Melamine poly(zinc phosphate) as flame retardant in epoxy resin: Decomposition pathways, molecular mechanisms and morphology of fire residues

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ABSTRACT

Synergistic multicomponent systems containing melamine poly(metal phosphate)s have been recently proposed as flame retardants. This work focuses on the decomposition pathways, molecular mechanisms and morphology of the fire residues of epoxy resin (EP) flame retarded with melamine poly(zinc phosphate) (MPZnP) to explain the modes of action and synergistic effects with selected synergists (melamine polyphosphate (MPP) and AlO(OH), respectively). The total load of flame retardants was always 20 wt.%. The decomposition pathways were investigated in detail via thermogravimetric analysis coupled with Fourier transform infrared spectroscopy. The fire residues were investigated via elemental analysis und solid-state nuclear magnetic resonance spectroscopy. The morphology of intumescent fire residues was investigated via micro-computed tomography and scanning electron microscopy. EP + (MPZnP + MPP) formed a highly voluminous residue that showed structural features of both EP + MPZnP and EP + MPP, resulting in a highly effective protection layer. EP + (MPZnP + AlO(OH)) preserved the entire quantity of phosphorus content during combustion due to the formation of $Zn_2P_2O_7$ and $AlPO_4$.

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1. Introduction

Epoxy resins and their fiber reinforced composites exhibit excellent mechanical and electrical properties and have therefore become an important material in lightweight construction and for electrical and electronic equipment [1,2]. However, the inherent flammability of epoxy resins makes the use of flame retardants necessary for many of their typical applications. Until recently, halogenated compounds were widely used as flame retardants for epoxy resins, but these are currently being phased out due to environmental concerns [3,4] and replaced with metal hydroxides, melamine derivatives and phosphorus-based compounds [5−11].

Melamine polyphosphate (MPP) is an effective and versatile halogen-free flame retardant that combines the benefits of phosphorus-based and melamine-based additives and often exhibits synergy with other flame retardants in epoxy resins and in other polymeric materials [12−17]. Melamine poly(metal phosphates) (MPMeP), recently commercialized under the brand name Safire® [18,19], have been proposed as an "enhanced version" of MPP and were investigated as flame retardants in polyamide by Bourbigot et al. with promising results [20−22].

One kind of MPMeP, melamine poly (zinc phosphate) (MPZnP), was investigated as a flame retardant in epoxy resin to assess its performance and synergy in performance with other flame retardants [23]. Synergistic effects were observed between MPZnP and MPP as well as between MPZnP and boehmite (AlO(OH)), as evident from UL 94 classification and the forced flaming behavior in cone calorimeter investigations. These observations gave reason to study in greater detail the interaction between MPZnP, MPP, AlO(OH) and the EP matrix during the decomposition.

This work provides a deeper understanding of how MPZnP works as a flame retardant in epoxy resin by presenting a detailed investigation of the decomposition pathways, molecular mechanisms and the morphology of the fire residues via thermogravimetry coupled with Fourier transform infrared spectroscopy (TGA-

FTIR), [27]Al and ^{31}P solid-state nuclear magnetic resonance spectroscopy (NMR), elemental analysis, micro-computed tomography (μ-CT) and scanning electron microscopy (SEM).

2. Experimental

2.1. Materials and specimen preparation

Unless stated otherwise, all raw materials were used as received. DGEBA (Araldite MY740) was purchased from Bodo Möller Chemie GmbH (Offenbach, Germany) and isophorone diamine from Merck KGaA (Darmstadt, Germany). MPZnP was provided by Floridienne Chimie[†] (Ath, Belgium). Boehmite (Apyral AOH 30) was kindly donated by Nabaltec AG (Schwandorf, Germany) and MPP (Melapur 200 70) by BASF SE (Ludwigshafen, Germany).

DGEBA, IPDA and the flame retardants were combined in a glass beaker and mixed thoroughly with a mechanical stirrer for at least 10 min. The total load of flame retardants was 20 wt.% in all cases (Table 1). The mixture was poured into open aluminum molds and ceramic molds with a height of 3 mm and put into an oven for 30 min at 80 °C, 30 min at 110 °C and 60 min at 160 °C.

The materials were slowly cooled down to room temperature to prevent cracking and then cut down to plates of 100 mm × 100 mm for cone calorimeter tests. Some amount of each material was cryogenically grinded to obtain powdered material for thermal analysis.

The specimens for μ-CT were prepared using custom made ceramic molds with removable edges and an inner surface area of 100 mm × 100 mm. By curing the mixture of DGEBA, IPDA and flame retardants inside the ceramic mold, perfect attachment of the specimen to the bottom of the mold was ensured. The fire residues for μ-CT were prepared by burning the materials inside the special ceramic mold using the cone calorimeter at an irradiation of 50 kW/m² and a starting distance of 35 mm. For strongly intumescent materials, the distance was gradually increased during combustion to avoid physical contact between the specimen and the heating cone to ensure undisturbed growth of the fire residue.

