Epoxy resin/phosphonium ionic liquid/carbon nanofiller systems: Chemorheology and properties

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Abstract. Epoxy nanocomposites with commercial carbon nanotubes (CNT) or graphene (GN) have been prepared using phosphonium ionic liquid [trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl) phosphinate, IL-f]. IL-f served simultaneously as nanofiller dispersing medium and epoxy resin catalytic curing agent. An influence of IL-f/epoxy weight ratio (3, 6 and 9/100, phr), carbon nanofiller type and content on viscosity of epoxy compositions during storage at ambient temperature was evaluated. Curing process was controlled for neat and CNT or GN modified epoxy compositions (0.25–1.0 wt% load) using differential scanning calorimetry and rheometry. Epoxy nanocomposites exhibited slightly increased glass transition temperature values (146 to 149°C) whereas tan δ and storage modulus decreased (0.30 to 0.27 and 2087 to 1070 MPa, respectively) as compared to reference material. Crosslink density regularly decreased for composites with increasing CNT content (11 094 to 7020 mol/m^3). Electrical volume resistivity of the nanocomposites was improved in case of CNT to 4·10^1 Ω·m and GN to 2·10^5 Ω·m (nanofiller content 1 wt%). Flame retardancy was found for modified epoxy materials with as low GN and phosphorus content as 0.25 and 0.7 wt%, respectively (increase of limiting oxygen index to 26.5%).

Keywords: *nanocomposites, epoxy resin, ionic liquid, carbon nanofillers*

1. Introduction

Ionic liquids (ILs) have been applied as sole cross-linkers for epoxy resin [1–5] or admixtures for epoxy systems cured with conventional hardeners that allowed to modify the properties of the final epoxy materials [3, 6–8]. ILs have been used together with polyamine or anhydride hardeners in order to modify epoxy curing process as well as materials glass transition temperature [7, 8], lubrication [6], or to improve (nano)filler dispersion [9–11].

The epoxy compositions with the most often used 1-alkyl-3-methylimidazolium ILs exhibited pot life at ambient temperature: 50–60 days where counteranions were chloride or tetrafluoroborate (3 wt parts/ 100 wt parts of epoxy resin, 3 phr) [4, 12]. That parameter was shortened to 30 days when 1-butyl-3-methylimidazolium (BMIM) with dicyanamide

anion [2] or even to 3 days when BMIM with thiocyanate anion [5] was used (at 3 phr). Phosphonium ILs have also been tested as epoxy crosslinking agents by Soares *et al.* [6] and Silva *et al.* [13]. It has been found that aliphatic phosphonium IL [trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl) phosphinate, IL-f] allowed to obtain epoxy materials with good thermomechanical properties and high thermal stability [13]. Glass transition temperatures of the epoxy materials crosslinked solely with ILs were often above 150°C [2, 4, 5, 13].

The important advantages of applying ILs for liquid epoxy resin catalytic curing are their low loadings (typically 3–9 phr) as well as fast and easy miscibility with other liquid components resulting in technological feasibility [5]. However, there is another advantage of ILs, i.e. ability to disperse carbon

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nanofillers before or during their introduction into epoxy systems [9, 11, 14].

Nanocomposite materials with epoxy resin matrix including those modified with carbon nanofillers are widely applied as adhesives, encapsulants, and coatings in various areas of industry. An incorporation of carbon nanostructures, especially carbon nanotubes (CNT) and graphene (GN) into epoxy material is a great challenge. Successful enhancement of mechanical and electrical properties could be reached only when the nanofiller was well dispersed within polymer matrix. It makes possible to minimize carbon nanofiller content necessary to obtain electrical percolation. Generally, CNTs and GN have tendencies to form heavily entangled or agglomerated structures, respectively. It was found that using room temperature ILs was one of the effective approaches of dispersing carbon nanofillers [15–17].

Guo *et al.* [9] and Hameed *et al.* [11] applied imidazolium ILs as dispersing media for expanded graphite (EG) and multiwalled CNT (MWCNT) introduced subsequently into epoxy resins [curing agents were polyoxypropylene diamine (Jeffamine D230) or 4,4′-methylenedianiline, respectively]. EG was ground with IL (BMIM hexafluorophosphate) and mixed with epoxy resin under stirring [9]. MWCNT suspension in epoxy resin containing [BMIM] tetrafluoroborate was prepared by sonication and mechanical stirring [11].

In one of the recent works [5] GN (0.25–1.0 wt%) has been mixed with deep eutectic ionic solvent (based on choline chloride and trihydroxymethylpropane), then sonicated and afterwards simply mixed with epoxy resin containing BMIM thiocyanate. The term 'deep eutectic solvents' (DESs) describes mixtures of some cationic compound, typically ammonium halogenate (e.g. choline chloride) and polar compound bearing –OH, –COOH or –CONH$_2$ moieties able to form hydrogen bonds with anion of the former. DESs exhibit substantially lower melting point (usually below 100°C) than any of the components [18]. DESs share many ILs characteristics, however are inexpensive, easy to prepare, nontoxic and often biodegradable. These features allow them to play multiple roles in polymers and related materials [19].

