Imidazolium and Deep Eutectic Ionic Liquids as Epoxy Resin Crosslinkers and Graphite Nanoplatelets Dispersants

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ABSTRACT: Two types of ionic liquids (IL), i.e., molecular ionic 1-butyl-3-methylimidazolium thiocyanate ([BMIM]SCN) and deep eutectic solvent (DES) based on choline chloride and tris(hydroxymethyl)propane, as well as their mixture have been used as epoxy resin curing agents. [BMIM]SCN showed the highest catalytic activity toward epoxy resin polymerization as compared to up today used ILs. Curing process of epoxy resin was investigated at ambient temperature (storage time up to more than 60 days) and elevated temperatures (80–200°C) using rheometry and DSC techniques. Thermomechanical analysis allowed to determine an influence of IL type and content on composites crosslinking density, glass transition temperature, and tan δ values. Graphite nanoplatelets (GNP) was dispersed in DES and then in DES/IL/epoxy resin composition prepared, cast, and cured to obtain nanocomposite material. Electrical volume resistivity of the nanocomposites with 0.25–1 wt % GNP increased with nanofiller content up to the highest value of $2.8 \times 10^6\ \Omega \cdot \mathrm{cm}$. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40401.

KEYWORDS: composites; ionic liquids; thermosets; nanotubes; graphene and fullerenes; thermal properties

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INTRODUCTION

The crosslinking of epoxy resin may occur by the addition or ionic polymerization reaction. One-component epoxy compositions exhibiting latent properties that enable prolonged storage at ambient temperature are particularly important from application viewpoint. The ionic liquids (ILs) have been tested as latent crosslinkers for epoxy resins[1–4] or admixtures for epoxy systems cured with conventional hardeners that allowed to modify the properties of the final epoxy material.[3,5–7]

The important advantages of applying ILs for liquid epoxy resin curing are their low loadings as well as fast and easy miscibility with other liquid components resulting in technological feasibility.

The investigated epoxy compositions with the most often used 1-alkyl-3-methylimidazolium ILs (where alkyl was butyl or ethyl) exhibited rather long pot lives at ambient temperature (3 wt parts/100 wt parts of epoxy resin, 3 phr): 50–60 days when counteranions were chloride or tetrafluoroborate.[4,8] When 1-butyl-3-methylimidazolium (BMIM) IL with dicyanamide anion[2] or phosphonium type of IL [1-hexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl) phosphinate][9] was used the ambient gelation time of the epoxy systems decreased to about 30 days. However, acceptable properties of the final epoxy material precured at ambient required high postcuring temperature (80–125°C).[9]

Moreover, ILs have been used with conventional polyamine hardeners, as modifiers of epoxy materials, i.e., glass transition temperature depressant,[5] and inner lubricant[6,7] added in rather low concentration 1–5 wt %.

Term "ILs" is used for molecular compounds consisting of organic cations and anions with melting points below 100°C, often liquid at room temperature. However, there is another category of liquid substances known—as deep eutectic solvents (DESs), i.e., mixtures of some cationic compound typically ammonium halogenate (e.g. choline chloride; ChCl) and polar compound bearing —OH, —COOH, or —$CONH_2$ moieties able to form hydrogen bonds with the former.[10] Compared to conventional ILs (i.e., molecular ionic compounds) DESs share many of their characteristics, however, are inexpensive, easy to prepare, nontoxic, and usually biodegradable. For those similarities, the both classes of mentioned ionic solvents, i.e., molecular ILs and eutectic mixtures are commonly called ILs.

The first announcement on DES usage as curing agent for epoxy resin has been reported recently.[8] ChCl/imidazole (ChCl/IM) composition was prepared by mixing of components in 1 : 1 weight ratio and used as epoxy resin hardener (1–9 phr) at 135°C.

