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## Epoxy resin crosslinked with conventional and deep eutectic ionic liquids

**Summary** — Molecular ionic liquid, *i.e.* 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl) and eutectic mixture of imidazole with choline chloride (IM + ChCl) have been used as epoxy resin hardeners. An influence of [EMIM]Cl and IM + ChCl content on pot life of epoxy compositions and runs of crosslinking process has been evaluated using DSC and ARES rheometry techniques. Epoxy compositions with [EMIM]Cl showed latent properties (pot life up to 50 days) while the systems with IM + ChCl gelled after few days. Comparative measurement of thermomechanical ( $T_g$ ,  $\tan \delta$ ) and mechanical properties (tensile, flexural and shear strength on aluminum substrates) as well as thermal decomposition of epoxy composites have been performed. Composite epoxy materials crosslinked with [EMIM]Cl exhibited more elastic properties (lower  $T_g$  and higher  $\tan \delta$  values) and generally better mechanical features than those hardened with imidazole + choline chloride eutectic mixture.

**Keywords:** epoxy resin, ionic liquid, eutectic mixture, thermal analysis, curing characteristics, epoxy compositions.

ŻYWICE EPOKSYDOWE USIECIOWANE KONWENCJONALNYMI LUB GŁĘBOKO EUTEKTYCZNYMI CIECZAMI JONOWYMI

**Streszczenie** — W artykule opisano zastosowanie molekularnej cieczy jonowej: chlorku 1-etylo-3-metyloimidazoliowego ([EMIM]Cl) i mieszaniny eutektycznej imidazolu z chlorkiem choliny (IM + ChCl) jako utwardzaczy żywicy epoksydowej. Metodami DSC oraz reometrii ARES zbadano wpływ zawartości [EMIM]Cl i IM + ChCl na czas życia kompozycji epoksydowej oraz przebieg procesu sieciowania. Kompozycje epoksydowe z [EMIM]Cl cechowały się długim czasem życia (do 50 dób w temperaturze pokojowej), podczas gdy układy z IM + ChCl żelowwały po kilku dniach. Dokonano także porównawczej oceny właściwości termomechanicznych ( $T_g$ ,  $\tan \delta$ ), mechanicznych (wytrzymałość na rozciąganie, zginanie oraz ścinanie spoin klejowych na podłożu aluminiowym) oraz odporności termicznej kompozytów epoksydowych. Kompozytowe materiały sieciowane wobec [EMIM]Cl wykazywały większą elastyczność (niższe wartości  $T_g$  i większe wartości  $\tan \delta$ ) oraz ogólnie lepsze właściwości mechaniczne niż utwardzane mieszaniną eutektyczną imidazolu i chlorku choliny.

**Słowa kluczowe:** żywica epoksydowa, ciecz jonowa, mieszanina eutektyczna, analiza termiczna, sieciowanie, kompozycje i kompozyty epoksydowe.

### INTRODUCTION

Epoxy materials are applied in various areas of industry. A wide range of curing agents and broad range of properties make possible for their commercial applications, such as: coatings, adhesives, cast systems, laminates and various composite materials [1]. As far as one-component epoxy resin/crosslinking agent compositions are concerned — especially important are these

exhibiting latent properties. Latency enables for rather long storage of such epoxy compositions at ambient temperature and fast curing after heating above 100 °C or by irradiation with UV or microwave.

Thermally initiating agents are based on tertiary and quaternary nitrogen compounds, BF<sub>3</sub> adducts, anhydrides, phenolic derivatives or dicyandiamide (DCDA). Some of latent hardeners, *e.g.* complexes of imidazole with metal cations [1–4], BF<sub>3</sub> adducts and DCDA are solid at ambient temperature what causes some problems with homogeneous dispersity of the curing agent in

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epoxy resin and could result in inhomogeneous cure. Ionic liquids (ILs), known as „green solvents“, are candidates for very broad practical usage. ILs can be used as media to perform the polymerization processes [5], solvents or plasticizers for synthetic polymers [6, 7] or polysaccharides (cellulose or lignocellulose biomass and starch) [8–11], catalysts [12] and for other purposes. ILs have also been tested as latent crosslinkers for epoxy resins [13–15]. The first announcement on using IL (1-butyl-3-methylimidazolium tetrafluoroborate) [BMIM]BF<sub>4</sub> for epoxy resins curing was described by our research team in 2003 [13]. The number of relevant works concerning epoxy materials crosslinked with ILs is very limited [14, 15]. The reasons are probably: rather high prices of ILs and insufficient knowledge about the chemistry and material science of epoxy resin/IL systems. Besides [BMIM]BF<sub>4</sub> some other ILs have been used for epoxy resin crosslinking, *i.e.*: 1-ethyl-3-methylimidazolium dicyanamide [EMIM]N(CN)<sub>2</sub> [14] and *N,N'*-dioctadecylimidazolium iodide [DODIM]I [15].

