



Flame retardancy of phosphorus-containing ionic liquid based epoxy networks



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ARTICLE INFO

Article history:

Received 1 July 2016

Received in revised form

7 October 2016

Accepted 14 October 2016

Available online 15 October 2016

Keywords:

Ionic liquid

Epoxy networks

Flame retardancy

Phosphorus flame retardant

ABSTRACT

Various amounts of a phosphonium ionic liquid (IL169) were used as curing agents as well as flame retardants of epoxy prepolymer in order to prepare epoxy networks with improved fire properties. The flame retardancy of these resins was investigated using thermogravimetric analysis (TGA), pyrolysis-combustion flow calorimetry (PCFC) and cone calorimetry. Phosphonium ionic liquid significantly reduced flammability without further addition of flame retardants due to the high amount of phosphorus (up to 3.69 wt%). The Peak of heat release rate decreases from 1099 kW/m² to 300 kW/m² in cone calorimeter at 35 kW/m² when incorporating 30 phr of IL169. Phosphorus modifies pyrolysis pathway, promotes charring and may act as flame inhibitor. The char layer protects the underlying polymer, leading to a high unburnt polymeric fraction. Char properties were studied using PCFC, Raman spectroscopy and X-ray tomography. Phosphorus improved the graphitization of the char and its thermo-oxidative stability.

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1. Introduction

Epoxy resins are widely used in many applications, including composite and coating industries. They are among the highest flammable thermosets together with unsaturated polyesters. Thus, many efforts have been made to improve the flame retardancy of these resins in order to extend their applications [1]. Phosphorus-based additives have been used as alternatives to halogen-based flame retardants (FRs) while some of the latter were banned due to environmental concerns [1–4]. Phosphorus-based epoxy monomers or curing agents have also been investigated as flame retardants [5–10]. Indeed, the reactive approach seems to be slightly more efficient, allows maintaining transparency, and is believed to suppress possible migration of flame retardants over time [11–12]. More recently, biobased additives or reactive hardeners have been developed [11,13] and some fully biobased and flame retarded epoxy resins have been synthesized [14].

According to the literature, phosphate and phosphonate-based

FRs act mainly in condensed phase by promoting charring of the epoxy resin [5–6]. Intumescent mono-component solutions led to a significant reduction of flammability. Phosphorus compounds decompose into phosphoric acids resulting in the dehydration of the epoxy resin which is necessary for promoting charring. However, the presence of phosphorus compounds could also reduce the thermal stability of the resin. Phosphinate and phosphine oxide-based FRs may be more active in gas phase, decreasing the combustion efficiency. The extent of flame retardancy depends primarily on the phosphorus content (typically higher than 1 wt%).

Ionic liquid (IL)-based epoxy resins are a new class of epoxy thermosets [15]. According to the literature, Livi et al. have demonstrated that the basicity of the ionic liquids (phosphinate, phosphate or dicyanamide) initiates the epoxy polymerization and binds covalently to the network through an anionic polymerization. These new curing agents of epoxy prepolymer lead to networks with enhanced final properties such as an excellent thermal stability, higher hydrophobic behavior and good thermo-mechanical properties [16–20]. Thanks to the great diversity of IL, properties can be finely tuned [21]. The thermal stability and flammability of ILs have already been studied, and vary to a great extent depending

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on their nature [22–23]. While some ionic liquids contain phosphorus groups, low-flammability epoxy resins can be expected without further addition of flame retardants.

The objective of this article is to assess the flame retardancy of epoxy resins crosslinked with various amounts of a phosphorus-based ionic liquid (namely IL169). The modes-of-action of phosphorus were identified and the properties of the char formed during burning were investigated in detail.

2. Experimental

2.1. Materials

Diglycidyl ether of bisphenol A (DGEBA) based epoxy prepolymer (DER 332) with an epoxide equivalent weight (EEW) of 175 g mol^{-1} was purchased from DOW Chemical Company. Jeffamine D230 was supplied by Huntsman and was used as conventional curing agent. Phosphonium ionic liquid: Tributyl(ethyl) phosphonium diethyl-phosphate named IL169 was kindly provided by Cytec, Inc. All the chemical structures are shown in Fig. 1.

To prepare samples, DGEBA and curing agents (i.e. Jeffamine D230 and IL169) were mixed with a suitable ratio under stirring at room temperature for 30 min. The mixture was then degassed in an ultrasonic bath for 15 min, and was poured into silicone molds prior to curing. The ratio between DGEBA and curing agents as well as the curing and post-curing conditions are presented in Table 1.

2.2. Differential scanning calorimetry

Differential Scanning Calorimetry thermograms (DSC) of epoxy/amine and epoxy/IL networks were recorded using a DSC Q20 TA instruments from 20 to 250 °C during heating at a rate of 10 K min^{-1} under nitrogen flow of 50 mL min^{-1} .