Throckmorton *et al.* [14] used GN or single walled CNT (SWCNT) to obtain paste in IL (1-ethyl-3-methylimidazolium dicyanamide, EMIM). They used 3-roll mill with regulated rollers rotation, the number of repeated mixing cycles and constant gap between rollers (20 µm). Cured EMIM/epoxy resin materials (with high IL content 17.6 phr) exhibited very low electrical network percolations; $1.7 \cdot 10^{-2}$ and $8.6 \cdot 10^{-5}$ vol% for GN and SWCNT, respectively.

In literature more tedious methodology of epoxy resin/CNT/ionic liquid nanocomposite manufacturing was also reported [20, 21]. Wang and Guo group applied imidazolium IL chemically functionalized CNT for epoxy nanocomposites preparation. Multistep procedure was used: (i) sulfoxylation of –COOH groups present at CNT surface defects with SOCl$_2$, (ii) reaction of formed acid chloride moieties with –NH$_2$ groups of 3-aminopropylimidazole, (iii) introduction of epoxy groups on imidazole ring with simultaneous quaternization of nitrogen atom (thus creating imidazolium ionic liquid structure) as a result of reaction with epichlorohydrin, (iv) preparation of CNT-IL/curing agent solvent dispersion (aromatic diamine, EpiCure W, was used as a hardener) by sonication (4 h/room temperature + 3 h/60°C), (v) addition of epoxy resin into the CNT-IL/curing agent solvent dispersion; shear mixing (0.5 h/80°C) and additional sonication (0.5 h/80°C), (vi) degassing and curing (4 h/120°C). The final nanocomposite materials exhibited electrical conductivity $8.4 \cdot 10^{-3}$ S/cm (1 wt% CNT-IL loading) and tensile strength increased ca. 36% (0.5 wt% CNT-IL) [21].

Considering the studies mentioned above continuation of research on application of other ILs in conjunction with carbon nanofillers to develop high performance epoxy resin nanocomposites is reasonable. In this work, the epoxy resin/IL systems with the mentioned phosphonium IL-f and CNT or GN content were investigated with the aim of obtaining nanocomposite epoxy materials with improved thermomechanical, electrical as well as flame retardancy features.

2. Experimental
2.1. Materials
Epoxy resin: bisphenol A-based low molecular weight Epidian 6 (E6); epoxy equivalent 185 g, (viscosity 18 000 mPa·s at 23°C), Organika Sarzyna, Poland was used. Trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate (>95%, Sigma-Aldrich) was used as curing agent for epoxy

resin and as a medium for carbon nanofiller dispersing. Two different types of carbon nanoparticles were applied: (i) graphene obtained by vapor deposition technology with specific surface >750 m²/g, layer thickness <2 nm, particle diameter <0.1 μm, carbon layer number <3 (Graphene Technologies, USA), and (ii) multiwall nanotubes, Nanocyl NC7000, with specific surface 250–300 m²/g, average length 1.5 μm, average diameter 9.5 nm, carbon content 90 wt% (Nanocyl, Belgium).

2.2. Preparation of carbon dispersions and epoxy compositions

The neat epoxy compositions were obtained by mixing of epoxy resin with IL-f at ambient temperature. The IL-f content was 3, 6 and 9 wt parts/ 100 wt parts epoxy resin.

The carbon nanofillers were introduced into the epoxy compositions in two different ways. GN in the amount of 0.25, 0.5 or 1.0 wt% (relation to epoxy resin) was added into IL-f and then homogenized by sonication (2 h, amplitude 50%, frequency 50 Hz, UP 200S, Hielscher GmbH, Germany). Subsequently, GN dispersion in IL-f was manually mixed with epoxy resin for 10 min. CNTs (0.25, 0.5 or 1.0 wt% in relation to epoxy resin) were dispersed in epoxy resin by ultrasonication for 2 h. Next, IL-f was added into the epoxy composition and the systems mixed manually for 10 min. Constant amount of IL-f (9 phr) was adjusted in all epoxy compositions with carbon nanofillers. Eventually, the epoxy compositions were cured in teflon mold at 120°C for 2 h. The resultant samples were used for further investigations. Differentiation of carbon nanofiller dispersion methodology was performed because of specific features of GN and CNT nanofillers. Carbon nanotubes need a large amount of wetting agent, i.e. IL-f, to obtain a uniform dispersion with viscosity enabling handling. Applied amount of ionic liquid (9 phr) was too low to be efficiently used as CNT dispersing medium. For that reason CNTs were first dispersed in epoxy resin and afterwards IL-f was introduced into epoxy/CNT composition.

