Ionic liquids and thermosetting polymers: a critical survey

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Thermosetting polymers are widely used as industrial materials due to good heat resistance, dimensional stability and chemical resistance. Designing novel networks still remains an exciting and emerging field of research. The present paper substantiates the applications of ionic liquids (ILs) for the design of advanced thermoset derivatives. The peculiarities of the curing behavior of resins in the presence of ILs and the main properties of the cured thermosets are analyzed. The utilization of ILs in thermosetting polymers as catalytic agents, plasticizers, electrolytes or porogens is highlighted. Diverse ILs can be incorporated into a polymer matrix to achieve better final properties. To make the review more substantial, basic ideas about ILs are first outlined.

Keywords: thermosets, ionic liquids, catalytic agent, porogen, ionic conducting agent.

Introduction.

Ionic liquids (ILs) are the subject of widespread interest as green alternatives to conventional organic solvents. Most of the ILs are commercially available from several suppliers. Ideally, ILs are non-flammable, optically clear and are relatively inexpensive to manufacture [1]. Many ILs exhibit a wide temperature range of liquid state up to about 300 °C, providing the opportunity to carry out high-temperature reactions. Being composed entirely of ions, these novel multifunctional agents so called as «designer solvents» have extremely low vapour pressure and low volatility. As a result of one or more of these characteristic properties, ILs have already been found useful in the polymer chemistry for diverse applications [2–5]. The combinations of ILs unusual properties with cross-linked polymers exhibit various interesting properties [6–12]. Unfortunately, if there is no any strong interection between polymer and IL a latter can easily exude from the polymer network making the properties of the material uncontrollable that is unacceptable from the viewpoint of application.

In this way, herein, we are going to review the using of ILs for a wide range of applications in thermoset materials that could be important for further spread of ILs. The application of ILs in thermosets has quickly advanced from using them as a reaction media to application as functional additives. Certainly, innovation in this field requires the control of their structure at nanoscale and addition of ILs can be a new and facile method to manage the morphology and properties of thermoset polymers as well as to widen their application.

Ionic liquids.

ILs may be considered as a class of salts with a melting temperature below 100 °C. The story of ILs begins with the first report of the preparation of ethylammonium nitrate salt using the reaction of ethylamine with nitric acid having melting point of 12 °C in 1914 [13]:

$$EtNH_2 + NHO_3 = [EtNH_4][NO_3]. \qquad (1)$$

Despite this the interest have developed after the discovery of binary ILs made from mixtures of aluminum (III) chloride and N-alkylpyridinium [14] or 1,3-dialkylimidazolium chloride [15]. Nevertheless, a major drawback of all chloroaluminate (III) ILs, their moisture sensitivity remained unresolved. In particular, Wilkes and Zawarotko
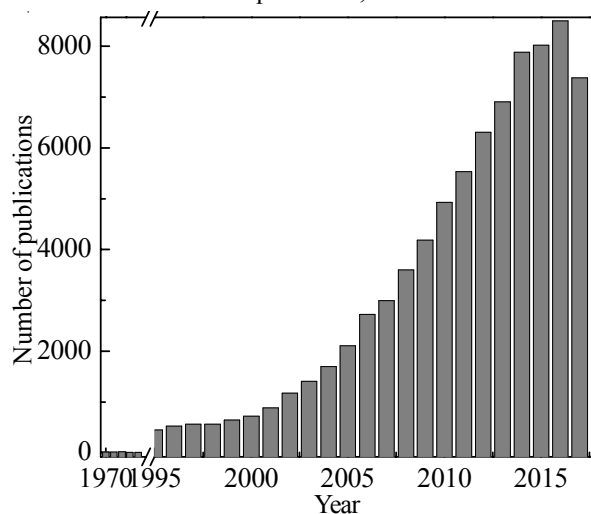

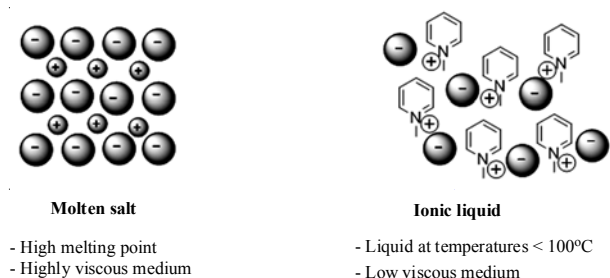Fig. 1. Publications on ILs as determined from the ISI Web of Science® (on December 12, 2017)

Molten salt
- High melting point
- Highly viscous medium

Ionic liquid
- Liquid at temperatures < 100°C
- Low viscous medium

Fig. 2. Schematical image of ionic structure of molten salts and ILs

Fig. 3. Structure of commonly used cations and anions species for ILs

[16] prepared and characterized the air and water stable 1-ethyl-3-methylimidazolium ILs with different anions.

Over the last two decades a large variety of ILs have been investigated marked by an exponential growth in a number of publications represented by the yearly increase starting from near 10 in 1990 to more than 7000 papers published last year (Fig. 1). The first publications on using ILs in polymers have appeared in 2002 and than increased quickly in the last two decades and a summary on their applications and properties may be found in a number of review articles [17–23] and book [24]. There is no doubt that this area of research has been an important point of polymer chemistry as well.

ILs are self-dissociated and do not need a solvent to dissociate into cations and anions that uniquely distinguish them from classical salts like NaCl, KBr. What is the difference between a molten salt and an ILs? Both molten salts and ILs are liquid salts containing only ions (Fig. 2). However, in molten salts, there are symmetric cations and anions making the lattice well packed and hence it requires a large energy to break the lattice. In contradistinction to molten salts ILs cations have irregular shape preventing crystal packing [25–27]. Therefore, molten salts melt above 100 °C ($T_{\text{melt NaCl}} = 801$ °C, $T_{\text{melt KCl}} = 770$ °C), a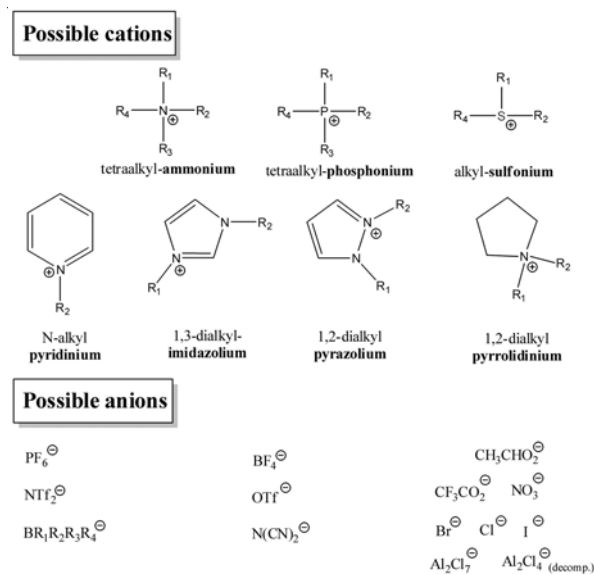nd ILs melt much below that temperature (in particular, Room temperature ILs (RTIL) are liquid already at an ambient temperature).

