Polymer Degradation and Stability 94 (2009) 2101–2106

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Short note

Thermal degradation of a reactive flame retardant based on cyclotriphosphazene and its blend with DGEBA epoxy resin

Mustapha El Gouri*, Abderrahim El Bachiri, Salah Eddine Hegazi, Mohamed Rafik, Ahmed El Harfi

Laboratory of Macromolecular & Organic Chemistry, Department of Chemistry, Faculty of Sciences, Ibn Tofaïl University, P.O.Box 133, 14000 Kenitra, Morocco

ARTICLE INFO

Article history:
Received 13 July 2009
Received in revised form
12 August 2009
Accepted 17 August 2009
Available online 27 August 2009

Keywords:
Synthesis
Epoxy resin
Flame retardant
Phosphazene
TG-FTIR

ABSTRACT

Hexaglycidyl cyclotriphosphazene (HGCP) was synthesized, and characterized by FTIR, ^{31}P, ^{1}H, and ^{13}C-NMR. This compound was used as a reactive flame retardant to blend with commercial epoxy resin DGEBA (Diglycidyl ether of bisphenol A). Its effect on the DGEBA decomposition pathways was characterized by studying both gas and solid phases produced during thermogravimetric analysis (TGA). The gases evolved during TGA in air were studied by means of thermogravimetry coupled with Fourier transform infrared spectroscopy (TG–FTIR), while the solid residues were analysed by FTIR and scanning electron microscopy (SEM). The results showed that HGCP presents a good dispersion in DGEBA, and the blend thermoset with 4,4′-methylene-dianiline (MDA) curing agent leads to a significant improvement of the thermal stability at elevated temperature with higher char yields compared with pure DGEBA thermoset with the same curing agent. Improvement has also been observed in the fire behaviour of blend sample.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

The objective of adding a flame retardant to a polymer is to increase the resistance of the material to ignition and to reduce the flame spread, so that the flame does not grow, but self extinguishes, while at the same time having minimal degradation of polymer properties. The resultant products are still combustible, and the use of the flame retardant is to minimize, not eliminate, the fire risk associated with the use of a polymer in a specific application. The use of flame-retardants may prevent a small fire from becoming a major catastrophe. Approximately 80% of fire deaths can be attributed to smoke inhalation [1].

There exist two approaches to achieve flame retardancy in polymers, generally known as the ‘additive’ type and the ‘reactive’ type. Additive type flame-retardants, which are widely used, are generally incorporated into polymers by physical means. This obviously provides the most economical and expeditious way of promoting flame retardancy for commercial polymers. Nevertheless, a variety of problems, such as poor compatibility, leaching, and a reduction in mechanical properties, weaken the attraction. The application of reactive flame-retardants involves either the design of new, intrinsically flame retarding polymers or modification of existing polymers through copolymerization with a flame retarding unit either in the chain or as a pendent group.

In recent years, there has been considerable interest in the phosphazene-based family of materials because they not only have a wide range of thermal and chemical stabilities, but also can provide improved thermal and flame-retardant properties to polymers and their composites [2,3]. Hexachlorocyclotriphosphazene is a versatile starting oligomer for the synthesis of phosphazene-based polymers. The chlorine groups attached to the phosphorus atoms are easily substituted by various nucleophiles to form reactive cyclotriphosphazenes.

Cyclotriphosphazene, as a ring compound consisting of alternating phosphorus and nitrogen atoms with two substituents attached to the phosphorus atoms, exhibits unusual thermal properties such as flame retardancy and self-extinguishability [4,5]. Cyclotriphosphazene has several advantages as a reactive flame-retardant functional oligomer. First, the flexible synthetic methodology can be developed for preparation of cyclotriphosphazene-based copolymers with various substituents, which allows us to obtain multifunctional initiators or terminators with ease. Second, thermal and non-flammable properties of the cyclotriphosphazene moieties can be conferred to the resulting polymers, especially, of low molecular weights [6–9].

Therefore, when cyclotriphosphazenes are incorporated into the network of thermoset polymers, they can increase the thermal properties and flame retardancy of the polymers because of phosphorous and nitrogen flame-retardant synergy. The reason is that

---

* Corresponding author. Tel.: +212 537329400; fax: +212 537329433.
E-mail address: gouri_mustapha@yahoo.fr (M. El Gouri).

0141-3910/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymdegradstab.2009.08.009

the thermal decomposition of the phosphazene-based polymers is an endothermic process, and phosphate, metaphosphate, polyphosphate generated in the thermal decomposition form a non-volatile protective film on the surface of the polymer to isolate it from the air; meanwhile, the non-flammable gases released such as CO_2, NH_3 and N_2 cut off the supply of oxygen so as to achieve the aims of synergistic flame retardancy [10,11]. The phosphazene-based polymers have more effective flame retardancy than any other flame-retardants, making them a new focus [12,13]. However, the phosphazene-based polymers used as a flame-retardant component with epoxy resins are seldom reported [14].

In this study we use a new reactive flame retardant based on hexaglycidyl cyclotriphosphazene (HGCP). It exhibits very good compatibility with and efficiency in conventional epoxy resin (DGEBA). This flame retardant is non-toxic, environmentally friendly material because it is free of halogen atoms. It does not contribute additional quantities of smoke due to the unique mechanism of "intumescence". The decomposition temperature is over 250 °C, suitable for epoxy resins, various processing and fabrication.