2.3. Methods

The viscosity of epoxy compositions with carbon nanoparticles was determined using stress rheometer (Rheometric Scientific, USA) at room temperature, a plate-plate system, ø = 40 mm, a gap of 1 mm.

The storage time for epoxy resin/crosslinker compositions at ambient temperature was determined on a basis of viscosity measurements during storage at 23–25°C using rheometer.

The curing process of epoxy compositions was investigated using differential scanning calorimeter (DSC, Q-100, TA Instruments, USA), at a heating rate of 5°C/min in the temperature range of 30–220°C and rheometer (Rheometric Scientific) at the same measurement schedule.

The glass transition temperatures (T_g), tan δ values and storage moduli were determined using dynamic mechanical thermal analysis (DMTA, Q – 800, TA Instruments) with dual cantilever, at heating rate of 2°C/min from 30 to 250°C, frequency 1 Hz.

Thermogravimetric analysis (TGA, Q500, TA Instruments) was performed using platinum pan under 25 mL/min air flow, in temperature range 40–800°C at a heating rate of 10°C/min.

The volume electrical resistance of cured composites with different carbon nanofiller content was tested at room temperature in accordance with IEC 93:1980 and ASTM D 257-99 (Keithley 8009 with a set of electrodes, Keithley Instruments, Inc., USA).

The limiting oxygen index (LOI) of the nanocomposites was measured using oxygen concentration meter (GOX 100, Greisinger Electronic GmbH, Germany) at room temperature, in accordance with PN-EN ISO 4589-2. The test was based on the determination of oxygen content (%) in a gas mixture of O_2 and N_2. The thin strips (5×1×0.25 cm) of each material were clamped vertically and ignited at the top.

3. Results and discussion

3.1. Influence of storage time, nanofiller type and content on viscosity of epoxy compositions

Viscosity changes during storage of epoxy compositions with increasing IL-f content in a range 3–9 phr were controlled up to 8 days (Table 1). It was clear that introduction of IL-f into epoxy resin caused slight decrease of viscosity when measured directly after components mixing (day 0). However, after 2-days storage rather high differences were found, i.e.: (i) from 13.3 → 16.5 Pa·s for the composition with the lowest IL-f content, (ii) it was almost doubled for medium IL-f content (13.0 → 24.1 Pa·s, 6 phr), and (iii) up to 8-times increase (12.9 to ca. 105 Pa·s) for the system with the high-

Table 1. Viscosity change of epoxy compositions with various content of phosphonium phosphinate ionic liquid (IL-f) during storage at room temperature

Composition acronym	Viscosity (days after component mixing) [Pa·s]				
	0	**2**	**4**	**7**	**8**
E6/IL-f_3	13.3±0.10	16.5±0.4	18.3±0.2	520.4±1.5	gel
E6/IL-f_6	13.0±0.10	24.1±0.3	258.1±1.2	gel	–
E6/IL-f_9	12.9±0.01	104.8±0.8	gel	–	–

est IL content, (iv) extremely high viscosity jump was found for E6/IL-f_6 after 4-day storage (almost 20 times, i.e. to 258 Pa·s), whereas composition containing the highest amount of IL-f showed gelation (i.e. viscosity above 3000 Pa·s) after that time.

Silva *et al*. [13] have reported recently that the pot lives of epoxy compositions containing 2.5, 5 and 10 phr IL-f at room temperature were: 26, 8 and 4 days, respectively, i.e. slightly longer than reported in here (more significant difference was found for system with the lowest IL-f content). It does mean that IL-f belongs (together with [BMIM] thiocyanate [5]) to the most reactive ionic liquids applied up today for epoxy resin crosslinking.

From applied view point an effect of carbon nanofiller presence on relevant epoxy compositions viscosity (η) is essential. In Table 2 the viscosities of epoxy systems with the highest content of IL-f (9 phr) and CNTs or GNs (0.25–1 wt%) were collected. Slight increase of η could be observed for composition filled with GN, from 12.9 for neat system up to 16.9 Pa·s for composition with 1 phr load. As it was already mentioned, the compositions with GN were first dispersed in IL-f by sonication and then introduced into epoxy resin. More significant influence of CNT on epoxy systems viscosity was observed. Even low CNT content (0.25 wt%) resulted in almost 3.5-times increase of epoxy composition viscosity (12.9 → 47.7 Pa·s) whereas η increased 16-times (up to >200 Pa·s) for 1 wt% load. The procedure of composition preparation was in that case different: CNTs were introduced into epoxy resin, then the system was sonicated and mixed with the curing agent.

3.2. Curing process of epoxy compositions

Curing process of epoxy resin/IL-f systems with various crosslinking agent content (3–9 phr) was investigated by rheometric and DSC techniques in a range from 40 up to 220°C with temperature gradient increase 5°C/min.