For scanning electron microscopy (SEM) of the fire residues, small pieces were carefully cut out both from the surface and from an inner layer of the residues and then gold coated.

2.2. Measurements

For thermogravimetric analysis (TGA), a TG 209 F1 Iris from NETZSCH (Selb, Germany) was used. A sample (powder) of 10 ± 0.1 mg was heated from 30 to 900 °C under nitrogen, applying a heating rate of 10 °C/min. Two measurements were performed and the results averaged for each material. For TGA coupled with Fourier transform infrared (FTIR) spectroscopy, the TG 209 F1 Iris was coupled with a Tensor 27 (Bruker, Germany) FTIR spectrometer. The transfer line between both devices and the spectrometer's gas cell were heated to 250 °C to avoid condensation of the pyrolysis products.

Cone calorimeter (FTT, East Grinstead, UK) investigations were performed in accordance with ISO 5660. An irradiation of 50 kW/m² was applied with a distance of 35 mm between heating cone and specimen, taking into account the intumescence of some materials. It was pointed out in previous investigations that increasing the distance from 25 to 35 mm does not significantly alter the homogeneity of the applied heat flux [24,25]. Samples were measured using a retainer frame including an additional simple thin wire cross to prevent them from buckling before ignition. Results were calculated for a sample surface area of 100 cm² despite the retainer frame, as the combustion of the specimens included the edges beneath the frame. Since some samples did not exhibit a distinctive point of flameout due to excessive intumescence, flameout was declared when the smoke production dropped below 0.01 m²/s. This criterion was applied to all systems for comparability. Two measurements were performed and averaged for each material. A third specimen was measured whenever the first two measurements deviated from each other by more than 20% in any characteristic parameter.

μ-CT of the fire residues was performed with a custom made setup consisting of a 225 kV X-ray source XWT 225-SE (X-RAY WorX, Garbsen, Germany), a rotatable table and a 2048 × 2048 pixel detector PE 1621 (Perkin Elmer, Waltham, USA), as described in Ref. [26]. An accelerating voltage of 40 kV and a filament current of 600 μA were applied.

SEM micrographs were recorded with a Zeiss EVO MA 10 (Zeiss, Oberkochen, Germany) at an acceleration voltage of 10 kV.

Elemental analysis (EA) was done by Mikroanalytisches Laboratorium Kolbe (Mühlheim an der Ruhr, Germany).

^{27}Al and ^{31}P solid-state NMR experiments were performed on a Bruker Avance 600 spectrometer (B0 = 14.1 T). All experiments were carried out at room temperature using a 2.5 mm magic angle sample spinning (MAS) probe. The MAS frequency was 25 kHz for [27]Al and 12.5 kHz for ^{31}P NMR. Data analysis was performed with the software TopSpin version 2.1. ^{31}P MAS NMR spectra were recorded at a Larmor frequency of 2042.9 MHz using a 90° pulse of 4 μs, and high power ^{1}H TPPM (two pulse phase modulation) decoupling was carried out with a 15° two pulse phase modulation (TPPM) sequence [27]. The repetition time was 300 s to ensure full spin-lattice relaxation, and 16 scans were accumulated. In addition, [1]H—[31]P cross polarization (CPMAS) was carried out using a CP contact time of 2 ms, a repetition time of 2 s and 32 scans. The ^{31}P spin lock field was held constant while the ^{1}H spin lock field was ramped down to 50% of its initial value. [1]H TPPM decoupling was applied as well. [31]P chemical shifts (δ) relative to hydroxyapatite are reported as a secondary standard at 2.3 ppm. ^{27}Al MAS NMR measurements were run at a Larmor frequency of 156.3 MHz using a selective 90° pulse of 2 μs and repetition times of 2 s. No ^{1}H decoupling was required because of the high MAS frequency of 25 kHz. 128 scans were accumulated. [27]Al chemical shifts (δ) relative to the narrow octahedrally coordinated signal of YAG are reported at 0.6 ppm.

Table 1
Prepared materials: Composition (loading of flame retardants), phosphorus, and nitrogen content.

Material	MPZnP in wt.%	MPP in wt.%	AlO(OH) in wt.%	P Content in wt.% ± 0.2	N content in wt.% ± 0.4
EP	–	–	–	–	3.1
EP + MPZnP	20	–	–	2.7	8.9
EP + MPP	–	20	–	2.8	6.7
EP + AlO(OH)	–	–	20	–	2.5
EP + (MPZnP + MPP)	10	10	–	2.8	10.0
EP + (MPZnP + AlO(OH))	10	–	10	1.4	5.7