The most common classes of cations and anions are illustrated in Fig. 3. The structural design of ILs is playing a very important role as the major properties may be easily controlled by composing of ionic pair (10^{18} potential structures [28]). In this way, their properties can be varied dramatically by creation of unique combinations of cations, anions and chains lengths. The change of anion can drastically affect physical properties of ILs such as hydrophilicity, viscosity and melting point as well as thermal stability. On the basis of reported data, the relative thermal stability of imidazolium ILs containing some common anions decreases in the following order: $[BF_4]^-$ (450 °C) > $[I]^-$ (303 °C) > $[Cl]^-$ (285 °C) > $[N(CN)_2]^-$ (275 °C) > $[SCN]^-$ (226 °C) [29–32]. The purity of ILs is a very important issue and

Table. Comparison of ionic liquids with organic solvents [20]

| Property	Organic Solvents	Ionic Liquids
Number of solvents	>1,000	>1,000,000
Applicability	Single function	Multifunction
Catalytic ability	Rare	Common and tunable
Chirality	Rare	Common and tunable
Vapour pressure	Obeys the Clausius-Clapeyron Equation	Negligible under normal conditions
Flammability	Usually flammable	Usually nonflammable
Solvation	Weakly solvating	Strongly solvating
Tunability	Limited range of solvents available	Unlimited range means «designer solvents»
Polarity	Conventional polarity concepts apply	Polarity concept questionable
Cost	Normally inexpensive	2 to 100 times the cost of organic solvents
Recyclability	Green imperative	Economic imperative
Viscosity/cP	0,2–100	22–40,000
Density/g cm^{-3}	0,6–1,7	0,8–3,3
Refractive index	1,3–1,6	1,5–2,2
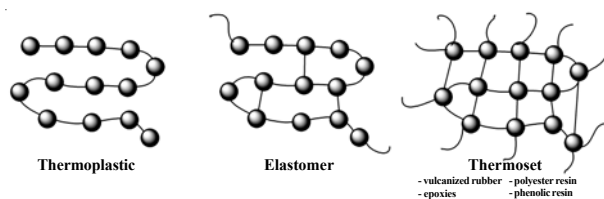
Fig. 4. Schematical image of structure of thermoplastics, elastomers and thermosets

the influence of major contaminants such as water and chlorine ion on some of their physical properties has been discussed by Seddon *et al.* [33].

Most of ILs are considered as green solvents, due to their ability to be reused/recycled, to replace toxical industrial volatile organic compounds (VOCs) [34], and to solve the following problems: *(i)* loss of solvent by uncontrolled evaporation, and *(ii)* traces of solvent in final product. In addition to the interactions existing in VOCs (hydrogen bonding, dipole–dipole and van der Waals interactions), ILs have ionic interactions (mutual electrostatic attractions or repulsion of charged particles), which make them very miscible with polar substances. Generally speaking, ILs have properties that are quite different from those of organic solvents (cf. Table).

Applications of ILs in thermosetting polymers.

It is well known that highly crosslinked structures *via* covalent bonds is directly responsible for the high mechanical strength and high thermal stability, but at the same time provides a poor elasticity or elongation compared with thermoplastics or elastomers (Fig. 4). Unlike thermoplastics, thermosets retain their strength and shape even when heated.

In this context, the generation of high performance thermosetting polymers in the presence of ILs may thus constitute an interesting challenge.

In the next sections the application of ILs in epoxy based thermosets as catalysts, curing agents, electroconductive components, plasticizers, and porogens is presented. Additionally, using of ILs in high performance Cyanate Ester Resins (CER) will be discussed as well.

Epoxy resins.

Ionic liquids as catalytic agents.

ILs represent an exciting new class of catalytic or/and crosslinking agents for thermosetting polymers, especially for epoxy resins [35–43]. First trial of using 1-butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF$_4$] IL for crosslinking of epoxy resin was described by Kowalczyk and Spychaj in 2003 [36].

Maka *et al.* prepared and investigated the epoxy compositions with ILs possessing the imidazolium cation with alkyl chains of different length (butyl or decyl), and different anion type ([N(CN)$_2$]$^-$, [BF$_4$]$^-$, [Cl]$^-$), the ILs concentration was varied as well (1, 3, or 9 phr) [41]. On the basis of the results, the authors concluded that *i*) the curing process started at lower temperature (120–150 °C) when ILs with [N(CN)$_2$]$^-$ anion were applied, in compari-

son with those containg [BF$_4$]$^-$ anions (200–240 °C); *ii*) the alkyl chain length of imidazolium cation influenced slightly the onset temperature curing range: for decyl substituent, 200–240 °C, and butyl, 210–230 °C; *iii*) as a rule bimodal exotherms appeared on DSC thermograms, the first was placed at a lower temperature range above 110 °C (compositions with ILs and basic [N(CN)$_2$]$^-$ anion) and the second was placed above 250 °C (compositions with ILs bearing [BF$_4$]$^-$ anion). The observed bimodal exotherms and FTIR absorption bands at 1740–1750 cm^{-1} were explained by the proposed mechanism of epoxy resin anionic polymerization initiated by thermal decomposition products of 1,3-dialkylimidazolium liquids.

Palmese's team [42] used 1-ethyl-3-methylimidazolium dicyanamide [EMIM]N(CN)$_2$ in a range of 1–9 weight parts per 100 parts of epoxy resin and found a lower crosslinking temperature than that reported by Kowalczyk and Spychaj for [BMIM][BF$_4$]. Maka *et al.* [44] performed comparison of two dicyanamide ILs with various cation types: imidazolium, *i.e.* 1-ethyl-3-methylimidazolium dicyanamide ([EMIM]N(CN)$_2$) and phosphonium, *i.e.* (trihexyltetradecyl phosphonium dicyanamide ([THTDP]N(CN)$_2$). The composition of neat epoxy resin with 9 wt. parts [EMIM]N(CN)$_2$ exhibited latency of above 45 days, whereas the composition containing 9 wt. parts [THTDP]N(CN)$_2$ demonstrated a pot life of above 70 days. However, it should be noted, that materials cured with 6 wt. parts [THTDP]N(CN)$_2$ showed higher transparency ($\approx$ 85 %) in comparison to that with 3 wt. parts [EMIM]N(CN)$_2$ (black opaque).