The results were presented in Figure 1 and Table 3. Rheometric and heat flow curves were consistent. The relevant values for viscosity jumps followed the order 145°C > 130°C > 125°C for E6/IL-f with 3, 6 and 9 phr, respectively. The temperature of exothermal peak maximum determined by DSC were: 133°C > 123°C > 118°C, respectively. It was also found that onset exothermal temperatures for the investigated systems (evidenced start of gelation process) were influenced by IL-f amount rather in low extent (101–106°C). The effect of crosslinking exothermic reaction extended importantly when IL-f content in epoxy system increased from 3 to 6 phr

Table 3. Curing characteristics for the system E6/IL-f and for epoxy compositions with carbon nanofillers from DSC measurements
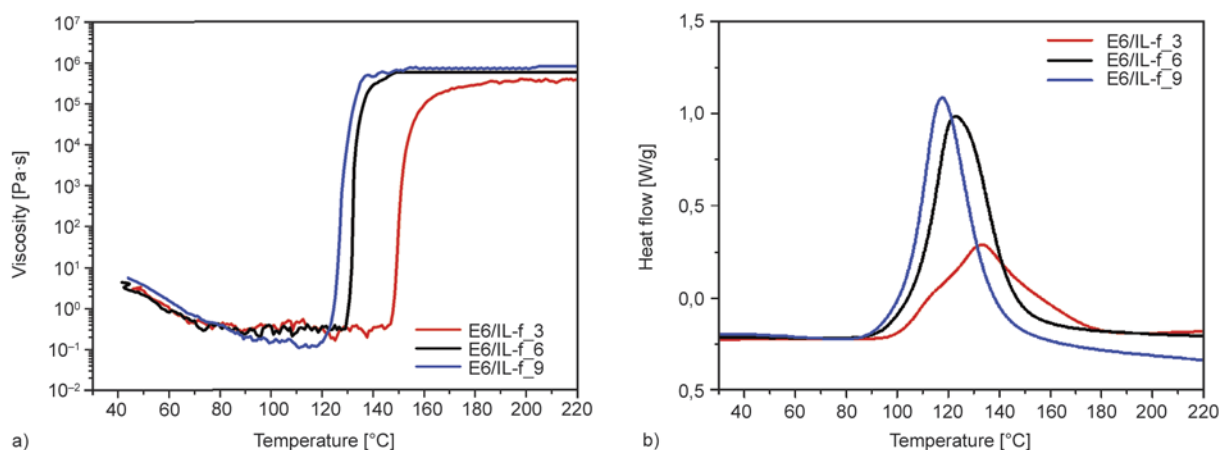
Composition acronym	Onset exotherm temperature [°C]	Maximum exotherm temperature [°C]	ΔH [J/g]
E6/IL-f_3	101	133	225
E6/IL-f_6	106	123	398
E6/IL-f_9	102	118	403
E6/(IL-f_9/GN_0.25)	100	125	388
E6/(IL-f_9/GN_0.50)	108	123	383
E6/(IL-f_9/GN_1.00)	101	122	417
(E6/CNT_0.25)/IL-f_9	100	126	388
(E6/CNT_0.50)/IL-f_9	101	126	382
(E6/CNT_1.00)/IL-f_9	99	126	394

Table 2. Viscosity of epoxy compositions with 9 phr of phosphonium phosphinate ionic liquid (IL-f) and various content of carbon nanofillers directly after preparation
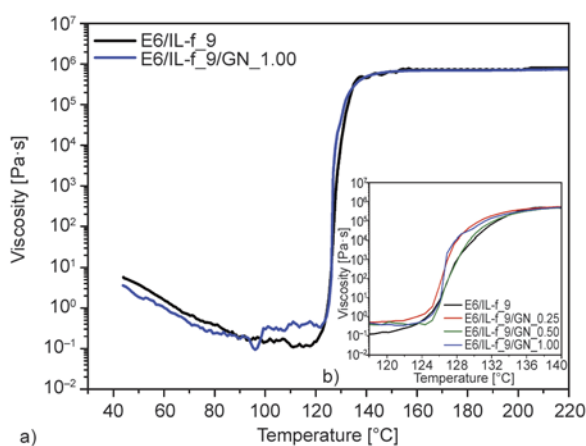
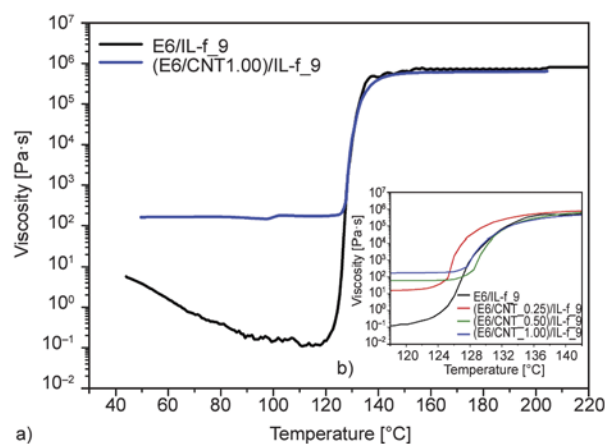| Composition acronym [GN in IL]	Viscosity [Pa·s][*]	Composition acronym [CNT in E6]	Viscosity [Pa·s][*]
E6/(IL-f_9/GN_0.25)	15.1±0.10	(E6/CNT_0.25)/IL-f_9	47.7±0.3
E6/(IL-f_9/GN_0.50)	15.8±0.10	(E6/CNT_0.50)/IL-f_9	89.2±0.5
E6/(IL-f_9/GN_1.00)	16.9±0.05	(E6/CNT_1.00)/IL-f_9	206.5±0.8