Carbon nanofillers have been utilized for preparing nanocomposite materials with enhanced electrical properties. In such

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Table I. Characteristics of Ionic Liquids or Their Components

Choline chloride (ChCl), mp = 247°C	1,1,1-Tris(hydroxymethyl) propane (TMP), mp = 56–58°C	1-Butyl-3-methylimidazolium thiocyanate ([BMIM]SCN), a dark yellow liquid

systems, well dispersion of carbon structures, i.e., nanotubes (CNT) or graphite nanoplatelets (GNP) is crucial to obtain very low percolation thresholds. It is known that molecular ILs as well as DESs can be used as dispersing media of CNT or GNP.[11–15]

For example, Guo et al.[11] applied BMIM hexafluorophosphate (PF_6^-) as dispersing agent of expanded graphite (EG) for manufacturing epoxy/EG composites cured with polyoxypropylenediamine (Jeffamine D-230). High concentrated few-layer graphene dispersions in 1-hexyl-3-methylimidazolium PF_6^- have been obtained by Mariani et al.[14]

Gutierrez et al.[15] used CNT dispersed in ChCl/ethylene glycol (1 : 2 mol/mol) as a medium for *in situ* resorcinol/formaldehyde polycondensation.

Basing on the studies mentioned above, one can conclude that in order to develop epoxy materials with new properties the research on application of other ILs of the both types, i.e., molecular compounds and eutectic mixtures for epoxy resin curing (including system with carbon nanofillers) should be continued.

In this work, the epoxy resin/IL systems based on BMIM thiocyanate ([BMIM]SCN) were described. Additionally, a combination of [BMIM]SCN with new DES based on ChCl and tris(hydroxymethyl)propane (TMP) was shown to be effective as a crosslinker of epoxy resin as well as dispersing medium for GNP.

EXPERIMENTAL

Materials

Epoxy resin: bisphenol A-based low molecular weight Epidian 6 (E6); epoxy equivalent 185 g/equiv. (viscosity 15,000 mPa · s at 23°C), Organika Sarzyna, Poland, and 1,1,1-tris(hydroxyl methyl)propane 1,1,1-tris(hydroxymethyl)propane (>98%), 1-butyl-3-methylimidazolium thiocyanate ([BMIM]SCN) (>98%), as well as choline chloride (>98%), products of Sigma-Aldrich were used. GNP, Grade 3-industrial grade with surface area of 600–750 m^2/g, average 10–15 carbon layers, an average thickness of 8–10 nm, and the typical particle diameters of approximately 2 μm, product of CheapTubes. All components were used as received (or prepared).

Deep eutectic mixture has been prepared by mixing ChCl with TMP in 1 : 1 molar ratio at ambient temperature and then heated up to 100°C for 2 h to obtain a colorless liquid product. This eutectic mixture is liquid at ambient temperature (its melting point is ca. 30°C determined by DSC measurement). In Table I, the chemical structures of [BMIM]SCN and the components used for preparation of (ChCl+TMP) DES were presented.

The epoxy compositions for curing or storage tests were obtained by mixing of epoxy resin with [BMIM]SCN and/or ChCl+TMP at ambient temperature using manual mixing. The [BMIM]SCN content was 1, 3, and 9 phr, whereas ChCl+TMP 9 phr, and the mixture of [BMIM]SCN and ChCl+TMP 3 and 9 phr, respectively.

GNP in the amount of 0.25, 0.5, or 1.0 wt % has been manually mixed with ChCl+TMP and then homogenized by ultrasonication (2 h, amplitude 50 %, frequency 50 Hz, UP 200S, Hielscher, Germany). The GNP dispersion has been mixed manually with epoxy resin and next with [BMIM]SCN for 10 min.

Methods

The storage time for epoxy resin/crosslinker compositions was determined on a basis of viscosity measurements at 23–25°C up to 72 days using ARES rheometer (Rheometric Scientific), a plate–plate system $\phi = 40$ mm, a gap of 1 mm.

The curing process of epoxy compositions was investigated using differential scanning calorimeter DSC Q-100 (TA Instruments) and ARES rheometer at a heating rate of 5°C/min in temperature range of 30–300°C.

Glass transition temperatures, tan δ and crosslinking density values were determined using dynamic mechanical thermal analysis DMTA Q–800 (TA Instruments) with dual cantilever, and heating rate of 2°C/min from 30 to 250°C, frequency 1 Hz. The samples for DMTA measurements were prepared by curing the epoxy composition at 120°C/2 h (for E6_[BMIM]SCN and, E6_(ChCl+TMP)+[BMIM]SCN compositions) and 200°C/2 h (E6_ChCl+TMP) in Teflon mold.