In order to supplement the state of art in the field of curing process and the properties of materials based on epoxy resin/IL compositions very recently we have investigated the influence of imidazolium cation size, anion type, as well as the IL content on latency, thermal cure characteristics and thermomechanical properties the respective materials [16]. Five imidazolium liquid salts have been used: [BMIM]BF<sub>4</sub>, 1-butyl-3-methylimidazolium dicyanamide [BMIM]N(CN)<sub>2</sub> and three salts of 1-decyl-3-methylimidazolium, *i.e.* chloride [DMIM]Cl, tetrafluoroborate [DMIM]BF<sub>4</sub> and dicyanamide [DMIM]N(CN)<sub>2</sub> [16].

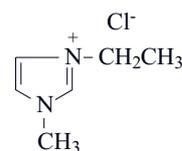
Deep eutectic solvent (DES) is a term used for ionic mixture with substantially lower melting point (usually below 100 °C) than each of the components [17]. Compared to conventional ILs (which are ionic compounds) DESs share many their characteristics, however are inexpensive and easy to prepare, moreover in many cases biodegradable. These both classes of ionic solvents, *i.e.* conventional molecular ILs and eutectic mixtures are commonly called „ionic liquids“.

In this paper crosslinking of epoxy resin with 1-ethyl-3-methylimidazolium chloride [EMIM]Cl and with eutectic mixture of imidazole and choline chloride (IM + ChCl) (1:1 wt./wt.), as well as the properties of cured epoxy materials are investigated. According to the authors knowledge it is the first trial to use DES for epoxy resin curing.

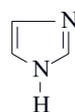
## EXPERIMENTAL

### Materials

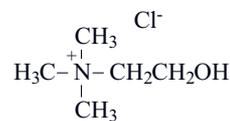
Epoxy resin: bisphenol A-based low molecular weight Epidian 6 (E6); epoxy equivalent 185, (viscosity 18 000 mPa·s at 23 °C), Organika Sarzyna, Poland, has been used. Conventional ionic liquid, *i.e.* [EMIM]Cl was



1-ethyl-3-methylimidazolium chloride  
(I)



imidazole  
(II)



choline chloride  
(III)

obtained from BASF [>95 %, melting temperature  $T_m = 77–79$  °C, Formula (I)]. Deep eutectic mixture based on imidazole [IM, 98 %,  $T_m = 89–91$  °C, Formula (II)] and choline chloride [ChCl, 99 %,  $T_m = 302$  °C, Formula (III)] (both from Sigma-Aldrich) has been prepared by mixing the components in a weight ratio 1:1 at ambient temperature and then heated up to 100 °C for 2.5 h, to obtain a colorless liquid product. The mixture exhibited melting point *ca.* 71.3 °C as compared with 89–91 °C and 302 °C for IM and ChCl, respectively.

### Preparation and investigation of epoxy resin compositions

[EMIM]Cl was homogenized with E6 resin at elevated temperature (60 °C). Eutectic mixture IM + ChCl or IM itself was mixed with E6 at elevated temperature (50 °C) and then stored for longer investigation at ambient temperature. The weight ratio of tested crosslinkers to epoxy resin was 1, 3 and 9 parts/100 parts of resin (phr). Because of anionic mechanism of epoxy resin polymerization with imidazole based catalysts their amounts were kept below 10 phr, similarly like in relevant research works [4, 13–16] (nonstoichiometric relations between epoxy resin and catalysts).

### Methods of testing

– The following tests were performed for epoxy compositions before curing and for crosslinked materials: storage time, rheometric tests during heating, differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), thermogravimetric analysis, heat distortion temperature determination, mechanical measurements.

– The storage time for epoxy resin/crosslinker compositions at ambient temperature has been determined on the basis of viscosity measurements during storage at 23–25 °C for 1–60 days using ARES rheometer (Rheometric Scientific), a plate-plate system  $\phi = 40$  mm, a gap of 1 mm.