[*]measured on rheometer, room temperature

Figure 1. Change of viscosity – (a) and heat flow – (b) during curing process of epoxy resin with IL-f measured by rheometry and DSC, respectively

Figure 2. Rheometric curves of epoxy compositions with dispersion of IL-f_9 and various contents of GN (0.25–1.00 wt%) during curing process: at wide temperature range (40–220°C) – (a) and narrow temperature range (120–140°C) – (b)

Figure 3. Rheometric curves of epoxy compositions with various contents of CNT dispersed in the resin (0.25–1.00 wt%) during curing process at wide temperature range (40–220°C) – (a) and narrow temperature range (120–140°C) – (b)

(225 → 398 J/g), whereas additional amount of the ionic liquid caused only minor ΔH increase (up to 403 J/g).

Curing of epoxy resin/IL-f/carbon nanofiller compositions was also followed by rheometric measurements (Figures 2 and 3). The following conclusion could be made on a basis of these results: (i) the viscosity of GN filled epoxy compositions decreased from 10 → 5 Pa·s during heating from 40 to 120°C. An influence of IL-f on viscosity is hardly visible. Fast gelation process was performed at 120–135°C. Slight shift of rheometric curves to lower temperature values for E6/IL-f/GN_0.25 and E6/IL-f/ GN_1.00 was found in relation to the neat system E6/IL-f_9, (ii) rheometric curves for CNT modified epoxy compositions showed distinct differences in comparison to E6/IL-f_9 neat system. Significant

viscosity increase at 100°C with increasing CNT content could be noted as followed: E6/IL-f_9: $2 \cdot 10^{-1} <$ (E6/CNT_0.25)/IL-f_9: $2 \cdot 10^{1} <$ (E6/CNT_0.50)/IL-f_9: $7 \cdot 10^{1} <$ (E6/CNT_1.00)/IL-f_9: $1.5 \cdot 10^{2}$ Pa·s. The gelation process performed in slightly wider temperature range (i.e. 120–140°C) when compared to the systems modified with GN. The lowest amount of CNT applied resulted in rheometric curve shift to lower temperatures (range from 124–132°C, in relation to the three other investigated compositions, Figure 3).

3.3. Properties of epoxy nanocomposites
For the E6/IL-f/carbon nanofillers cured system thermomechanical, thermal, electrical resistance and flammability tests were performed.

3.3.1. Thermomechanical and thermal properties

The crosslinking of the epoxy composition containing 3 phr IL-f was not efficient enough, as it could be seen from DMTA results in Table 4 (low values of glass transition temperature, T_g, and storage modulus, as well as high tan δ value). Higher contents of catalytic curing agent (6 and 9 phr) in epoxy compositions allowed to obtain epoxy materials with acceptable thermomechanical parameters, i.e. T_g (145–146°C), storage modulus (2097–2446 MPa) and tan δ (0.30–0.34). Crosslinking density parameter was estimated on a basis of Equation (1) [22, 23]:

$$\nu_e = \frac{E_r}{3RT_r} \tag{1}$$

where E_r is storage modulus at 'rubbery' state, i.e. at $T_r = T_g + 30$, R is universal gas constant. The values of ν_e for epoxy materials cured with 6 and 9 phr IL-f were rather high (12 758 and 11 094 mol/m³, respectively) – significantly higher than for epoxy systems cured with BMIM thiocyanate (2113 and 7181 mol/m³; using 9 and 3 phr of IL, respectively). That ν_e value difference was caused mainly by relatively high storage moduli values at 'rubbery' state (i.e. above 175°C) when IL-f was applied as crosslinking agent (Table 4).