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

The volume electrical resistance of cured composites was tested in accordance with IEC 93:1980 and ASTM D 257-99 (two-probe method) using Keithley Instruments, Inc. with a set of electrodes (Keithley 8009). Electrical resistivity measurements were performed for E6_[BMIM]SCN, neat E6_(ChCl+TMP)+[BMIM]SCN and the latter containing 0.25, 0.5, and

Table II. Composition of Epoxy Resin Systems with Ionic Liquids and Graphite Nanoplatelets

Composition acronym	Epoxy resin (Epidian 6)	Molecular ionic liquid (1-butyl-3-methylimidazolium thiocyanate) (phr)	Eutectic mixture (ChCl and TMP) (phr)	Graphite nanoplatelets (wt %)
E6_[BMIM]SCN 1	100	1	–	–
E6_[BMIM]SCN 3	100	3	–	–
E6_[BMIM]SCN 9	100	9	–	–
E6_(ChCl+TMP) 9	100	–	9	–
E6_(ChCl+TMP) 9 + [BMIM]SCN 3	100	3	9	0.25
				0.5
				1.0

1.0 wt % GNP. The content of [BMIM]SCN in relevant curing compositions with ChCh+TMP was 3 phr. The samples for electrical volume resistance measurements were cast in Teflon molds and cured at 80°C/2 h. The extraction of selected cast composites with distilled water was performed for 48 h by immersing a specimen in water at ambient temperature (beaker 1 L volume); immersion medium was changed after 24 h. Subsequently, the samples were dried for 24 h and tested on volume electrical resistivity.

RESULTS AND DISCUSSION

Curing Process of Epoxy Resin/IL Compositions

Storage Time at Room Temperature. The content of both ILs used for epoxy resin curing is given in Table II. The results of viscosity changes for epoxy compositions containing of 1, 3, or 9 phr [BMIM]SCN are presented in Figure 1. It may be seen that these systems exhibited substantially shorter storage times in comparison to data presented earlier.[1,2,4,8] Also recently reported epoxy systems with phosphonium phosphinate[9] reacted slower at ambient temperature than relevant compositions with [BMIM]SCN. In dependence on the IL/epoxy resin weight ratio, the composition gelled at room temperature after about 8, 3, and 2 days for 1, 3, and 9 phr imidazolium IL used, respectively. The epoxy resin with imidazolium IL often behaved as latent compositions as their pot life at normal conditions was longer than 6–8 weeks.[1,2,4,8] The highest values of storage time were found for epoxy systems cured with [BMIM]BF_4 (3 phr, above 60 days[4]) and [EMIM]Cl (3 phr, above 50 days[8]). Shorter storage time at room temperature, i.e., 30 days was noted for compositions with dicyanamide anion: [BMIM]$N(CN)_2$ (3 phr)[4] as well as with phosphonium phosphinate IL (2.5 phr).[9] So, the epoxy/[BMIM]SCN system exhibits the shortest pot life of the IL-cured epoxy compositions reported up today and can be precured at ambient before final curing at high temperature.

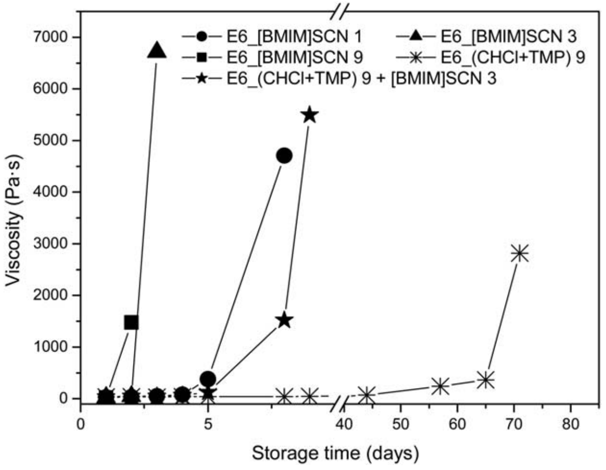


Figure 1. Viscosity change during epoxy composition storage at ambient temperature.