2. Experimental

2.1. Materials

Cyclotriphosphazene, 4,4′-methylene-dianiline (MDA) (Aldrich chemical company) and 2,3-epoxy-1-propanol (ACROS chemical company, 99%) stored at temperature of 4 °C to 6 °C, DGEBA (Epon828). All these materials were used without any further purification.

2.2. Instrumentation

Infrared spectra were recorded on a Vertex 70 FTIR spectrophotometer using KBr technique.^{1}H, ^{13}C, and ^{31}P nuclear magnetic resonance (NMR) Spectra were obtained on a Bruker AVANCE 300 NMR Spectrometer using $CDCl_3$ as solvent. Chemical shifts (δ-scale) are quoted in parts per million and following abbreviations are used: s = singlet; m = multiplet. Thermogravimetric analysis (TGA) were carried out on an SETARAM thermogravimetric analyzer (The SETSYS evolution) with a heating rate of 10 °C/min from room temperature to 600 °C under air atmosphere.

The DSC measurements were carried out using a PYRIS6 DSC in nitrogen atmosphere, with a heating rate of 10 °C/min under N_2 from 40 to 300 °C. UL 94 standard test carried out in terms of the method proposed by Underwriters Laboratory. It was used to evaluate the fire retardancy properties of the materials.

The microstructures of blend and the chars were recorded using "MEB ENVIRONNEMENTAL" scanning electron microscope (SEM).

2.3. General procedure of synthesis of hexaglycidyl cyclotriphosphazene (HGCP)

In the dry-box, a solution of 4 g of (2,3-epoxy-1-propanol) (0.054 mol) in 28.5 ml of toluene containing 5.41 g of triethylamine (0.053 mol) was prepared at room temperature. The mixture was cooled with an ice-water bath. A solution of 3 g of hexachlorocyclotriphosphazene (0.0086 mol) in 15 ml of toluene was very slowly dropped in with vigorous stirring (during a 3 h) while keeping the reaction mixture cool. After the addition was completed, the stirring was continued for another 45 h at room temperature. The reaction mixture was filtered to remove triethylamine hydrochloride salt as a precipitate produced from the reaction. The toluene solvent was removed by rotary evaporation. The obtained product was then dissolved in dichloromethane, washed with water, and dried over Na_2SO_4. A brown viscous product was finally obtained after removal of dichloromethane under vacuum, with a yield of about 73%.

2.4. Sample preparation

Epoxies (HGCP, DGEBA and there blend) were warmed to melt and the curing agent (Scheme 1) added and mixed until homogeneous. The resin-hardener mixture was then poured into preheated moulds and cured in a forced convection oven to make samples.

The mixture of the epoxy resin with 4,4′-methylene-dianiline (MDA) curing agent before the crosslinking was carried out according to the protocol adopted by Levan [15]. The formulations and cure schedules were as follows:

* The samples were prepared by mixing stoichiometric amount of MDA and epoxy resins HGCP, DGEBA and their blend.
* The samples thus prepared underwent a cycle of heating: one night at 70 °C,3 h at l00 °C,2 h at 120 °C,1 h at 140 °C and 30 min at 150 °C.

3. Results and discussions

3.1. Characterization of hexaglycidyl cyclotriphosphazene (HGCP)

In this paper we describe the synthesis of phosphazene substrate containing epoxide functionality (HGCP: hexaglycidyl cyclotriphosphazene) by direct reaction with 2,3-epoxy-1-propanol.

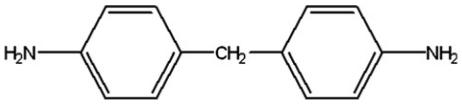
For the synthesis of (HGCP) one route is followed as outlined in the previous paragraph.

The method involves the addition of a solution of $[NPCl_2]3$ in toluene to a solution of TEA in toluene containing 2,3-epoxy-1-propanol which can afford a (HGCP). This route leads to the exclusive formation of hexaglycidyl cyclotriphosphazene. This was confirmed by the ^{31}P NMR spectra of the crude reaction mixtures which show a resonance signal at +9.32 ppm, characteristic of the (HGCP) and disappearance the signal at +20 ppm which indicates the presence of hexachlorocyclotriphosphazene.

Indeed, as reported in previous work [16–18], all compounds models show sharp singlet in the ^{31}P NMR spectra, located between $\delta + 9$ ppm and +10 ppm, to indicate a complete equivalence of the three phosphorus atoms present in the cyclophosphazene ring. These facts are considered a convincing evidence that the phosphazene ring is not destroyed during the synthetic work. This is in agreement also with the ^{31}P NMR data for our compound (HGCP), where only sharp singlet is showed at +9.32 ppm.

Moreover, ^{1}H and ^{13}C NMR spectra of the product confirm the chemical structure of the cyclophosphazene substituents and show that epoxy groups are attached to the cyclophosphazene nucleus. In fact, multiplets are observed in the ^{1}H NMR spectra of this compound in the range between 2.5 and 4,5 ppm attributable to the oxirane ring. While in ^{13}C NMR spectra we observed singlets: 44.6, 49, 69.5 ppm.

The analysis IR, realized on the product confirms the results mentioned above: Bands around 852 cm^{-1} (absorption indicates the oxirane ring), 2911, 2950 cm^{-1} (asymmetric and symmetric



Scheme 1. Chemical structure of 4,4′-methylene-dianiline (MDA) using as curing agent for epoxy resins.

Download English Version:

https://daneshyari.com/en/article/5203774

Download Persian Version:

https://daneshyari.com/article/5203774

Daneshyari.com