhibited effective cellulose dissolution, as validated by employing a 5% wt. cellulose solution. The decision to substitute [EMIM][Cl] in the model system known in literature, with [EMIM][DCA] stemmed from the recognized crosslinking properties, which are well documented in prior studies. Analysis of the curing process using DSC indicated that the inclusion of cellulose in the resin mixture did not markedly influence the curing temperatures (T_{onset} , T_{max} ,

T_{endset}). Scanning electron microscopy revealed the in situ generation of cellulose fibers during mixing with epoxy resin, displaying high compatibility with the resin matrix and minimizing defects. The addition of cellulose demonstrated promising outcomes: a substantial increase in glass transition temperature (T_g) to nearly 100 °C in System B with cellulose, indicating heightened thermal stability; improved Heat Deflection Temperature (HDT), signaling enhanced resistance to deformation under temperature influence; and a noteworthy rise in Vicat Softening Temperature (VST) by 160 °C, emphasizing superior resistance to plastic deformation. However, the Charpy Impact Test (CIT) revealed a 50% reduction in impact strength, showing the composite to be more brittle.

However, it is important to note the shortcomings of the proposed solutions, which include the observed increase in the brittleness of the cellulose-reinforced biocomposite structures. Potential future applications could involve addressing the brittleness issue by optimizing the cellulose-reinforced biocomposite composition. In addition, further research could focus on developing methods to mitigate the observed increase in brittleness while maintaining the improved thermal and mechanical properties of the biocomposite structures. This could involve investigating different curing processes, alternative cellulose sources, or the incorporation of additives to enhance the overall performance of the biocomposites. Applications that prioritize increased thermal stability and stiffness over high roughness typically involve environments or conditions in which structural integrity and resistance to deformation under elevated temperatures are paramount. In certain industries such as aerospace, automotive, and electronic, while surface roughness may be a consideration for certain esthetic or functional requirements, the primary focus is on ensuring the structural integrity, thermal performance, and mechanical strength of the composite materials. Therefore, materials with enhanced thermal stability and stiffness are preferred to withstand demanding operating conditions and extend the service life of the components.

Acknowledgments The authors of this paper would like to acknowledge Paulina Nadobna for conducting the SEM measurements.

Author Contributions Conceptualization, DZ; methodology, DZ and AS; formal analysis, DZ and AS; investigation,

DZ and AS; resources, MS; validation, DZ and MS; writing—original draft preparation, DZ; writing—review & editing, AS, HM and MS; funding acquisition, MS; supervision, MS.

Funding This work was supported by the National Science Centre (Poland), project SONATA BIS (No. 2017/26/E/ST8/01059) entitled “Multifunctional composite systems based on epoxy resins with ionic liquids as a crosslinking initiators”.

Data availability No datasets were generated or analysed during the current study.

Declarations

Ethical approval This research article does not contain studies involving human participants or animals performed by any of the authors.

Consent for publication All authors have approved the final version of the manuscript.

Competing interests The authors declare no competing interests.

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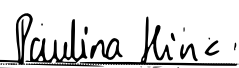
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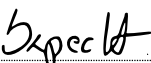
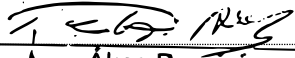
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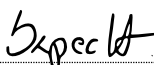
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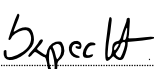
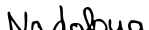
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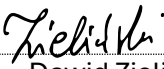
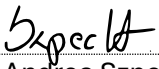
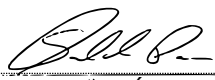
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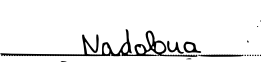
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