The storage time of epoxy resin with DES ChCl+TMP (9 phr) was above 72 days in comparable conditions. The (ChCl+TMP)/epoxy resin weight ratio was selected on a basis of earlier experience with ChCl/IM system[8] as well as taking into consideration the DES content necessary for efficient dispersion of GNP in epoxy matrix. The storage time of epoxy resin/(ChCl+TMP) (9 phr) + [BMIM]SCN (3 phr) system was reduced to about 9 days (Figure 1). This composition was selected for manufacturing of epoxy material filled with GNP because of the ability for effective nanofiller dispersion and acceptable curing characteristics. Additionally, DES (ChCl+TMP) is more convenient than earlier used ChCl/IM due to its lower melting point (30°C), whereas ChCl/IM melts at 70°C.

Curing at Elevated Temperatures. The stability of the ILs anions plays an essential role in some applications.[16] In almost all cases, nucleophilic attack of the IL anion in reverse Menschutkin-type reaction to yield neutral products is possible (Scheme 1).[17] The decomposition reaction is S_N2 process that results in a mixture of *N*-alkylimidazoles and 1-alkylhalides. In general, remarkable differences in decomposition temperature values were observed by changing the anion in imidazolium ILs. On a basis of reported data,[16,18,19] the relative thermal stability

X^- R N+ N → N N + XR + N N R

Scheme 1. Imidazolium salt thermal decomposition.

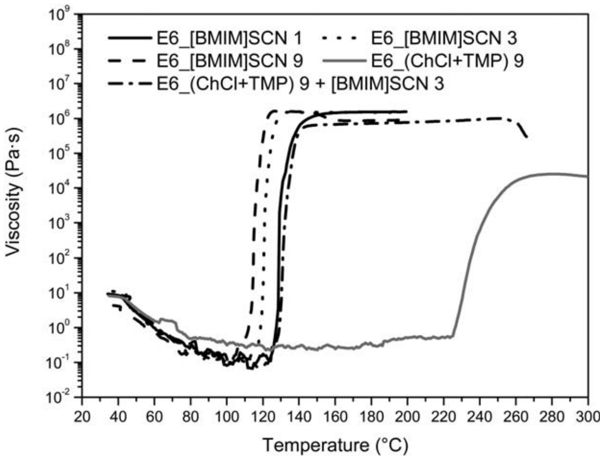


Figure 2. Rheometric curves of epoxy compositions with ionic liquids.

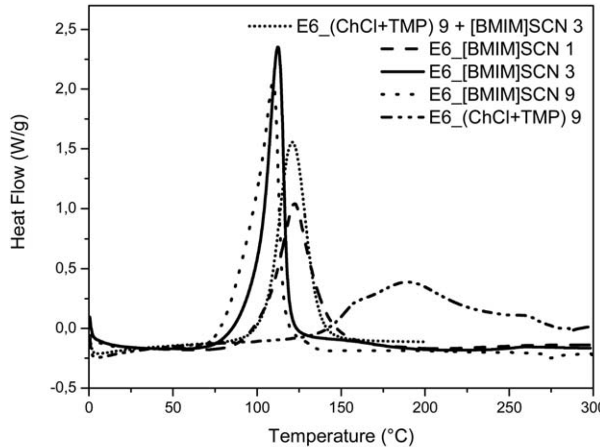


Figure 3. DSC thermograms of epoxy compositions with ionic liquids.

of selected anions in imidazolium ILs decreased in the following order: $BF_4^- > Cl^- > N(CN)_2^- > SCN^-$.

Imidazole or its alkyl derivatives formed during ILs thermal decomposition are able to initiate epoxy resin anionic polymerization resulting in resin crosslinking. The reaction mechanism was examined in several reports, e.g., refs. 20 and 21, with consistent conclusions. The detailed scheme of epoxy resin anionic polymerization in a presence of imidazolium ILs has been presented recently.[4] Crosslinking of epoxy resin at elevated temperatures using [BMIM]SCN, ChCl+TMP, or their mixture was investigated using rheometric and DSC techniques. The rheometric curves were presented in Figure 2. It is clear that with increasing imidazolium IL content the beginning of steep viscosity increase was shifted to lower temperatures (from ca.125 to 110°C for 1 and 9 phr, respectively). The observed range of gellation temperatures is about 60–70°C lower than for the epoxy resin systems with other relatively high active imidazolium liquid crosslinker, i.e., $[BMIM]N(CN)_2$.[4] The relevant comparison can be made on a basis of DSC and rheometric data presented in Figures 2 and 3, Table III and results from ref. 4. It does mean that the presence of thiocyanate anion results in higher catalytic activity of [BMIM]SCN in anionic epoxy polymerization than other used BMIM ILs.