2.3. Thermogravimetric analysis

Thermogravimetric analyses (TGA) were performed using a Setsys Evolution apparatus (Setaram). $10 (\pm 2)$ mg-samples were heated under nitrogen flow (100 mL/min) at a heating rate equal to 10 °C/min from room temperature to 900 °C.

2.4. Pyrolysis-combustion flow calorimeter

Flammability was investigated using a pyrolysis combustion flow calorimeter (PCFC) which was developed by Lyon and Walters [24]. The sample ($3 \pm 1 \text{ mg}$) was first heated from 80 to 750 °C at 1 °C/s in a pyrolyzer under nitrogen flow and the degradation products were sent to a combustor where they were mixed with oxygen in excess at 900 °C. In such conditions, these products were fully oxidized. The heat release rate (HRR) was then calculated by oxygen depletion according to Huggett's relation (1 kg of consumed oxygen corresponds to 13.1 MJ of released energy) [25]. All materials were tested twice at least. The variation in main data (peak of heat release rate, total heat release and heat of complete combustion) was lower than 10% and the variation in the temperature of pHRR was around 10 °C .

The thermo-oxidative stability of residues from cone calorimeter was also studied in PCFC according to method B, i.e. in aerobic pyrolysis, for various oxygen fractions in pyrolysis chamber (from 0.01 to 0.4) as proposed elsewhere [26]. The temperature of char degradation is the temperature at which the HRR reaches 50 W/g .

2.5. Cone calorimeter

Some flame retardant effects (as barrier effect or flame

inhibition) are not effective in PCFC. Therefore fire behavior was also studied using a cone calorimeter (Fire Testing Technology) which is a powerful tool to investigate the fire behavior of polymers. A horizontal sample sheet of $100 \times 100 \times 3 \text{ mm}^3$ was placed at 2.5 cm below a conic heater and isolated by rock wool. The samples were exposed to 35 kW/m^2 in well-ventilated conditions (air rate 24 L/s) in the presence of a spark igniter to force the ignition. HRR was determined according to oxygen depletion (Huggett's relation) as in PCFC. This test was performed according to the ISO 5660 standard. All materials were tested twice with a good repeatability. The variation on main data (time-to-ignition, peak of heat release rate, total heat release, smoke extinction area, residue content and effective heat of combustion) was lower than 10% except for pHRR of 10IL and the char content was 20IL (15–20% of variation).

2.6. Raman spectroscopy

Raman spectra were carried out to study the graphitization of the chars. Spectra were measured using a Horiba Jobin Yvon LabRAM Aramis spectrophotometer fitted with a 532 nm laser and a $200 \text{ }\mu\text{m}$ confocal pinhole. The laser was focused using a $\times 10$ objective. All spectra were obtained with an integration time of 30 s accumulation of 4 spectra recorded in the spectral range $800\text{--}1900 \text{ cm}^{-1}$.

2.7. X-ray tomography analyses

X-ray tomography is a powerful tool to assess the morphology of the char [27–29]. To obtain 3D visualization of the inner residues, a fraction of $30 \times 30 \times 30 \text{ mm}^3$ of the residue collected from cone calorimeter test was analyzed using non-destructive Analysis X-ray micro-tomography EasyTom with a LaB6 filament and a flat panel with a resolution of 2320×2336 . The volume of material is $30 \times 30 \times 30 \text{ mm}^3$ with a resolution of 34 microns. The volume reconstruction was obtained from a set of 1900 slices obtained after 1800 rotations. The diagram of the analysis is shown in Fig. 2.

2.8. Scanning electron microscopy coupled with Energy Dispersive X-ray spectroscopy (SEM-EDX)

Chars were observed using a FEI Quanta 200 scanning electron microscope and char composition (C, O, P atoms) was determined by Energy Dispersive X-ray spectroscopy (EDX) using Oxford INCA Energy 300 system and a detector of 133 eV (at Mn). For each char, the composition of at least three zones was analyzed. Note that hydrogen content cannot be measured using SEM-EDX.

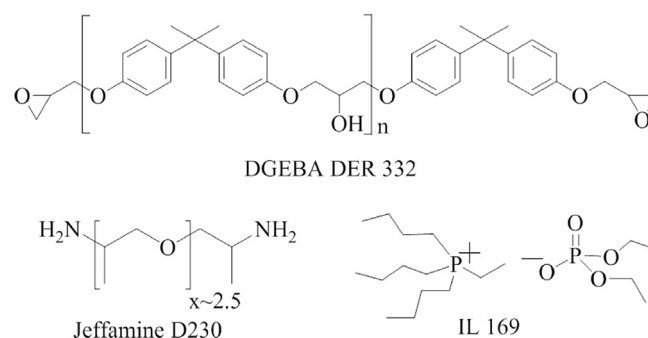


Fig. 1. Chemical structures used in this study.

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