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High performance epoxy composites cured with ionic liquids

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ABSTRACT

Two ionic liquids (ILs) with the same dicyanamide anion and various cation types: imidazolium and phosphonium as catalytic agents of epoxy resin have been compared. Neat epoxy materials cured with imidazolium IL exhibited above 45 days latency, high thermal performance, i.e. glass transition temperature (above 190 °C), low tan δ (0.17), and stability (395 °C/5% weight loss), whereas with phosphonium IL – pot life above 70 days, similar tan δ value and high transparency (85%). Carbon nanotubes modified epoxy composites cured with imidazolium dicyanamide IL showed bulk electrical resistivity in a range 10^7–10^3 Ω·m for carbon filler content 0.0625–0.25 wt.%. These features designate developed materials for various engineering applications.

Introduction

The ionic liquids (ILs) can be used as catalytic epoxy resin crosslinkers solely [1–7] or in combination with other conventional hardeners, such as polyamines [3,8–11] or anhydrides [12,13]. Epoxy compositions with ILs exhibited latency at room temperature which could be regulated in a rather wide range from a few days (e.g. 3–4, for systems with 1-butyl-3-methylimidazolium thiocyanate, [BMIM]SCN, [7] or phosphonium phosphinate derivative [6,14]) up to ca. 50 days (imidazolium ILs with chloride or tetrafluoroborate anions [4,5]) when used in similar weight ratio to epoxy resin (3 parts per 100 parts of resin, 3 phr). Besides the mentioned latent character, to important advantages of ILs as epoxy resin curing agents belong low loading (usually 3–9 phr), fast and easy miscibility as well as homogeneity with liquid epoxy resin (before and after curing process) resulting in technological feasibility. In addition, ILs can play multifunctional role in epoxy material acting as polymer matrix modifier [8,15] or carbon nanofiller dispersing agent [9–12,14] as well.

Until today, imidazolium type ILs have been more often applied in epoxy resin systems than phosphonium ones [14]. However, the reasons why one might be interested in a phosphonium IL, even in industrial process, include its availability and cost. Phosphonium salts are manufactured on multiton scale [16,17]. Recently, phosphonium ILs have been tested as epoxy resin crosslinkers used independently [6,14] or in combination with aromatic polyamine [18]. Soares at al. [18] published limited DSC and FTIR results on epoxy resin curing process with some imidazolium (1,3-bis octadecylimidazolium iodide) and phosphonium ILs (octadecyltriphenyl phosphonium hexafluorophosphate). However, according to our best knowledge, up to now, no systematic study on simultaneous an influence of the imidazolium and phosphonium ILs on epoxy resin curing process and properties of the relevant materials has been reported. On the other side it seemed that known features of epoxy materials cured with ILs could be improved by careful selection of IL type and concentration as well as by introduction of modifying ingredient, e.g. carbon nanotubes in low loading to obtain high performance epoxy materials.

Epoxy materials filled with carbon nanotubes (CNT) can be used for various engineering applications, like electrical conductive adhesives [12], antistatic or corrosion resistant coatings [19,20], electromagnetic shielding materials [21] or with thermally improved features [22,23]. Considering polymeric materials exhibiting enhanced electrical features the amount of filler is a critical aspect allowing to change material properties from insulator to conductor. Percolation threshold depends on many factors, such as: aspect ratio, allignment, functionalization, processing, polymer type etc. [24].

In this work two ILs with the same counteranion: imidazolium type, i.e. 1-ethyl-3-methylimidazolium dicyanamide, [EMIM]N(CN)$_2$, and phosphonium derivative, i.e. trihexyltetradecyl phosphonium dicyanamide, [THTDP]N(CN)$_2$, were used as

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the curing catalysts to obtain epoxy materials (also CNT modified) with enhanced performance. The study had two main goals: (i) scientific: to compare curing characteristics of epoxy systems depending on the ILs cation type, (ii) to enhance technological and utility properties of the epoxy compositions and composites for industrial usage.

Experimental

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. Trihexyltetradecyl phosphonium dicyanamide (≥95%), Sigma–Aldrich, and 1-ethyl-3-methylimidazolium dicyanamide (≥95%) from Iolitec Ionic Liquid Technologies GmbH, Heilbronn, Germany were used as epoxy resin curing catalysts (Table 1). Multiwall carbon nanotubes (CNT), Nanocyl NC7000, with specific surface 250–300 m^2/g, average length 1.5 μm, average diameter 9.5 nm, carbon content 90 wt.% (Nanocyl, Belgium) were applied for epoxy composite preparation when $[EMIM]N(CN)_2$ was used as epoxy crosslinking catalyst.