– The curing process of the epoxy compositions has been investigated using ARES rheometer and DSC Q-100

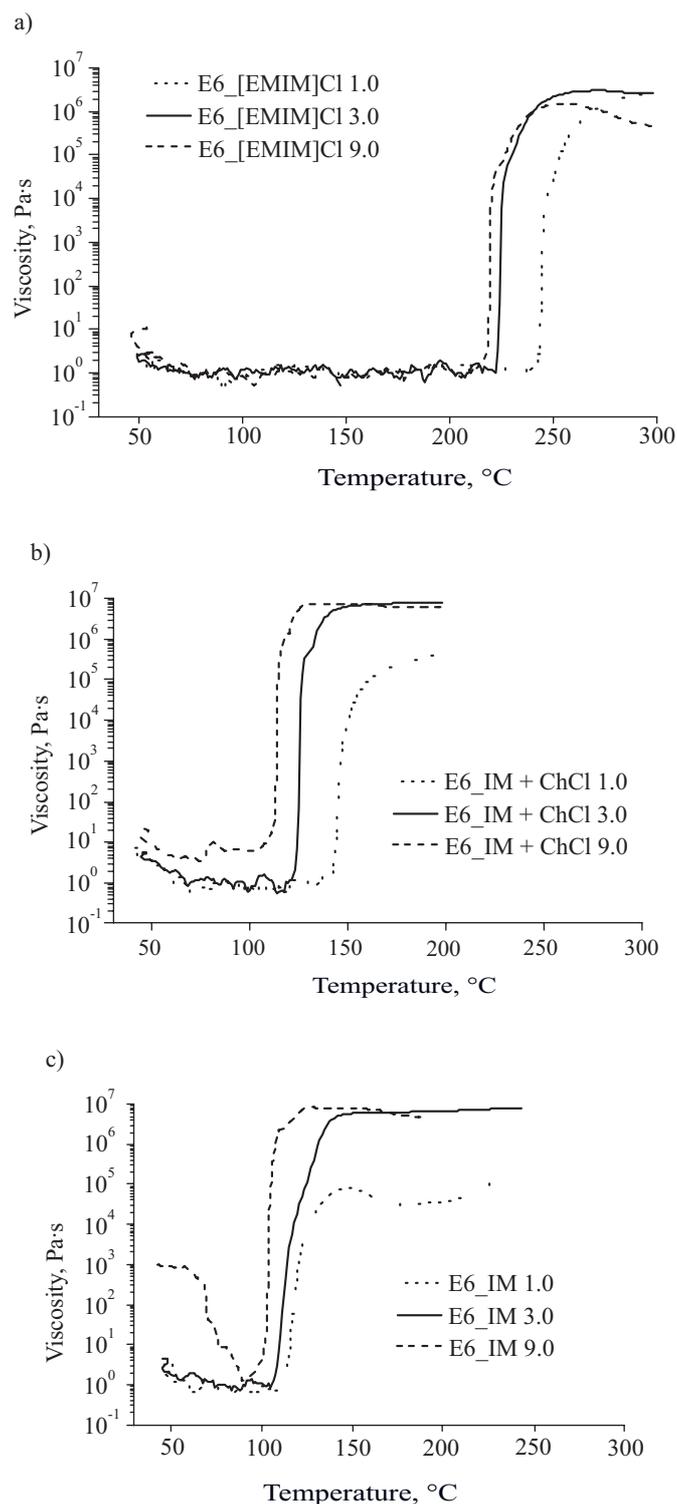


Fig. 1. Rheometric curves of curing process of the epoxy resin/ILs and epoxy resin/IM compositions with various concentrations of crosslinkers

(TA Instruments) at the heating rate of 5 °C/min in the temperature range of 30–300 °C.

– The glass transition temperatures and  $\tan \delta$  values of epoxy resin/IL materials have been determined using DMTA Q-800 (TA Instruments) with dual cantilever, at the heating rate 2 °C/min from 30 to 200 °C and frequency 1 Hz. Because reactivity of [EMIM]Cl and IM/ChCl

towards epoxy resin differs substantially, *i.e.* the former causes fast curing above 220 °C, whereas the eutectic mixture above 115 °C (see Fig. 1) samples for DMTA measurements have been cast into teflon moulds and hardened at 240 °C/4 h for E6/[EMIM]Cl and 135 °C/2 h for E6/IM + ChCl.

– Thermogravimetric analysis (TGA) has been conducted on TGA Q-5000 (TA Instruments) in nitrogen atmosphere in temperature range 40–900 °C, with heating rate 10 °C/min.

– Heat distortion temperature has been measured using Donserv D-VICAT/HDT-2/300/SA according to PN-EN ISO 75 (method A, position on a flat).

– Mechanical properties of hardened epoxy materials have been determined using Instron 4026 machine (Instron Corporation) (tensile strength according to PN-EN ISO 527-1, flexural strength according to PN-EN ISO 178, and shear strength for aluminum plates 100 × 25 × 15 mm, according to PN ISO 4587 and PN-69/C-89300).