The epoxy composition containing 9 phr IL-f was selected for preparing nanocomposite with carbon nanofillers. The presence of CNTs as well as GNs affected thermomechanical properties of epoxy nanocomposites in rather low extent. T_g slightly increased from 146 to 149°C; no regular tendency in dependence to filler type and content has been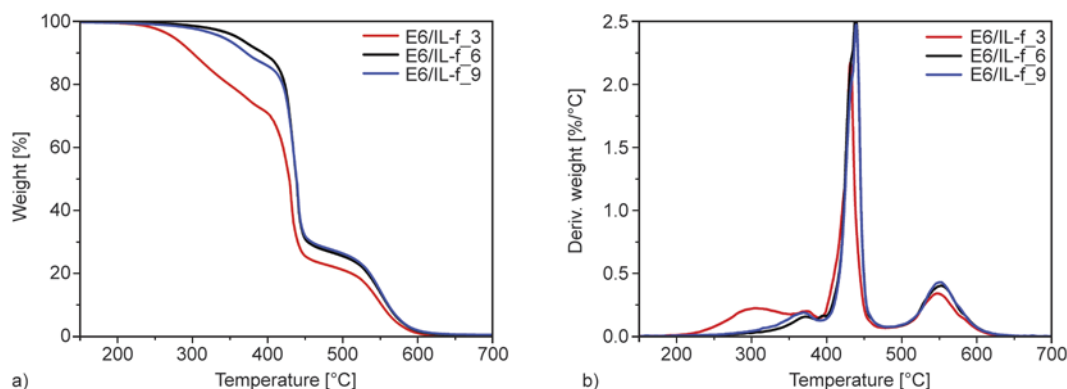 observed. The tan δ values decreased from 0.30 to 0.27 with CNTs or GNs content increase (Table 4). The storage modulus changed depending on carbon nanofiller kind: (i) clear and significant decrease (2087 → 1070 MPa) for neat epoxy materials and that filled with the highest (1.0 wt%) amount of CNTs, respectively, (ii) irregular changes when the other nanofiller was used: E6/IL-f_9/GN_0.50 (2172 MPa) and E6/IL-f_9/GN_1.00 (1995 MPa). Similarly, crosslink densities regularly decreased for materials containing CNTs:
neat epoxy (11 094 mol/m³) > (E6/CNT_0.25)/IL-f_9 (9965 mol/m³) > (E6/CNT_0.50)/IL-f_9 (7810 mol/m³) > (E6/CNT_1.00)/IL-f_9 (7020 mol/m³). Nanocomposites with GN exhibited maximum ν_e values in a range of nanofiller contents 0.25–0.50 wt% (12 841–12 852 mol/m³) whereas for neat epoxy materials and that filled with the highest GN content crosslink densities were lower and rather similar (11 094 and 12 025 mol/m³, respectively).

Putz *et al.* [24] considered three possible mechanisms for T_g variation referred to CNT nanoparticles presence in epoxy resin: (i) changed thermal conductivity could affect curing kinetics resulting in impeded attainment of consistent crosslink density (T_g ↓), (ii) network disruption leading to effective ν_e decrease (T_g ↓), (iii) interphase creation of thin films (T_g ↑ or ↓). Some data considering decreased [24, 25] or increased [24–26] T_g values for epoxy materials caused by CNT presence, have been reported. The possible explanation of observed T_g and tan δ variation related to introduction of carbon nanofillers could be enhancing interaction between carbon nanoparticles (perfectly wetted with IL) and epoxy network. Epoxy polymerization caus-

Table 4. Characteristic parameters for epoxy materials cured with IL-f and modified with carbon nanofillers from DMTA and TGA measurements

Composition acronym	DMTA					TGA		
	T_g [°C]	tan δ	Storage modulus* (glassy state) [MPa]	Storage modulus** ('rubber' state) [MPa]	Crosslink density [mol/m³]	$T_{5\%}$ [°C]	$T_{10\%}$ [°C]	$T_{max.DTG}$ [°C]
E6/IL-f_3	44	1.27	800	0.0	n.d.	275	300	431
E6/IL-f_6	145	0.34	2446	139.7	12 758	360	394	438
E6/IL-f_9	146	0.30	2087	124.6	11 094	340	372	439
E6/(IL-f_9/GN_0.25)	148	0.29	2043	144.7	12 852	349	384	439
E6/(IL-f_9/GN_0.50)	149	0.27	2172	144.7	12 841	345	384	439
E6/(IL-f_9/GN_1.00)	146	0.28	1995	134.6	12 025	336	371	438
(E6/CNT_0.25)/IL-f_9	147	0.28	1930	108.8	9 965	354	393	438
(E6/CNT_0.50)/IL-f_9	147	0.27	1633	82.6	7 810	347	376	434
(E6/CNT_1.00)/IL-f_9	149	0.27	1070	79.1	7 020	358	398	435

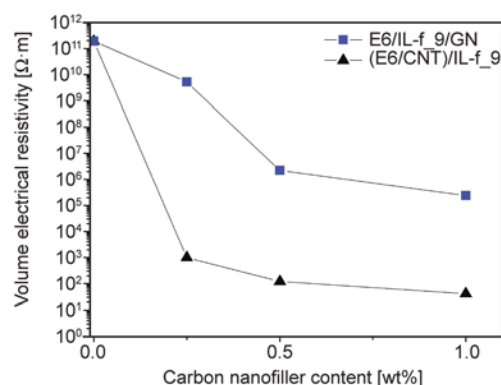n.d. – not determined, *determined at 40°C, **determined at $T_g + 30$

Figure 4. TGA (a) and DTG (b) curves for neat E6/IL-f epoxy materials

ing network formation began directly on carbon surface. In result thin interphase between epoxy network and carbon surface could be formed, resulting in T_g increase (tanδ decrease) because of some retarding dynamics in the system. Network disruption mechanism could be responsible for storage modulus as well as crosslink density decrease, especially for CNT modified nanocomposites.