Until today, imidazolium-based ILs have been more often applied in epoxy resin systems than phosphonium ones [45]. On the contrary, the presence of phosphonium salts exerted only a marginal effect on the curing process. However, the reasons why one might be interested in phosphonium ILs, even in industrial processes, include their availability and cost.

As discussed in the literature [35–36], imidazolium-based ILs act as curing agents for the epoxy systems at high temperature. Liebner *et al.* [46] suggested that such ILs may undergo a thermal decomposition leading to formation of imidazole and other decomposition products. In an early study, Farkas and Strohm, reported about high catalytic activity of imidazoles for curing of epoxy resins, proving that the imidazole became permanently attached to the polymer chain [47]. The curing kinetics and mechanisms of diglycidyl ether of bisphenol A (DGEBA) using imidazole and 1-methyl imidazole as curing agents were studied by Ghaemy and Sadjady [48]. Soares et al. [37] noted that the imidazolium-based IL participated in the curing process of the epoxy resin probably through its decomposition products (imidazole) generated at high curing temperature. Pyridinium-based ILs may also decompose at high temperature and produce pyridine, which is reported to act as a crosslinking agent for epoxy systems [49–51]. Maka *et al.* [40] also reported that reaction

activity of ILs toward epoxy resins was connected with its thermal decomposition characteristics. Easy decomposing ILs with dicyanamide and chloride anions were able to cross-link epoxy resin at 150 °C, whereas the reactions of temperature resistant ILs containing tetrafluoroborate anion occurred at temperature above 200 °C.

Ionic liquids as ionic conducting agents.

ILs are promising candidates for novel high performance electrolytes for electrochemical devices such as lithium ion batteries and electronic double layer capacitors. ILs have excellent ionic conductivity up to their decomposition temperature. Nevertheless, a drawback for practical application is that IL fluidity may cause liquid electrolyte leakage. Ohno and co-workers attempted to polymerize ILs composed of imidazolium substituted methacrylates [52–54]. However, polymerization of ionic compounds often reduces the molecular motion and provides low ionic conductivity. To solve this problem, polymers which have three dimensionally highly crosslinked structures and possess excellent physicochemical properties could be use.

Polymer networks confining an ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide (EMImTFSI), were prepared [55] by curing a mixture of bisphenol A diglycidyl ether (BADGE) and tetrafunctional epoxy resins with tetraethylenepentamine (TEPA) in the presence of ionic liquid. The ionic liquid confinement, ionic conductivity, mechanical strength, and morphology of the materials strongly depended on the ionic liquid content. At a low EMImTFSI content (<40 wt.%), the material tightly confined the ionic liquid and showed little ionic conductivity with a high Young's modulus. This seems reasonable because there are no freely mobile ions in the samples, in which rigid and glassy polymer network locally confine ions. At a high IL content (>40 wt.%), the material did not tightly confine the IL showing higher ionic conductivity. The microphase separation between the EMImTFSI and the epoxy networked polymer was observed by scanning electron microscopy (SEM). The ionic conductivity of the BADGE/TetradX/TEPA/(50 wt.%) EMImTFSI was equal to 0,1–0,12 S/m in the frequency range from 1to 100 KHz, which is quite high and corresponds to about 1/8 of the reported bulk EMImTFSI conductivity (0.84 S/m). Subsequently, Matsumoto et al. [56] synthesized the highly flexible ion conductive films of epoxy-based crosslinked polymer containing ionic liquid having a quaternary ammonium salt structure. The polymers having trimethylammonium bis(trifluoromethanesulfonyl)imide groups were synthesized by heating a mixture of diepoxide, glycidyl trimethylammonium bis(trifluoromethanesulfonyl)imide (GTMATFSI), and diamine curing reagent. Ethylene glycol diglycidyl ether (EGGE), poly(ethylene glycol) diglycidyl ether (PEGGE), and poly(propylene glycol) diglycidy ether (PPOGE) were used as diepoxides, and ethylene glycol bis(3-aminopropyl) ether (EGBA), poly(ethylene glycol) diglycidyl ether bis(3-
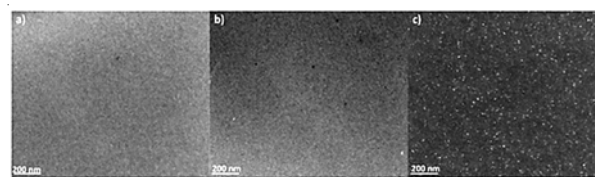

Fig. 5. TEM micrographs of epoxy networks cured with: a) 5 phr, b) 10 phr and c) 30 phr of phosphonium dicyanamide IL [57]

aminopropyl ether) (PEGBA), and polypropylene glycol bis(2-aminopropyl ether) (PPOBA) were used as diamine curing reagents. The obtained networks having quaternary ammonium structure showed high thermal stability (temperature of 5 wt. % decomposition above 270 °C), low crystallinity, low glass transition temperature, and good ionic conductivity. In particular, the crosslinked polymers consisting of poly(ethylene glycol) segments showed high ionic conductivity ($>1,0 \cdot 10^{-3}$ S/m) at room temperature and reached $5,8 \cdot 10^{-2}$ S/m for EGGE-GTMATFSI-1.2/PEGBA and $4,1 \cdot 10^{-2}$ S/m for PEGGE/GTMATFSI-1.2/PEGBA at 90 °C, which is also quite high for a solid polymeric material. These networks were mechanically strong and tough enough to produce self-standing thin films and will be useful materials for application as ionic conductive membranes in electrochemical devices.