For epoxy composition cured with (ChCl+TMP), the steep viscosity increase on rheometric curve was placed at very high-temperature region (ca. 220°C). The crosslinking of epoxy resin with (ChCl+TMP) is a chain homopolymerization process initiated by ammonium salt,[22] i.e., by ChCl. This process is very slow at room temperature whereas it is considerably accelerated above 200°C (see Table III, Figures 2 and 3). On the other hand, the rheometric curves for system cured with the mixture (ChCl+TMP 9 + [BMIM]SCN 3) as well as with [BMIM]SCN (1 phr) were quite similar (Figure 2). Such similarity could be also observed in a case of DSC thermograms for analyzed systems (Figure 3). The temperature values for maximum heat flow for E6/[BMIM]SCN were in the following order: 123°C (1 phr) >113°C (3 phr) >110°C (9 phr) (Table III). The beginning of the exothermic process was in a range of 70–85°C. With increasing [BMIM]SCN content in epoxy composition the enthalpy of curing reaction increased from 400 up to 523 J/g.

When (ChCl+TMP) was applied, epoxy curing process started at about 130°C and the onset temperature value of the exothermic peak (T_{max}) was around 189°C, whereas exothermic effect was the lowest (382 J/g) in relation to other tested epoxy compositions.

Considering the curing kinetics the epoxy resin hardened with (ChCl+TMP) 9 + [BMIM]SCN 3, that mixture behaved similarly to epoxy composition with the lowest imidazolium liquid content (i.e., [BMIM]SCN 1, Figure 3). So, an application of

Table III. Results of DSC and DMTA Measurements

	DSC		DMTA			
Composition acronym	T_{max}[a] (°C)	ΔH[b] (J/g)	T_g[c] (°C)	Storage modulus (MPa)	Tan δ	Crosslink density (mol/m^3)
E6_[BMIM]SCN 1	123	400	139	1810	0.32	5498
E6_[BMIM]SCN 3	113	437	181	1730	0.30	7181
E6_[BMIM]SCN 9	110	523	138	2060	0.87	2113
E6_(ChCl+TMP) 9	189	382	90	2150	0.97	1800
E6_(ChCl+TMP) 9+[BMIM]SCN 3	121	410	133	1890	0.63	1960

[a] Maximum temperature exothermic peak.
[b] Enthalpy values of crosslinking process.
[c] Glass transition temperature (determined from the maximum of tan δ).

Table IV. Volume Electrical Resistivity of Epoxy Composites

Composition acronym	Volume resistivity[a] ($\Omega \cdot$ cm)		
	Series I	Series II (before water treatment)	Series II (after water treatment)
E6_[BMIM]SCN 3	$2.8 \cdot 10^{11}$	$8.1 \cdot 10^{11}$	$3.8 \cdot 10^{11}$
E6_(ChCl+TMP) 9 + [BMIM]SCN 3	$1.3 \cdot 10^{10}$	$8.3 \cdot 10^{10}$	$1.4 \cdot 10^{10}$
E6_(ChCl+TMP) + [BMIM]SCN_GNP 0.25	$1.0 \cdot 10^{8}$	–	–
E6_(ChCl+TMP) + [BMIM]SCN_GNP 0.5	$1.3 \cdot 10^{7}$	–	–
E6_(ChCl+TMP) + [BMIM]SCN_GNP 1.0	$2.8 \cdot 10^{6}$	$8.2 \cdot 10^{5}$	$9.0 \cdot 10^{5}$

[a] Measured at 230 V; samples of both series were independently prepared.

the mixture of imidazolium IL [BMIM]SCN with DES (ChCl+TMP) allowed to cure epoxy resin at temperature below 130°C with reasonable exothermic effect.

Thermomechanical and Thermooxidative Properties of Epoxy Resin/IL Composites

DMTA results showed that the glass transition temperature of epoxy material crosslinked with 3 phr of [BMIM]SCN was 181°C (Table III). T_g values for samples with lower (1 phr) and higher (9 phr) [BMIM]SCN content were substantially lower (138 and 139°C, respectively). These results could suggest that samples with both extremes of IL levels, i.e., 1 and 9 phr are not enough good crosslinked or overplasticized by excessive amount of the hardener (in the latter case).