Inefficiently crosslinked epoxy material based on E6/IL-f_3 exhibited clearly lower temperatures of 5 or 10% mass losses in comparison to those cured with higher IL-f content. Generally, the materials containing medium amount of curing agent (6 phr) exhibited the highest temperatures of 5 and 10% mass losses (360 and 394°C, respectively). Some influence of carbon nanofiller addition on the nanocomposites thermal stability has been observed as well (Figure 4, Table 4). The temperatures values of 5 and 10 wt% losses were about 8–12°C higher for the materials modified with 0.25 and 0.50 wt% of GN than for the reference one. Even higher increase of the mass loss temperatures for the epoxy nanocomposites modified with CNT (up to 18 and 26°C, for 5 and 10% mass losses, respectively) has been noted. The temperature values at maximum mass losses were placed in rather narrow range from 431 up to 439°C.

3.3.2. Electrical volume resistivity

Electrical volume resistivity of the investigated epoxy materials was evaluated. The changes of that parameter as a function of filler contents were presented in Figure 5. The electrical resistivity of neat epoxy material was found to be $1.9 \cdot 10^{11}$ $\Omega \cdot$m. The both carbon nanofillers improved the electrical conductivity of epoxy matrix several orders of magnitude, however, the results for nanocomposites with

Figure 5. Volume resistivity of epoxy (nano)composites with GN and CNT as a function of nanofiller content

CNTs were substantially more pronounced. For the nanocomposites with GNs increasing filler content from 0.25 to 1 wt% caused reduction of electrical resistivity about 4 orders (from $5.2 \cdot 10^9$ to $2.4 \cdot 10^5$ $\Omega \cdot$m). An introduction of CNT into epoxy materials resulted in deep decrease of this parameter, i.e. altogether 8–10 orders of magnitude as compared to the reference neat epoxy material. In the range of CNT content 0.25–1.0 wt% electrical resistivity decreased to a lower extent from $1.1 \cdot 10^3$ to $4.1 \cdot 10^1$ $\Omega \cdot$m. It could be seen from Figure 5 that nanocomposites with CNT cured with phosphonium phosphinate ionic liquid exhibited percolation threshold below 0.25 wt% whereas these containing GN showed steadier decreasing electrical resistivity with growing nanoparticles content. These results were in qualitative agreement with recent literature data. Throckmorton *et al*. [14] have found that percolation threshold for epoxy nanomaterials modified with SWCNTs was ca. 2.5 order below that for GNP ($8.6 \cdot 10^{-5}$ and $1.7 \cdot 10^{-2}$ volume fraction, respectively). Both these values were close to the theoretical percolation thresholds predicted by power law

percolation theory model (for CNTs) or plate-like particle percolation theoretical models (for GNP) [14].

The obtained results showed that introduction of IL-f into preliminary sonicated epoxy resin/CNT system with afterwards simple mixing (without necessity of using more efficient dispersing technique) allowed to obtain epoxy nanocomposites with important improvement of electrical properties.
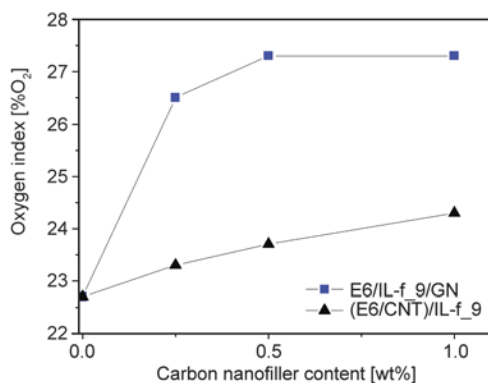
3.3.3. Limiting oxygen index

Phosphorus compounds represent important group of flame retardants including organic and inorganic phosphates $[(PO)_3PO]$, phosphites $[(PO)_3P]$, phosphonates $[(RO)_2PR']$, phosphinates $[(ROR'_2PO]$, phosphines $[R_3P]$, phosphine oxides $[R_3PO]$, and phosphonium salts $[R_4PX]$ [27]. As applied trihexyl(tetradecyl)phosphonium bis(2,2,4-trimethylpentyl)phosphinate contained phosphonium atom in cationic as well as in anionic part of IL, flame retardancy features of epoxy nanoycomposites cured with it were tested.