Livi *et al.* designed IL-containing polymer networks, which could be employed as new polymer electrolytes [57]. They used trihexyl(tetradecyl)phosphonium IL with dicyanamide counteranion as functional additives to synthesize nanostructured epoxy networks with very high mechanical properties and thermal stability (>400 °C). In addition, TEM micrographs (Fig. 5) showed formation of ionic clusters of the size of 20–30 nm with excellent distribution (characterized by the white spots) for the epoxy
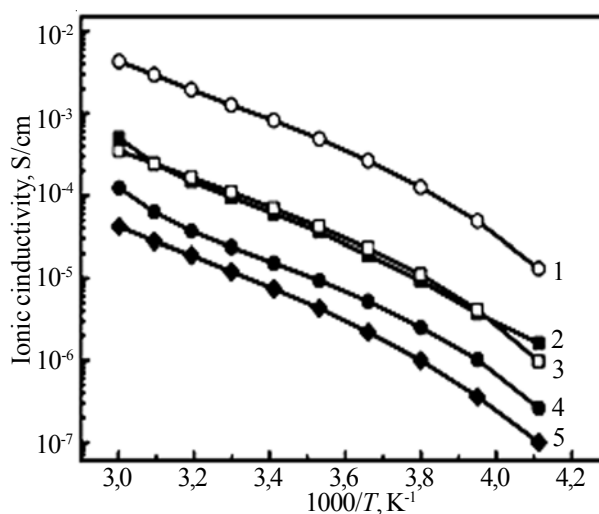

Fig. 6. Temperature dependence of ionic conductivity of samples with varying resin contents (wt.%): 1) 30; 2) 50; 3) 40; 4) 50; 5) 50. Samples 1, 3, 5 –based on MVR®444; 2 – VTM®57; 4 – VTM®266 [58]

network loaded with the highest concentration (30 phr) of this IL. These results are promising and open new perspectives in the field of energy where the IL can be used as ionic channels for lithium salts to ensure suitable conduction properties [57].

Shirshova *et al.* [58] prepared a series of epoxy resin-ionic liquid composites to identify the optimum system microstructure required to achieve a high level of multifunctionality. Structural electrolytes based on fully formulated commercially available epoxy resins (pure one with trademark MVR®444 and toughened ones, MTM®57 and VTM2®66) were obtained by adding the mixture of bis(trifluoromethane) sulfonimide lithium salt (LiTFSI) and ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide (EMIM-TFSI) ionic liquid. At only 30 wt.% of structural resin and 70 wt.% of IL-based mixture, containing 17 wt.% of the Li salt, stiff monolithic plaques with thicknesses of 2–3 mm possessing room temperature ionic conductivity of 0,8 mS cm^{-1} and Young's modulus of 0,2 GPa were obtained. Detailed temperature-dependent ionic conductivity measurements were carried out using dielectric spectroscopy in a temperature range of -30 to 60 °C. The ionic conductivity was extracted from the plateau region of each dielectric spectrum (Fig. 6). The sample with the highest ionic conductivity across the temperature range was MVR®444 with 70 wt.% of IL-based mixture. Even at -20 °C, the ionic conductivity was equal to 0,05 mS·cm^{-1}. The room temperature conductivity was close to 1 mS·cm^{-1}, which is not only a desirable value for supercapacitor applications, but is also high enough to potentially consider thin films of MVR®444/30 as separation membranes for Li ion batteries.

Ionic liquids as plasticizers.

A plasticizer is a substance incorporated into a polymer to increase its flexibility, workability or distensibility. Normally, plasticizers have a large influence on physical, chemical, and electrochemical properties of modified polymers: for instance, they reduce melt viscosity, tempera-ture of a second order glass transition (T_g) or elastic modulus of a polymer. The plasticizers used in the industry are mostly derivatives of phthalates, which represent approximately 70 percent of the market. However, due to their toxicity, academic and industrial researchers have been looking for new plasticizers. In fact, RTILs have the necessary qualities of a good plasticizer: *i*) excellent melting properties, *ii*) minimal interaction with resins at room temperature and *iii*) non-volatility at ambient conditions. As one can conclude, RTILs can be utilized as efficient plasticizers to manage mechanical properties of thermosetting polymers, at that the chemical nature of organic cations and anions plays a significant role in distribution of ionic domains in the polymer matrix. According to the literature, imidazolium and pyridinium ILs lead to the formation of aggregates of ionic clusters, while phosphonium ILs generate a structuration at a nanoscale denoted as «spider-web» morphology [59]. Thus, it is possible to control the plasticization effect of thermosets by varying IL molar mass and chemical structure.

Lu *et al.* reported [60] a significant decrease in the T_g, of epoxy networks by using several types of ILs, and this effect was more pronounced in the systems modified with imidazolium-based ILs, than that in the systems containing phosphonium-based ILs. Sanes *et al.* reported that addition of the 1-octyl-3-methylimidazolium tetrafluoroborate [OMIM][BF$_4$] to epoxy resins enhanced chain mobility and provided a plasticizing effect as well as reduced friction coefficient and wear rate of the final materials [61].

Soares and coauthors successfully synthesized and used [37] *N,N'*-dioctadecylimidazolium iodide with long alkyl chains as a new additive for epoxy networks. The T_g value as determined at the maximum of the tanδ peak decreased as the amount of the IL increased. This behavior suggested a plasticizing effect of the IL imparted by the presence of the two long alkyl chains in its structure. The authors [37] noted that the storage moduli at temperatures below T_g were higher in the thermosets containing
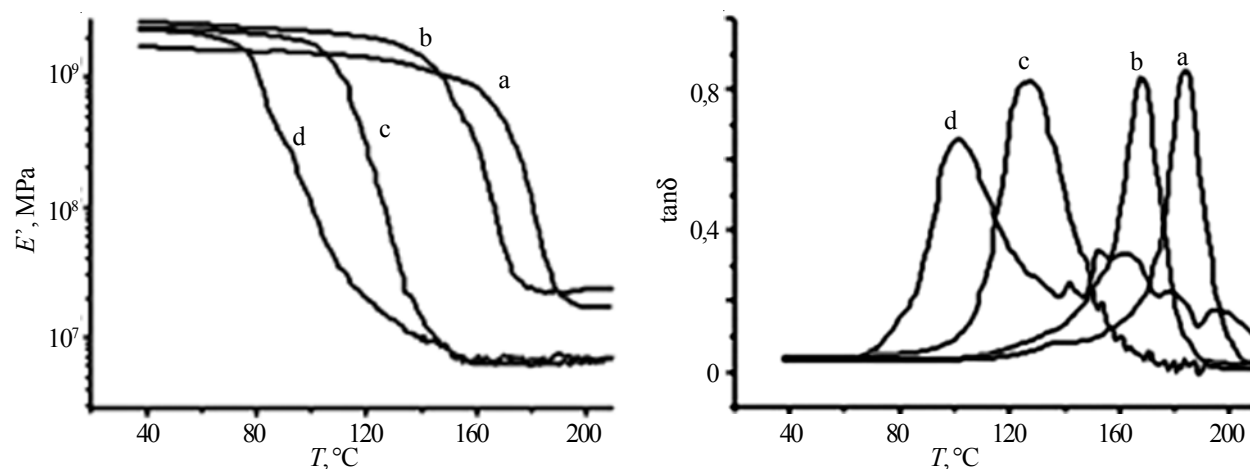

Fig. 7. Dynamical mechanical properties of DGEBA/IL/MCDEA networks as a function of the IL content: 0 (*a*); 1,0 (*b*); 2,5 (*c*); 5,0 phr (*d*) [37]

IL probably because of the good interactions between the components (Fig. 7). At temperatures above T_g, the modulus of the system containing 1 phr of IL was higher than that of pure epoxy network, indicating high interactions between the blend components. However, when increasing the amount of IL, the moduli in this region decreased, suggesting that the plasticizing effect imparted by the long alkyl groups in the IL molecules contributed more for this property than the interactions between the components. The T_g tendency found in DSC experiments was similar to that detected by DMA analysis and also confirmed the plasticizing effect of the IL.