In order to quantify differences of epoxy resin crosslinking effect, Υ_e parameter determining crosslinking density was estimated on a basis of eq. (1): [23,24]

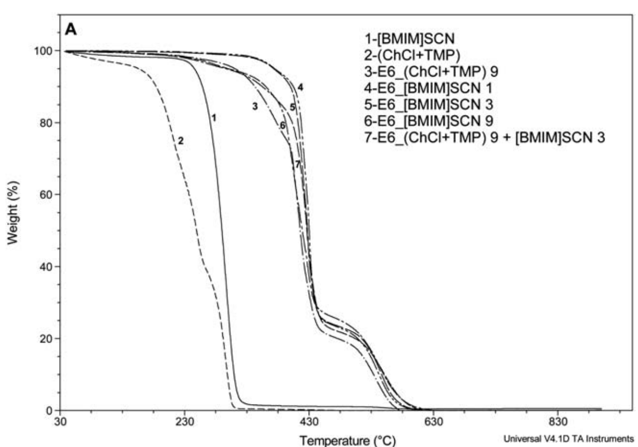
$$\Upsilon_e = E_r/3RT_r \quad (1)$$

where E_r is "rubber" modulus which can be regarded as storage modulus at T_g+30; R is universal gas constant; $T_r = T_g$+30.

Previous our prediction of crosslinking density decrease as well as observed overplasticization effect was supported by Υ drop (7181 →2113 mol/m^3), jump of tan δ (0.30 → 0.87) and increase of storage modulus (1730 → 2060 MPa) values with IL increase (Table III). The lowest [BMIM]SCN content applied (1 phr) was probably insufficient for effective crosslinking of epoxy resin, whereas the highest (9 phr) could result in a large number of initiating species formed at the expense of ether linkages, and eventually in reduced crosslinking density[2] as well as overplasticization. From the above it is evident that medium content of [BMIM]SCN (3 phr) seems to be optimal for epoxy resin curing.

Noticeable lower T_g value was observed for epoxy resin cured with (ChCl+TMP) 9 (90°C). Epoxy material cured with the mixture of both types of ILs exhibited slightly lower T_g value, i.e., 133°C, than the system crosslinked using 1 and 9 phr of [BMIM]SCN. The highest value of storage modulus E' was found for epoxy resin crosslinked with DES (2150 MPa) whereas for composition cured with the mixture of ILs reached 1890 MPa. The epoxy resin system crosslinked with (ChCl+TMP) (9 phr) exhibited the lowest crosslinking density, about threefold lower than reference sample with 3 phr [BMIM]SCN. Similarly, introduction of DES into E6_[BMIM]SCN 3 composition negatively influenced Υ value (7181→1960 mol/m^3).

The thermogravimetric curves (TG and DTG) of IL, DES as well as epoxy materials cured using ILs and their mixture were presented in Figure 4. It was shown that [BMIM]SCN began to decompose at about 200°C (2% mass loss) whereas



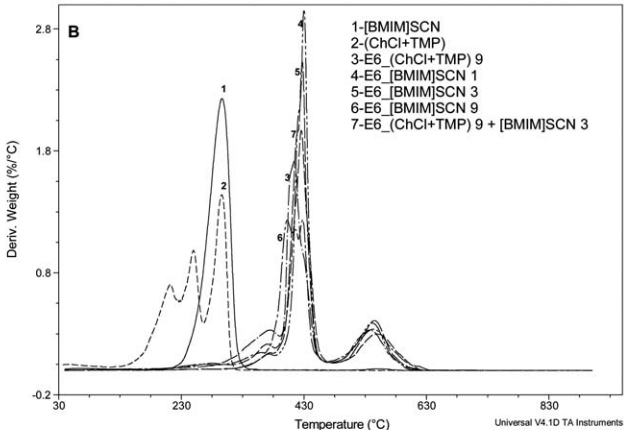


Figure 4. Thermogravimetric curves of cured epoxy compositions with ionic liquids and relevant ionic liquids alone: (a) TG curves and (b) DTG curves.