## RESULTS AND DISCUSSION

### Curing process of epoxy resin/IL compositions

#### Storage time at ambient temperature

The data on storage time of the investigated epoxy systems crosslinked with [EMIM]Cl, IM + ChCl as well as with IM are collected in Table 1. Epoxy compositions with conventional ionic liquid exhibited the highest latency. The viscosity of E6/[EMIM]Cl systems increased slowly for *ca.* 50 days [from a level of 20–45 up to *ca.* 280 Pa · s (25 °C)]. One can conclude that the epoxy compositions with [EMIM]Cl exhibited reasonable storage time up to *ca.* 50 days (Table 1). The viscosity changes of epoxy resin/molecular IL systems are similar to that reported in our earlier works [13, 16]. The highest similarity of investigated E6/[EMIM]Cl storage time with E6/[DMIM]BF<sub>4</sub> system was found [16].

The viscosity ( $\eta$ ) of epoxy compositions with IM + ChCl eutectic mixture has increased substantially faster than E6/[EMIM]Cl ones, exhibiting  $\eta$  level above 1100 Pa·s after 3 days of storage for E6/IM + ChCl 3.0, and extremely high (above 11 000 Pa · s) on the second day for E6/IM + ChCl 9.0. Epoxy resin with IM only (3.0 phr) showed even higher viscosity increase in comparison with the relevant E6/IM + ChCl system (up to above 2700 Pa · s on the 3<sup>rd</sup> day for E6/IM 3.0).

However, experiments performed here (at ambient or elevated temperature) don't allow evaluating clearly any influence of ChCl on curing kinetics of epoxy resin with IM. The reason is that constant weight ratio of the both components was kept in the experiments even if total concentration of the two components in the catalyst changed. Additional investigation with constant amount of IM and changeable ratios of ChCl should be performed to explain the mentioned influence.

**Table 1.** Viscosity changes of epoxy compositions with imidazole based crosslinkers during storage at the ambient temperature

Compositions acronym	Viscosity, Pa · s							
	days							
	1	2	7	19	37	43	49	60
E6/[EMIM]Cl 1.0	17.0 ± 0.9	21.2 ± 0.6	23.2 ± 0.8	45.9 ± 0.3	58.3 ± 1.2	114.5 ± 2.0	188.6 ± 2.5	542 ± 0.7
E6/[EMIM]Cl 3.0	25.9 ± 0.7	25.1 ± 0.9	28.9 ± 0.5	48.9 ± 0.8	85.8 ± 0.4	143.4 ± 3.3	279.2 ± 3.1	1245.3 ± 9.4
E6/[EMIM]Cl 9.0	44.9 ± 0.8	40.0 ± 0.4	45.8 ± 0.7	60.0 ± 1.1	63.5 ± 0.6	77.6 ± 1.6	134.7 ± 2.8	151.8 ± 1.1
	1	2	3	4	5			
E6/IM + ChCl 1.0	28.3 ± 0.7	37.9 ± 0.8	64.4 ± 0.8	125.9 ± 0.9	1055.4 ± 27.8			
E6/IM + ChCl 3.0	32.8 ± 0.9	128.0 ± 2.4	1134.4 ± 24.2	—	nm <sup>*)</sup>			
E6/IM + ChCl 9.0	46.1 ± 1.7	11 136.8 ± 38.6	—	nm	nm			
E6/IM 1.0	31.8 ± 0.6	86.5 ± 1.9	91.7 ± 1.6	236.6 ± 0.7	nm			
E6/IM 3.0	37.6 ± 1.3	340.9 ± 19.0	2745.1 ± 28.6	—	nm			

<sup>\*)</sup> nm — not measured, — extremely high viscosity.

### Curing performed at elevated temperatures

Two instrumental techniques have been used to follow curing process at elevated temperature, *i.e.* rheometry and DSC. The results of rheometric measurements are presented in Fig. 2. The rheometric curves of epoxy compositions with the three crosslinkers showed steep viscosity increase in various temperature ranges. The highest was found for E6/[EMIM]Cl at above 210 °C. The temperature of the fast viscosity increase dropped with the amount of the crosslinking agent from *ca.* 240 °C for E6/[EMIM]Cl 1.0 down to *ca.* 215 °C for E6/[EMIM]Cl 9.0 and from *ca.* 145 °C for E6/IM + ChCl 1.0 down to *ca.* 110 °C for E6/IM + ChCl 9.0. The temperature ranges of fast viscosity increase in the E6/IM + ChCl and E6/IM systems are about 100 °C lower, depending on the relevant crosslinker concentration. The comparison of rheometric curves of epoxy compositions containing IM + ChCl and IM only showed that the former one was shifted to higher onset temperatures (*ca.* 10–30 °C), and are placed at ranges 110–145 °C and 100–112 °C, respectively (Fig. 1).