Preparation of epoxy compositions, CNT dispersions and epoxy composites

The neat epoxy compositions were prepared by mixing epoxy resin with $[EMIM]N(CN)_2$ or $[THTDP]N(CN)_2$ at ambient temperature. The IL content was 1, 3, 6 and 9 wt. parts/100 wt. parts epoxy resin (phr). CNT (0.0625–1.0 wt.% in relation to epoxy resin) were dispersed in epoxy resin by ultrasonication for 2 h (amplitude 50%, frequency 50 Hz, UP 200S, Hielscher GmbH, Germany). Next, $[EMIM]N(CN)_2$ was added into the epoxy composition with CNT and the systems mixed manually for 10 min. Constant amount of $[EMIM]N(CN)_2$ (3 phr) was adjusted in all epoxy compositions and composites modified with CNT. Eventually, the epoxy compositions were cured in Teflon mold at 160 °C for 2 h. The resultant samples, i.e. compositions and composites were used for further investigations.

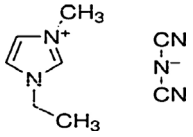
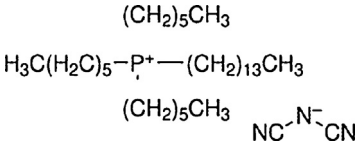
Methods

The viscosity of epoxy compositions with CNT was determined using stress rheometer (Rheometric Scientific, USA) at room temperature, a plate–plate system, $\phi = 40$ mm, a gap of 1 mm.

The pot life for epoxy resin/IL compositions at ambient temperature was determined on a basis of viscosity measurements during storage at 23 ± 2 °C using stress 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 30–300 °C and rheometer at the same measurement schedule.

Table 1
Ionic liquids used as epoxy curing catalysts.

1-Ethyl-3-methylimidazolium dicyanamide, $[EMIM]N(CN)_2$	
Trihexyltetradecylphosphonium dicyanamide, $[THTDP]N(CN)_2$	

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 3 °C/min from 30 to 250 °C, frequency 1 Hz.

Thermogravimetric analysis (TGA Q-500, 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 various CNT content was tested at room temperature in accordance with IEC 93:1980 and ASTM D 257-99 using Keithley Instruments, Inc., USA, with a set of electrodes (Keithley 8009).

Thermal conductivity of disk shaped composite samples was measured at room temperature using TPS 2500S apparatus (Hot Disk AB Company) with 7577S sensors.

Results and discussion

Pot life of epoxy compositions

Pot life of epoxy compositions with applied ILs was controlled during storage at ambient temperature by rheometric measurements. Relevant dependences are shown in Fig. 1. The both E6/IL systems exhibited prolonged storage time >45 days and >70 days when $[EMIM]N(CN)_2$ and $[THTDP]N(CN)_2$ was applied, respectively. That feature was to some extent dependent on IL/epoxy resin weight ratio. Increasing IL amount in epoxy composition resulted

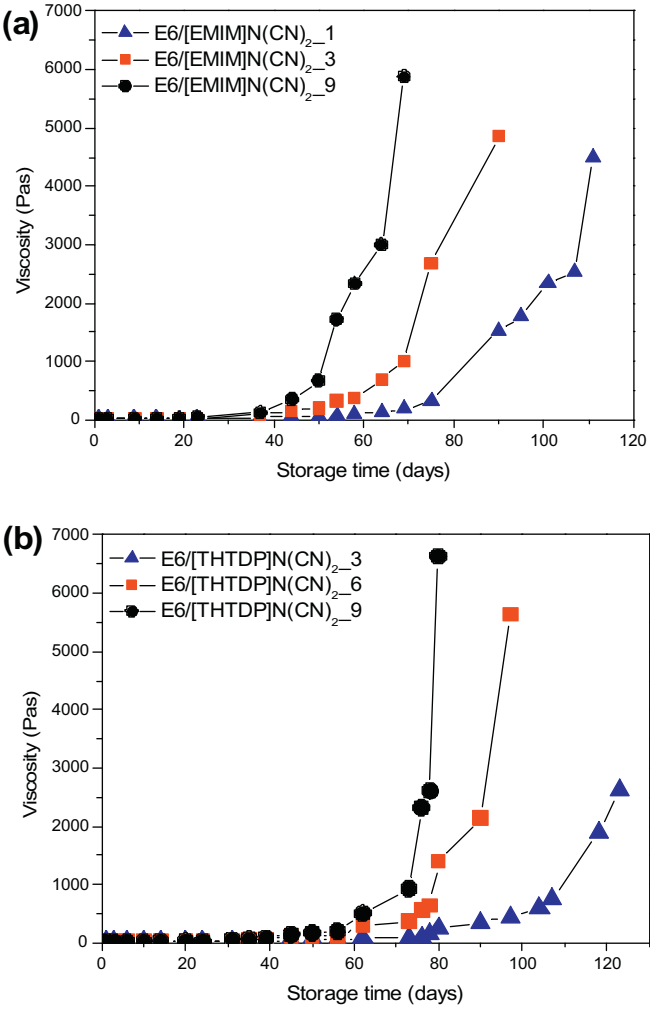


Fig. 1. Viscosity change of epoxy compositions during storage at room temperature: (a) E6/$[EMIM]N(CN)_2$, (b) E6/$[THTDP]N(CN)_2$ systems.