Ionic liquids as porogens.

The novel peculiarity of ILs as «designer solvents» is the possibility to design porous thermosets with the necessary properties for the specific applications. The basic requirements to porogens are as follows: *i*) boiling point higher than temperature of polymer synthesis; *ii*) inertness towards basic components of polymer synthesis; *iii*) predetermined ratio of polarity and solubility parameters of monomer, polymer, and porogen. The solubility parameter is crucial for a porogen selection, and it is used to compare the solvation, miscibility, and swelling properties of the components used. The consideration of nature and possible interactions of porogen-polymer, porogen-monomer(s), and porogen-initiator is also an important issue during synthesis of porous materials.

Mohamed *et al.* [62] reported that the closer the solubility parameters $|\Delta\delta|$ of a porogen, reactants (monomer/crosslinker), and polymer, the greater the surface area and the smaller the pore volume, while the smaller surface area and higher pore volume in porous polymers could be reached for higher difference in solubility parameters of the components used. The uni-modal (micro, meso, or macroporous) polymer can be obtained by varying the type and amount of a porogen. In addition to this, bi-modal (micro-meso, meso-macro, or micro-macro) porosity can be generated using a porogen mixture or varying the porogen ratio. A low molar mass porogen is generally preferred to obtain the smaller pore size, which results
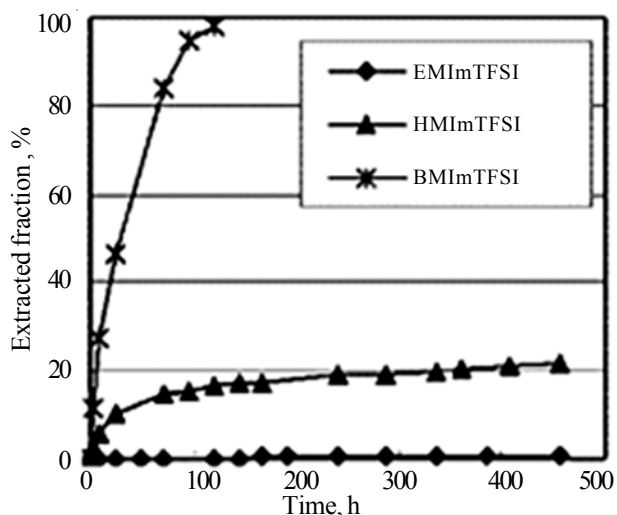

Fig. 8. Time dependence of the extracted ionic liquid fraction from films of BADGE/Tetrad-X/TEPA with [EMIm][TFSI], [HMIm][TFSI] and [BMIm][TFSI] (extraction solvent: acetone) [55**]**

into a greater surface area and vice-versa for a high molar mass porogen [63]. However, increasing the molar mass of a porogen increases the viscosity of the polymerization reaction composition, and it is recommended to use high molar mass porogens in combination with a porogen of low molar mass [64]. Therefore, the use of RTILs as porogens for the preparation of porous polymers [65–69] has some distinct advantages: *i*) ILs are thermally stable and nonvolatile and can be easily recycled; *ii*) the morphology and porous structure can be easily changed through a proper selection of the structural features of the IL used; *iii*) pore diameter can be managed by varying the amount of IL used; *iv*) due to extremely low viscosity, ILs can be used as porogens without using any additional solvent.

Nowadays, several researchers have studied the extraction of ILs from epoxy polymer networks, however no-one has reported on characterization of porous thermosets obtained thereof. Matsumoto and Endo [55]
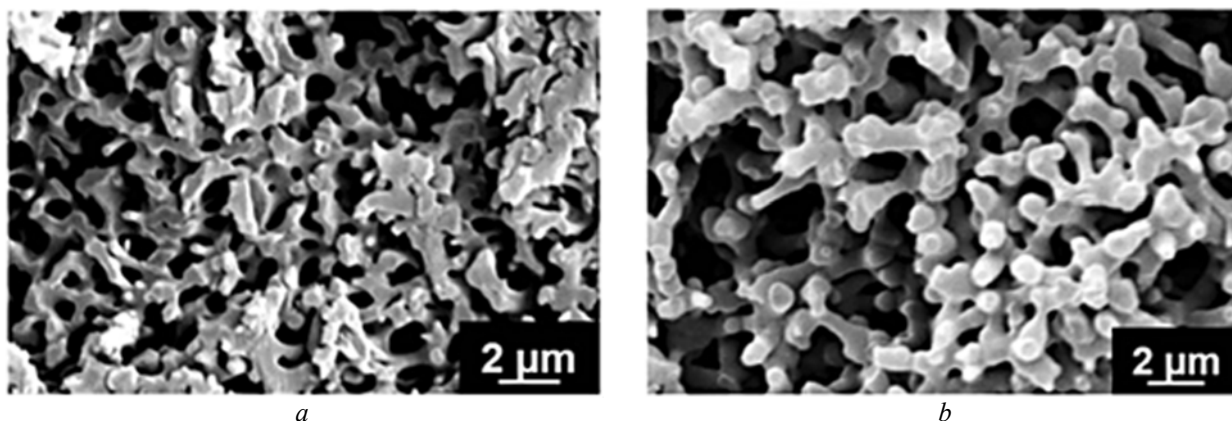