Different gel time observed for the investigated epoxy resin systems, *i.e.* the shortest for E6/IM, slightly longer for E6/IM + ChCl and the longest for E6/[EMIM]Cl (see Table 1 and Fig. 1) could be caused by the interaction between imidazole and ChCl (hydrogen bonding, relatively weak) or cation/anion type in [EMIM]Cl (strong electrostatic in the case of molecular ionic liquid). NH — group of unbounded IM can easily interact with epoxy group in the first reaction step (short gel time); in the case of eutectic mixture a proton of secondary amine is less accessible for direct reaction (medium gel time). On the other hand imidazolium liquid shows the lowest activity in reaction with epoxy groups because: (i) hydrogen atom on nitrogen atom is not present and (ii) high stability of the imidazolium compound is observed (dependent on basicity and thermal stability of IL) [16].

The data obtained from DSC measurements are shown in Fig. 2 and Table 2. The thermograms of

E6/[EMIM]Cl show distinct bimodal exothermic maxima, placed in lower (135–145 °C) and higher (216–242 °C) temperature regions. The onset temperature values of the first exothermic peaks are placed at 112–122 °C and slightly increased with imidazolium salt concentration (Table 2). Maximum temperature of the second predominant exothermic peak is shifted down with increasing amount of the crosslinker, whereas position the first peak is only slightly influenced by the IL concentration. The thermograms of epoxy materials with IM + ChCl (or IM itself) exhibited in principle unimodal shapes (solely bimodal character of the thermogram has been found for E6/IM 9.0 system) (Fig. 2).

**Table 2.** DSC characteristic parameters: onset and maximum exotherm temperatures and enthalpies of curing reactions for epoxy resin/IL compositions

Composition acronym	Onset temperature $T_0$ , °C	Maximum temperature $T_m$ (or $T_{m1}$ and $T_{m2}$ ), °C		Enthalpy $\Delta H$ (or $\Delta H_1$ and $\Delta H_2$ ), J/g	
E6/[EMIM]Cl 1.0	112.3	135.2	241.7	11.7	357.2
E6/[EMIM]Cl 3.0	117.5	145.4	232.2	21.9	491.1
E6/[EMIM]Cl 9.0	121.7	141.6	216.0	59.8	496.3
E6/IM + ChCl 1.0	103.6	118.6		159.8	
E6/IM + ChCl 3.0	98.8	116.7		376.9	
E6/IM + ChCl 9.0	92.7	110.7		384.3	
E6/IM 1.0	113.0	125.2		59.2	
E6/IM 3.0	104.6	119.5		281.7	
E6/IM 9.0	66.6	79.7	108.2	28.6	382.8

Different onset temperatures tendency than for E6/[EMIM]Cl system was observed for E6/IM + ChCl compositions, *i.e.* there was a decrease from 104 °C to 93 °C when the amount of eutectic crosslinker increased from 1 to 9 phr. Slow decrease of temperature exothermic