(ChCl+TMP) exhibited the same mass loss at 80°C, due to water evaporation. The melting points of choline chloride and TMP are 247 and 56–58°C, respectively. Heating ChCl above the melting point causes its gradual decomposition (no boiling point is accessible). TMP boils at 285°C. So, the second and third DTG maxima (ca. 250 and 290°C) for (ChCl+TMP) were assigned to the evaporation of degradation products of (ChCl+TMP) system. The comparison of TGA and DSC results showed that catalytic activity of [BMIM]SCN for epoxy resin curing started at 75–90°C, i.e., below its decomposition temperature determined by TGA measurements. DES based on ChCl and TMP exhibited curing activity above 130°C with maximum at about 190°C, i.e., before the first thermal decomposition stage.

The highest and comparable temperatures for 2% mass loss of epoxy materials crosslinked with 1 and 3 phr [BMIM]SCN were found 343 and 338°C, respectively. However, an increase of IL content to 9 phr resulted in distinguishingly lower temperature value (229°C). Similar tendency of changes was found for 5% mass losses, i.e., 372°C for epoxy material with 1 and 3 phr [BMIM]SCN and 288°C for E6_[BMIM]SCN 9.

The materials cured with DES or the mixture of [BMIM]SCN and (ChCl+TMP) exhibited lower values of 2 and 5% mass loss temperature than the composites containing 1 or 3 phr [BMIM]SCN. (235/297 and 250/312°C, respectively).

Epoxy Composites Filled with Graphite Nanoplatelets

The results of volume electrical resistivity of epoxy materials crosslinked with [BMIM]SCN and its mixture with (ChCl+TMP), including these filled with GNP were presented in Table IV (series I). It may be seen that introduction of DES into composition with [BMIM]SCN caused decrease of the mentioned parameter from $2.8 \cdot 10^{11}$ up to $1.3 \cdot 10^{10}$ $\Omega \cdot$ cm. Further increase of electrical conductivity was attained through addition of GNP: $1 \cdot 10^{8}$ $\Omega \cdot$ cm up to $2.8 \cdot 10^{6}$ $\Omega \cdot$ cm for 0.25 and 1 wt % nanoplatelets, respectively. These results shown that epoxy nanocomposites modified with GNP multilayer particles exhibited antistatic properties.

Applying a DES based on choline chloride and tris(hydroxymethyl)propane in epoxy composition allowed to obtain the acceptable degree of GNP dispergation in polymer matrix. Moreover, the electrical resistivity measurements were performed for selected nanocomposites after 48-h water treatment; the results were collected in Table IV (series II). The volume resistivity of specimen after water treatment was practically unchanged. It means that hydrophilic ILs and/or the products of their thermal degradation present in nanocomposite materials were confined in the epoxy network and together with incorporated commercial GNP allowed to improve the electrical volume resistivity about five orders of magnitude.

CONCLUSIONS

For the first time the curing of epoxy resin with [BMIM]SCN and new DES based on choline chloride and tris(hydroxymethyl)propane as well as their mixture has been reported. [BMIM]SCN exhibited higher curing activity toward epoxy resin in comparison to other imidazolium ILs earlier applied. Rather short pot life values of such epoxy systems (2–8 days) were found. Longer storage time was noted for epoxy composition containing DES (more than 60 days). The highest crosslinking density, glass transition temperature and the lowest tan δ values have been found for epoxy material cured with medium [BMIM]SCN content (3 phr): 7181 mol/m^3, 181°C, and 0.30, respectively. The epoxy composition cured with DES/[BMIM]SCN mixture resulted in materials with acceptable T_g and tan δ values (133°C and 0.63, respectively). Epoxy materials with lower [BMIM]SCN content (1 and 3 phr) were more thermally resistant as compared to these with the highest IL dose, as well as with DES or DES+[BMIM]SCN. Relevant temperatures of 5% mass losses for the two former epoxy materials were about 375°C, whereas for the latter 290–313°C. It has been found that DES could act as an effective GNP dispersing medium, which positively affected electrical volume resistivity of epoxy composites. Introduction of GNP dispersion into epoxy resin caused substantial improvement of electrical conductivity from two to four orders of magnitude, in dependence on nanofiller content ($1.0 \cdot 10^{8}$ $\Omega \cdot$ cm for 0.25 wt % up to $2.8 \cdot 10^{6}$ $\Omega \cdot$ cm for 1 wt % GNP). It means that graphite nanaplatelets were stably confined in the cured epoxy matrix after dispersion in hydrophilic dispersing DES.

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