Fig. 9. SEM micrographs of epoxy samples after extraction of different amounts of electrolyte (EMIM-TFSI + LiTFSI): a) 60 wt.%; b) 70 wt.% [58]

extracted the IL from polymer/IL composites in order to examine the morphologies of the cross-linked materials. Fig. 8 shows the results of acetone extraction of various ILs from BADGE/TEPA/IL epoxy network systems. The IL confinement was in the order EMImTFSI > HMImTFSI > BMImTFSI, which was the opposite order of the steric hindrance of the cations. The reason for this remained unknown, but the authors assumed that the hexyl or benzyl groups in the cationic part may increase the compatibility of the IL with the epoxy network that provides the enhanced segmental motion of the network, so the IL can easy escape from the network. Materials confining IL were insulating with a high Young's modulus, while those not confining IL were ion conducting with a low Young's modulus. SEM observation revealed that the drastic change of the fundamental properties of the epoxy materials could be due to the morphology transition of the materials, in which the IL transformed discrete phases to continuous phases in the epoxy-based networks. These
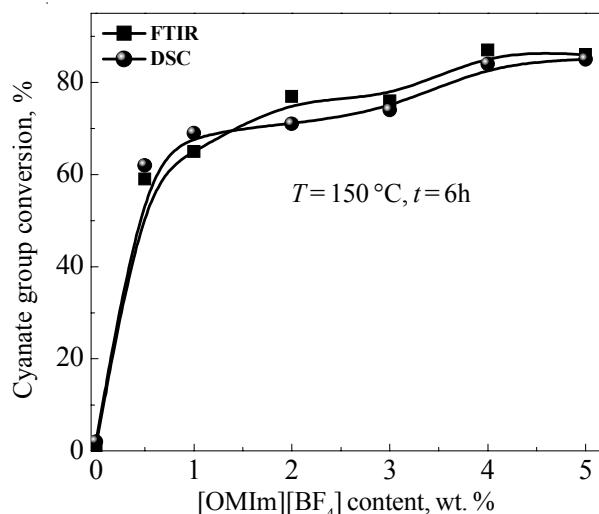

Fig. 10. Concentration dependence of CER monomer in the CER/[OMIm][BF$_4$] samples at heating at 150°C for 6 h
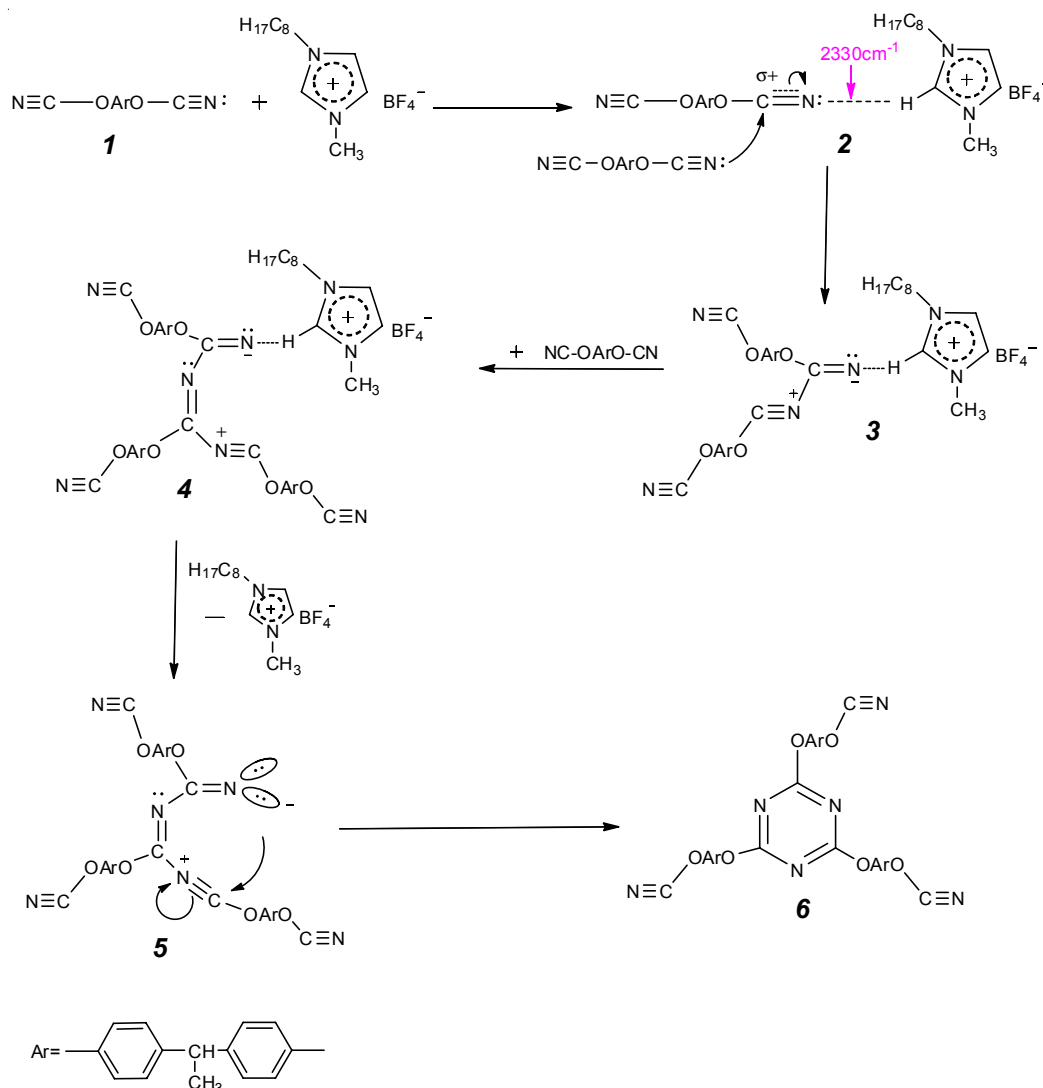

Fig. 11. The mechanism proposed for the [OMIm][BF$_4$]-catalyzed cyclotrimerization [71]

results suggest that the addition of IL can be a new and facile method to control the morphology of polymer networks.

Shirshova *et al*. [58] reported that there were no dimensional changes observed as a result of electrolyte (EMIM-TFSI + LiTFSI) extraction removing more than >95 wt. % of the original IL-based electrolyte content from an epoxy network (MVR®444). The SEM images of all the samples showed a bicontinuous morphology (Figure 9). It seemed likely that MVR®444 formed a fully miscible one-phase system at the cure temperature, but that phase separation occurred at an earlier stage during the polymerization as a result of its lower miscibility with the ionic liquid. The authors concluded that this system based on commercial components could be readily applied to the development of structural electrical energy storage composite devices.

Ionic liquids in Cyanate Ester Resins (CERs).