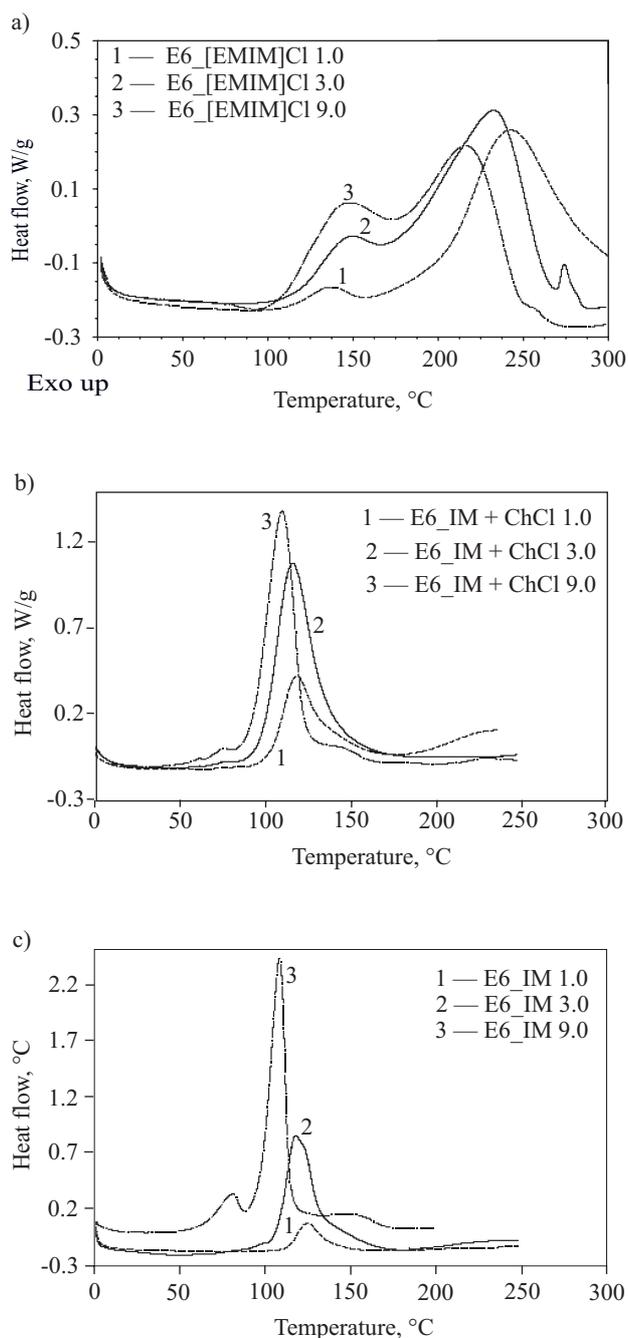


Fig. 2. DSC thermograms of epoxy resin/ILs and epoxy resin/IM compositions with various concentrations of crosslinkers

maxima for compositions with IM + ChCl mixture can be observed (119 °C→111 °C). This temperature range is substantially lower than for any other investigated epoxy resin ionic liquids systems, irrespectively of a type of anion [ $\text{Cl}^-$ ,  $\text{BF}_4^-$  or  $\text{N}(\text{CN})_2^-$ ] or length of alkyl substituent on imidazolium cations (above 162 °C) [16].

The enthalpy values of the second exothermic effect of epoxy resin cured with [EMIM]Cl were higher (496→357 J/g) than the first exotherm (60→12 J/g) and decreased with the grow of the crosslinker amount (ratios  $\Delta H_1/\Delta H$  and  $\Delta H_2/\Delta H$  were changed in the range 10.8–3.2 % and 89.2–96.8 %, respectively, Table 2). Higher

range of enthalpy changes of the curing reactions has been observed for E6/IM + ChCl compositions (160–384 J/g) with eutectic mixture content increase. The enthalpy values of E6/IM reactions were lower than those measured for both above discussed epoxy systems.

Imidazole can crosslink epoxy resin according to the anionic polymerization mechanism, similarly like tertiary amines [1]. The reaction mechanism of epoxy resin curing with imidazoles was examined in some reports [18, 19] and most authors have agreed upon. After the first step of reaction in which imidazole (or its derivative) reacts with an epoxy group to form 1:1 adduct, next (after  $\text{H}^+$  transfer) can be formed 1:2 adduct and then anionic polymerization of epoxy resin proceeds.

Quaternary ammonium salts are used usually as accelerators (catalysts) for epoxy resins crosslinked with carboxylic anhydrides, carboxylic acids or phenols. However, no literature data on an influence of quaternary ammonium salt on crosslinking of epoxy resin with imidazole(s) are known.

The mechanism of anionic polymerization of epoxy resin with imidazolium ionic liquids have recently been proposed by the authors [16]. As it has been found, onset thermal decomposition temperatures of molecular imidazolium ILs are mainly dependent on the type of anion and decrease in the range:  $\text{BF}_4^-$  (ca. 350 °C) >  $[\text{N}(\text{CN})_2]^-$  (ca. 250 °C) >  $\text{Cl}^-$  (ca. 215 °C) [16].