The limiting oxygen index test results were shown in Figure 6. Materials with LOI lower than 22% are flammable, with LOI between 22 and 25 are considered as self-extinguishing; when value of this parameter is above 26, the material reaches flame retardancy level [28]. All investigated epoxy materials exhibited LOI values above 22. Typical level of LOI for epoxy crosslinked with polyamines, e.g. triethylenetetramine is ca. 20 [29]. The LOI values of nanocomposites modified with CNTs were placed in a range from about 23 to 24.5, indicating that small amount (0.25–1.0 wt%) of CNTs in epoxy systems slightly improved flame retardancy. Epoxy nanocomposites modified with GN exhibited dis-

tinctly improved flame retardancy; for composites with 0.5 or 1.0 wt% GN LOI was above 27 (flame retardant). Even lower amount of GN applied (0.25 wt%) increased oxygen index parameter about 4 units from 22.5 up to 26.5%. Presented results indicated that GN was an effective flame retardant for epoxy nanocomposites cured with phosphonium phosphinate ionic liquid.

Our results on flame retardant properties of epoxy nanocomposites cured with phosphorus containing IL and modified with GN could be compared with relevant data recently published by Chiang *et al.* [30]. That research group used graphene oxide (GO) and reduced GO (rGO) functionalized with DOPO (9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide) known flame retardant for epoxy materials. The grafting efficiency for DOPO/rGO ratio was 19.9 wt%. GO as well as rGO functionalized with DOPO (DOPO-rGO) were used in amounts 1, 5 and 10 wt% relative to epoxy resin (i.e. for DOPO-rGO containing 0.2, 1.0 and 2.0 wt% P as well as 0.8, 4.0 and 8.0 wt% rGO, respectively). Introduction of 1–10 wt% GO resulted in some LOI value increase (from 20 up to 23% as compared to neat epoxy cured with diaminodiphenylmethane). DOPO-rGO used with mentioned above ratios allowed to reach LOI values to: 21, 25 and 26%, respectively. Similar flame retardancy effect was reached in our work using: (i) rather simple GN dispersion methodology as comparing with DOPO grafting on rGO [30], (ii) substantially lower concentrations of modifying components, i.e. IL-f (serving simultaneously as curing catalysts, GN dispersion medium and antiflamming compound) and GN, i.e. 0.5 wt% GN and ca. 0.7 wt% P, as compared to those from ref. [30] (8.0 wt% GO and 2.0 wt% P) to obtain LOI value 26–27%.

4. Conclusions

Epoxy compositions with CNT or GN in presence of phosphonium ionic liquid have been prepared. IL played triple function: carbon nanofiller dispersing medium, catalytic curing agent and antiflamming additive. The pot life values of neat epoxy systems were 4 up to 8 days for IL-f/epoxy weight ratio between 9 and 3 phr at ambient temperature. The viscosities of epoxy compositions containing GN were negligibly higher. On the other hand the same contents of CNT (0.25–1.0 wt%) in epoxy systems caused dramatic viscosity jump from ca. 13 up to

Figure 6. Oxygen index of epoxy (nano)composites with GN and CNT as a function of nanofiller content

207 Pa·s as measured directly after components mixing. With increasing IL-f content (3 → 9 phr) in epoxy resin the curing reaction started at lower temperatures as determined by rheometry (145 → 125°C) or DSC (133 → 118°C). Only slight influence of CNT or GN on curing characteristics of epoxy systems has been observed. Acceptable thermomechanical properties of IL-f cured epoxy neat materials were reported when at least 6 phr IL was applied (i.e. T_g 145–146°C, storage modulus 2097–2446 MPa, and tan δ 0.30–0.34). The both carbon nanofiller types slightly affected T_g and tan δ values (from 146 → 149°C and 0.30 → 0.27, respectively). However, storage modulus changed depending on nanoparticle type, i.e. significant decrease (2087 → 1070 MPa) for nanocomposites with CNT and irregular changes in narrow values range (2172 → 1995 MPa) with GN was observed. For crosslink density similar trend was observed, i.e. changes in rather wide range (11 094 → 7020 mol/m^3) for CNT modified materials and little difference for GN filled composite materials. Thermal resistance of epoxy material was improved when CNTs were added (18–26°C for 5 and 10% mass losses) and to a lower extent for GN modified materials (8–12°C). Electrical bulk resistivity decreased about 8 order of magnitude after inclusion of 0.25 wt% CNT to epoxy materials. The highest electrical conductivity, i.e. $4 \cdot 10^1$ Ω·m was registered for nanocomposite containing 1 wt% CNT. Higher resistivity exhibited epoxy materials modified with GN (up to $2.4 \cdot 10^6$ Ω·m). The presence of phosphonium phosphinate IL resulted in some improvement of LOI index for neat epoxy material (22.7 when compared to 20% for conventional epoxy materials cured with polyamine). However, few-layer GN caused high improvement of that parameter (up to 26.5 for 0.25 wt% load) in the nanocomposite. Such an epoxy nanocomposite material could be considered as electroconductive (below 10^5 Ω·m [31]) and flame retardant.

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