Throckmorton and Palmese in 2016 firstly reported [70] a new way to accelerate CER polycyclotrimerization by using dicyanamide (DCNA)-containing RTILs as a new catalytic system alternative to conventional catalysts normally based on metal acetylacetonates and nonyl phenol. Novel ionic thermosetting polymers, *i.e.* polycyanurates containing the ILs incorporated chemically directly into the triazine network, were thus synthesized. The catalytic effect was found in a number of dicyanamide-containing ILs with diverse cations, namely 1-ethyl-3-methyl imidazolium dicyanamide, 1-(3-cyanopropyl)-3-methyl imidazolium dicyanamide, 1-(2-hydroxyethyl)-3-methylimidazolium dicyanamide, 1-butyl-1-methyl-pyrrolidinium dicyanamide, and 1-butyl-3-methyl pyridinium dicyanamide. For comparison, the non-dicyanamide RTIL, 1-ethyl-3-methyl imidazolium tetrafluoroborate ([BMIM][BF_4]) was tested as a catalyst for CER polycyclotrimerization. It was found that the reaction kickoff temperature in CER/[BMIM][BF_4] system was significantly higher than that for the DCNA containing ILs. The following conclusions could be done on the basis of these results: *i*) RTILs of varying structures and concentrations accelerated curing of
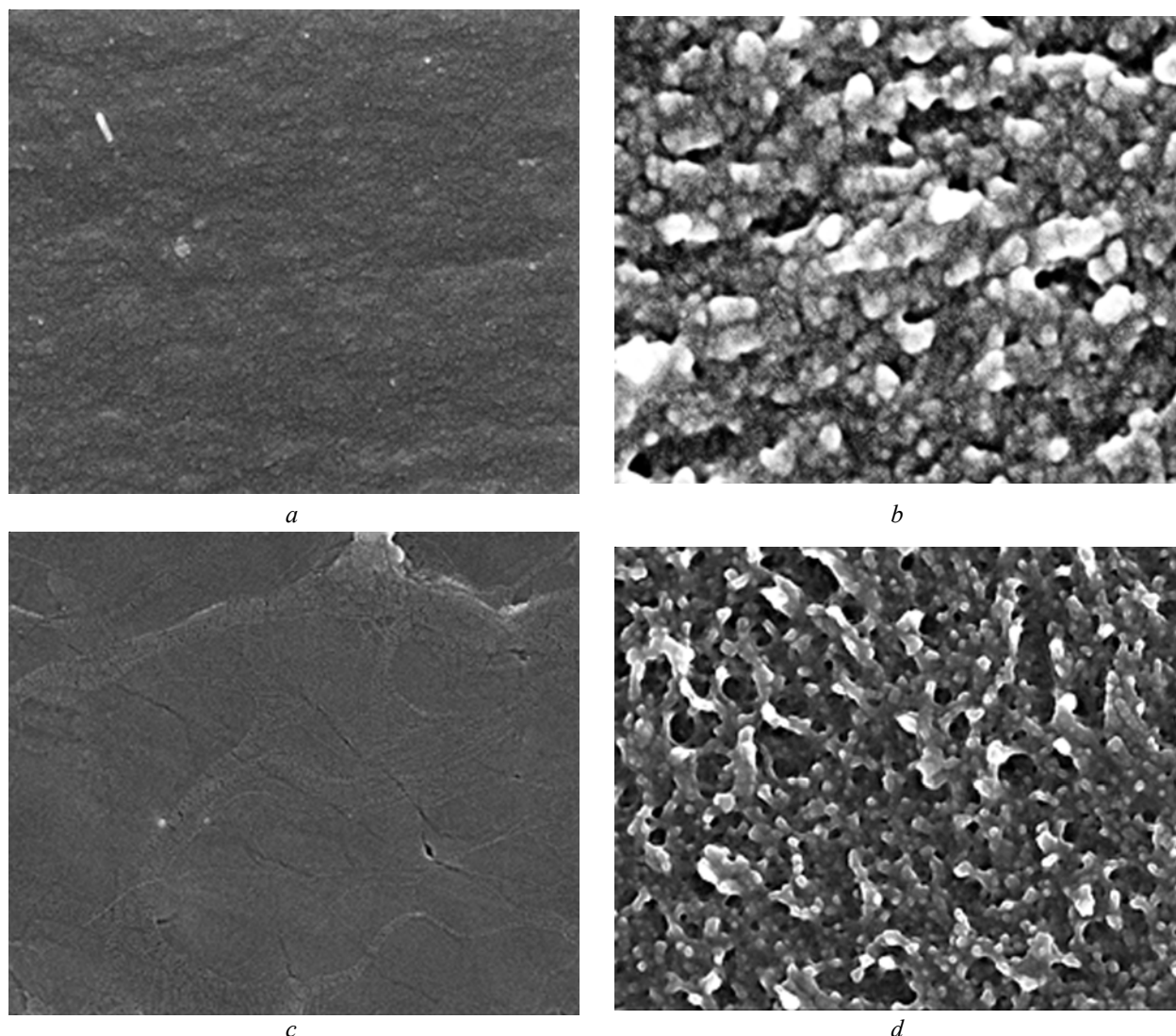

Fig. 12. Typical SEM micrographs of CER-based samples: CER$_{ext}$ (a), CER$_{20ext}$ (b), CER$_{40}$ (c), CER$_{40ext}$ (d) [72]
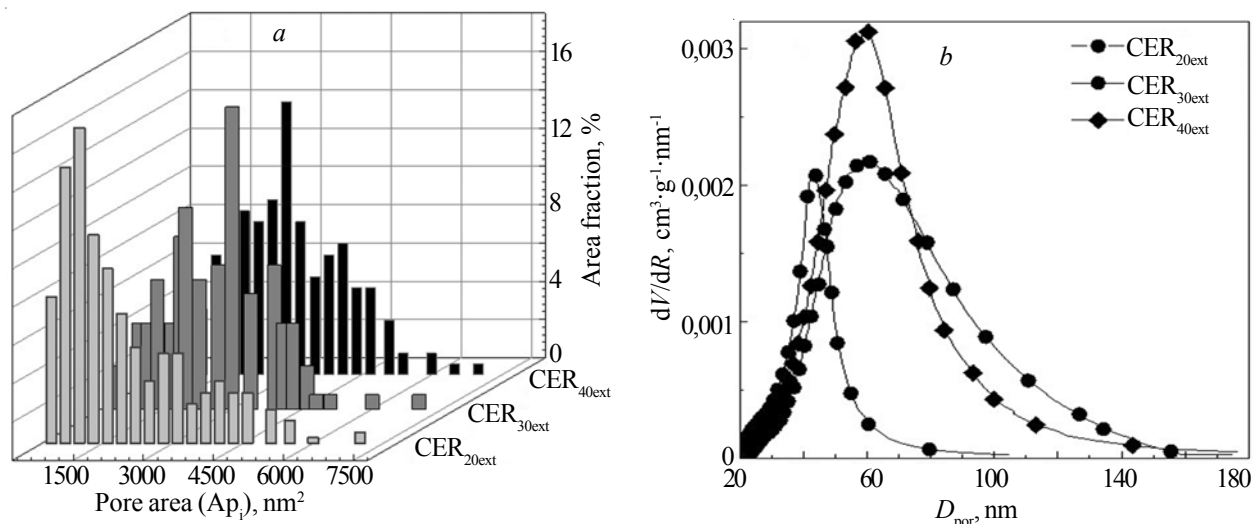
Fig. 13. a) Pore area distributions derived from SEM data for the nanoporous CER-based samples and b) Pore size distribution profiles derived from DSC-thermoporometry [72]