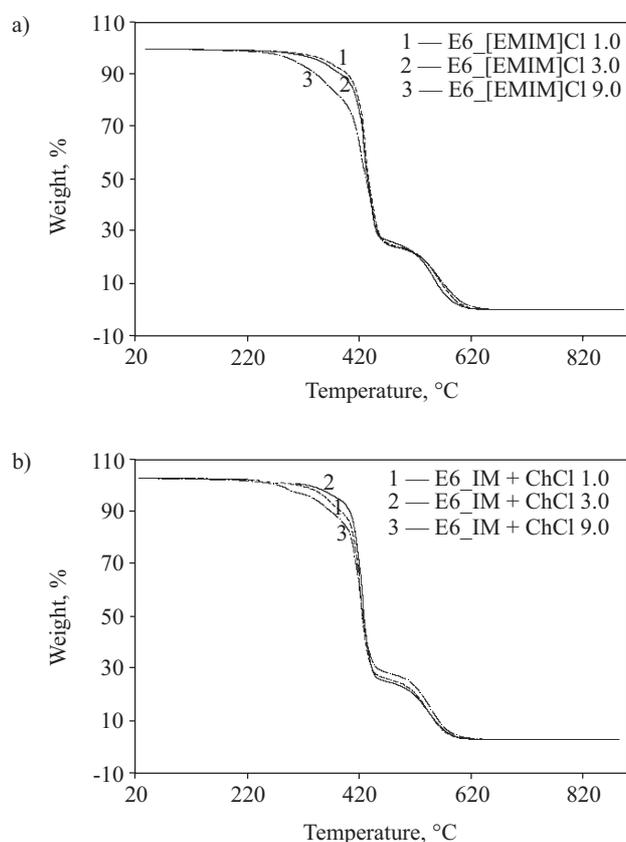


Fig. 3. Thermal gravimetric analysis of epoxy materials cross-linked with conventional ionic imidazolium liquid and with eutectic mixture of imidazole with choline chloride

The thermomechanical and thermal resistance properties of epoxy materials crosslinked with [EMIM]Cl and IM + ChCl are collected in Table 3. The values of  $\tan \delta$  and glass transition temperatures were determined by DMTA measurements and temperature losses by TGA method (Fig. 3). Glass transition temperatures of E6/[EMIM]Cl materials are in the range 107–109 °C for samples cured with 1 and 3 phr IL, respectively.

Increasing amount of imidazolium IL used for curing epoxy resin causes some decrease of  $T_g$  (107→92 °C) with maximum value for E6/[EMIM]Cl 3.0. Such a figure can be explained by formation of epoxy crosslinked material plastified by excess of IL used (*i.e.* above 3 phr). When considering  $T_g$  values for epoxy resin crosslinked with IM + ChCl system – other tendency has been observed, *i.e.* high jump from 85 up 156 °C while changing the amount of hardener from 1 up to 3 phr. The parameter is practically unchanged for the highest content of eutectic mixture hardener. The reason for large difference of  $T_g$  for epoxy materials hardened with the same concentration of both described systems (3.0 phr) may be connected with specific influence of the both catalytic crosslinkers used, *i.e.* (i) plastifying action of imidazolium liquid, (ii) presence of ChCl in eutectic mixture with IM, which may cause more dense crosslinking of epoxy resin, (iii) various molar ratios of the imidazole (or its IL derivative) applied for epoxy crosslinking process.

**Table 3. Thermomechanical properties and thermal resistance of the crosslinked epoxy resin/IL materials**

Composition acronym	Tan $\delta$	$T_g$ , °C	Temperature loss of 2 and 10 wt. % $T_2/T_{10}$ , °C	Heat deflection point °C
E6/[EMIM]Cl 1.0	1.16	107.4	320.9/401.1	85.0
E6/[EMIM]Cl 3.0	1.24	109.0	305.8/391.1	84.2
E6/[EMIM]Cl 9.0	1.68	92.3	272.6/345.6	63.0
E6/IM + ChCl 1.0	0.86	84.7	305.7/386.0	60.3
E6/IM + ChCl 3.0	0.38	157.1	321.7/409.1	134.0
E6/IM + ChCl 9.0	0.45	156.0	274.9/366.5	120.0

Tan  $\delta$  values for E6/[EMIM]Cl samples were higher (1.16–1.68) than for E6/IM + ChCl (0.86–0.38). These data give an information on the ratio of energy stored  $E'$  and dissipated as heat  $E''$  ( $\tan \delta = E''/E'$ ). Usually for polymer composites  $E'' < E'$ , *i.e.*  $\tan \delta$  are lower than 1. Lower values of the discussed parameter for the E6/IM + ChCl system prove higher crosslinking efficiency in comparison with the systems based on molecular IL agent or plasticization effect of molecular IL in cases of E6/[EMIM]Cl composite materials. Measured  $\tan \delta$  values for E6/[EMIM]Cl system above 1.0 were similar to those found for E6/[DMIM]Cl [16] and are characteristic for more elastic polymer composites.

Heat deflection temperatures (Table 3) correlated with measured  $T_g$  and  $\tan \delta$  values, *i.e.* were lower for E6/[EMIM]Cl (1.0 and 3.0 phr) materials (*ca.* 85 °C) in comparison with E6/IM + ChCl (3.0 and 9.0 phr) ones (120–134 °C).

From TGA measurements it was evident that the highest crosslinkers concentrations used in epoxy composites caused a decrease of 2 and 10 wt. % temperature losses about *ca.* 30–40 °C (Table 3). The highest thermal resistance, *i.e.* high temperature mass losses have been found for E6/[EMIM]Cl 1.0 and E6/IM + ChCl 3.0, (*i.e.*  $T_2/T_{10} = 321/401$  °C and  $T_2/T_{10} = 322/409$  °C, respectively).

**Table 4. Mechanical properties of the crosslinked epoxy resins/IL materials**

Composition acronym	Tensile strength MPa	Flexural strength MPa	Shear strength MPa
E6/[EMIM]Cl 1.0	38.3 ± 5.8	112.6 ± 9.1	20.0 ± 1.2
E6/[EMIM]Cl 3.0	44.0 ± 5.9	128.0 ± 7.5	19.8 ± 2.9
E6/[EMIM]Cl 9.0	11.8 ± 6.2	26.0 ± 10.9	18.2 ± 0.2
E6/IM + ChCl 1.0	44.3 ± 6.6	81.0 ± 7.8	8.6 ± 1.4
E6/IM + ChCl 3.0	25.4 ± 3.0	56.9 ± 8.7	11.1 ± 1.0
E6/IM + ChCl 9.0	24.0 ± 1.8	62.5 ± 5.9	12.6 ± 1.3

The comparison of mechanical measurement results showed that generally composites made of epoxy materials crosslinked with the lower two [EMIM]Cl concentrations exceed those with IM + ChCl (Table 4). The tensile strength results for E6/[EMIM]Cl (1.0 and 3.0 phr) are on similar level (38.3 and 44.0 MPa) and are statistically higher than relevant data for E6/IM + ChCl composites (44.0 and 25.0 MPa). The flexural strength for the epoxy materials with [EMIM]Cl (1.0 and 3.0 phr) were 1.4–2.2 times higher than those cured with IM + ChCl. Similarly, the shear strength of epoxy adhesives from E6/[EMIM]Cl on aluminum substrate were at least 50 % higher than those for joints based on E6/IM + ChCl (*ca.* 20 MPa in comparison with 8.5–12.6 MPa, respectively). Analysis of mechanical results showed that tensile and flexural strengths of E6/[EMIM]Cl 9.0 composite are substantially lower than for other materials. It can suggest that in that case the applied amount of ionic liquid was too high and caused extraordinary plasticization of the final epoxy material. In general, the best mechanical properties exhibited epoxy composite on a basis of E6/[EMIM]Cl 3.0 (Table 4).

## CONCLUSIONS

Comparative study of the curing process, thermomechanical, thermal resistance as well as mechanical properties of epoxy resin cured with imidazole based ionic liquids: 1-ethyl-3-methylimidazolium chloride and

eutectic mixture of imidazole with choline chloride was performed. Considering the curing processes the following may be concluded: (i) liquid epoxy compositions with [EMIM]Cl exhibit evidently longer storage time in comparison with compositions based on IM + ChCl mixtures (*ca.* 50 days and *ca.* 3 days, respectively), (ii) maximum temperature of the main exotherm of the curing epoxy resin with [EMIM]Cl is above 215 °C, *i.e.* about 100 °C higher than for the system crosslinked with eutectic mixture of imidazole with choline chloride, (iii) curing process of epoxy resin with [EMIM]Cl shows bimodal character with exotherms at 135–145 °C (slight: 3–10 % of total reaction enthalpy) and at 216–242 °C (predominant: 90–97 % of the total enthalpy).

The properties of cured epoxy composites with proper amounts of crosslinking agents: [EMIM]Cl (1 and 3 phr) and imidazole/choline chloride (3 and 9 phr) can be commented as follows: (i) epoxy materials cured with molecular ionic liquid are more elastic than those with eutectic mixture of imidazole as is seen on a basis of thermomechanical properties ( $T_g = 107–109$  °C,  $\tan \delta = 1.16–1.24$ , as compared with  $T_g = 85–157$  °C,  $\tan \delta = 0.38–0.45$ , respectively), as well as of heat deflection temperatures (*ca.* 85 °C and 120–134 °C, respectively), (ii) mechanical properties of composites cured with [EMIM]Cl are better than those crosslinked with eutectic mixture of imidazole.

The results allow for predictions that epoxy resin with 1-ethyl-3-methylimidazolium chloride can be potentially usable as one-component latent adhesive for metal joining. On the other hand epoxy composition with imidazole/choline chloride can be considered as convenient liquid system with few-days storage time designated for casting and offering improved thermal properties after curing.

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