CERs; *ii*) dicyanamide ILs were incorporated directly into the triazine network; *iii*) plasticization effect was fixed depending on RTIL content (0-10 wt.%) due to decrease in cross-linking density (nearly 100 °C decrease in T_g at 10 wt. % IL loading). Finally, the ionic thermoset structure presented a cured resin with ionically bound species that provided an excellent subject for future research in ionomers and nanocomposites.

Although the reaction mechanism of CER curing in the presence of DCNA-based ILs was investigated thoroughly, the mechanism of catalysis by non-dicyanamide RTILs was not discussed. Based on the studies mentioned above, one can conclude that in order to develop novel CER-based materials with new properties, research on application of other ILs should be continued.

These results prompted us to investigate the effect of other non-dicyanamide ILs on the kinetics of the CER system [71]. We found that small additions (0,5 – 5,0 wt.%) of 1-octyl-3-methylimidazolium tetrafluoroborate ([OMIm][BF$_4$]) significantly accelerated the kinetics of CER polycyclotrimerization. For samples containing [OMIm][BF$_4$], polycyclotrimerization of monomer took place even at the heating stage at 150 °C, while for pure monomer polycyclotrimerization practically did not occur (Fig. 10). A reaction mechanism was newly proposed *via* the involvement of a [CN]$^{\delta+}$ --- [OMIm]$^{\delta}$ complex as a key intermediate (Fig. 11). We assume that such catalytic effect of imidazolium-based ILs would take place with any dicyanate monomer.

To the best of our knowledge until 2017, no systematic studies on using ILs as porogens for producing porous CER networks have been reported. In our recent research [72], 1-Heptylpyridinium tetrafluoroborate IL ([HPyr][BF$_4$]) was chosen as a porogen for CER-based films. Complete IL removal was confirmed by determination of gel fraction contents, FTIR, ^{1}H NMR, and EDX spectroscopic analyses. Typical SEM images of CER films before extraction of

[HPyr][BF$_4$] (CER$_{40}$) and after extraction of the latter (CER$_{40ext}$) are presented in Fig. 12. As it was expected, both CER$_{ext}$ (pure CER after extraction) and CER$_{40}$ samples (Fig. 12a and Fig. 12c, respectively) exhibited compact and non-porous structures, whereas CER$_{20ext}$ and CER$_{40ext}$ samples (CERs containing 20 and 40 wt.% IL after extraction, Fig. 12b and Fig. 12d, respectively) displayed a nanoporous structure with pore diameters ranging from 25 to 170 nm, depending on their CER/IL composition. SEM and DSC-based thermoporometry were used as complementary techniques for nanopore characterization. Depending on the IL porogen content, the average pore diameter values were found in the range of 45–60 nm with pore size distributions of ~20–180 nm (Fig. 13). It is also noteworthy that an increase in the [HPyr][BF$_4$] content resulted in increasing pore diameters. The TGA curves showed high thermal stability of the nanoporous films obtained with an onset decomposition temperature near 300 °C. It should be stressed that the synthesis of CERs in the presence of IL was carried out without using any additional solvents or specific catalysts.

Conclusions.

Our review emphasizes the urgent need for understanding the role, efficiency and perspectives of an innovative class of componets, namely ILs with the potential to impact across many areas of thermosetting polymers. In the reviewed studies, we have found that ionic liquids can be effectively used as catalytic agents, plasticizers, electrolytes or porogens, thus providing a new route to the design of high performance materials. However, many challenges remain to be overcome, such as *i*) a better understanding of the interactions between the ILs and the polymer network; *ii*) suitable functionalization of the ILs for reactive modification of thermosets, and *iii*) separation/sorption properties of IL-based thermosets before and after extraction for membrane technologies; *iv*) compatibilizing effect of ILs in the hydrophobic polymer networks

filled with hydrophilic fillers.

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Іонні рідини та термореактивні полімери

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Сітчасті полімери завдяки високій термостійкості, стабільності розмірів і хімічній стійкості знайшли широке застосування в різних галузях промисловості. Однак, розробка нових термореактивних матеріалів досі залишається актуальною. У цій роботі обґрунтовано перспективність використання іонних рідин (ІР) для створення термореактивних полімерних матеріалів з покращеними характеристиками. Також проаналізовано особливості формування сітчастих полімерів за наявності ІР та основні властивості отриманих матеріалів. Згідно з проведеним аналізом літератури, ІР можна використовувати як каталізатори, пластифікатори, електроліти або порогени. Шляхом введення різноманітних ІР у полімерну матрицю можна досягнути покращення кінцевих властивостей матеріалів. Варто зауважити, що спочатку наводяться основні характеристики ІР.

Ключові слова: термореактивні полімери, іонні рідини, каталізатор, пороген, іон-провідний наповнювач.

Ионные жидкости и термореактивные полимеры

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Сетчатые полимеры благодаря высокой термостойкости, стабильности размеров и химической стойкости нашли широкое применение в разных отраслях промышленности. Однако, разработка новых термореативных материалов продолжает быть актуальной. В данной работе обосновано перспективность использования ионных жидкостей (ИЖ) для создания термореактивных полимерных материалов с улучшенными характеристиками. Также проанализированы особенности формирования сетчатых полимеров в присутствии ИЖ и основные свойства полученных материалов. Согласно проведенному анализу литературы, ИЖ могут использоваться как катализаторы, пластификаторы, электролиты или порогены. Введение различных ИЖ в полимерную матрицу приводит к получению материалов с улучшенными конечными свойствами. Стоит отметить, что сначала приводятся основные характеристики ИЖ.

Ключевые слова: термореактивные полимеры, ионные жидкости, катализатор, пороген, ион-проводящий наполнитель.