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Intrinsically flame retardant epoxy resin – Fire performance and background – Part II

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ABSTRACT

The flame retardant mechanism of a newly synthesized phosphorus-containing reactive amine, which can be used both as crosslinking agent in epoxy resins and as flame retardant, was investigated. The mode of action and degradation pathway were investigated by in situ analysis of the gases evolved during the degradation by thermogravimetric measurements coupled online with infrared (TG-EGA–FTIR) and mass spectroscopy (TG/DTA-EGA–MS) and by solid residue analysis by infrared (ATR) spectroscopic methods and X-ray photoelectron spectroscopy (XPS). It was observed that the main difference in the degradation of the reference and the flame retardant system is that the degradation of the latter begins at lower temperature mainly with the emission of degradation products of the phosphorus amine, which act as flame retardants in the gas phase slowing down the further degradation steps. At the high temperature degradation stage the solid phase effect of the phosphorus prevails: the formation of phosphorocarbonaceous intumescent char results in a mass residue of 23.4%. The ratio of phosphorus acting in gas phase and solid phase, respectively, was determined on the basis of thermogravimetric and XPS measurements.

1. Introduction

Epoxy resins have been commercially available for 60 years and have found use mainly in industrial applications where their exceptional characteristics such as good adhesion to many substrates; moisture, solvent and chemical resistance; low shrinkage on cure; outstanding mechanical and electronic resistance properties justify their higher costs compared to other thermosets. They are widely used as adhesives, surface coatings, laminates and matrix materials in electronic, transport and aerospace industries, however their thermal and fire resistance needs to be improved in many applications. Fire retardancy, as an outstanding requirement of safety, is one of the key challenges for society in our century. The increasing focus on the health and environmental compatibility of flame retardants has drawn the attention to the organophosphorous reactive flame retardants [1–3]. The new European Directive 2002/95/EC [4], requiring the substitution of some widely used brominated flame retardants (polybrominated biphenyls (PBB) and polybrominated diphenyl ethers (PBDE)) in new electrical and electronic equipment put in the market from 1 July 2006, also facilitates the development and increased use of phosphorus flame retardants. In the case of epoxy resins, the phosphorus-containing chemical unit providing the flame retardant effect can be incorporated into the epoxy component, the crosslinking agent or into both of them. From the many possible alternatives the combination of an aliphatic epoxy component – more difficult to flame retard than the aromatic ones – and a simple phosphorus-containing crosslinking agent was chosen.

In the current literature an increasing number of papers deal with the mode of action of reactive organophosphorous flame retardants in an epoxy resin matrix [3,5,6], however there are no references dealing with the degradation of aliphatic epoxy resin systems. Earlier studies focus on aromatic epoxy and aromatic phosphorus compounds such as DOPO and derivatives. Concerning the mode of action of organophosphorous flame retardants both condensed phase and gas phase actions have been reported, but only few systematic studies are available taking into account the chemical structure of the phosphorus compound, the chemical environment, and the interaction with the polymer matrix during

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degradation. Hergenrother et al. [6] found that with increasing oxidation state of phosphorus the condensed state action is increasing. Similarly, Braun et al. [3] observed that decreasing the oxidation state of phosphorus resulted in an increase of the flame retardancy, which was supposed to be explained by the increasing gas phase action. Nevertheless, no reference was found dealing with the determination of the ratio of phosphorus acting in solid phase and gas phase, respectively.

In this work the mode of action and degradation pathway of an aliphatic epoxy resin system was investigated by analysis of the gases evolved during the degradation by thermogravimetric measurements coupled with infrared and mass spectroscopy and by solid residue analysis by infrared spectroscopic methods and X-ray photoelectron spectroscopy. The ratio of phosphorus acting in the gas phase and solid phase, respectively, was determined on the basis of thermogravimetric and XPS measurements. The better understanding of the degradation mechanism is crucial for further improving the fire retardant performance of epoxy networks.

2. Experimental

2.1. Materials

The polymer matrix was ER type Eporezit AH-16 (non-modified, resin like reactive dilutant, epoxy equivalent: 160–175; viscosity at 25 °C: 800–1800 mPa s; density at 25 °C: 1.24 g/cm^3, hydrolysable chlorine content: 1.5 mass%) used with Eporezit T-58 curing agent (amine number: 460–480 mg KOH/g; viscosity at 20 °C: 100–200 mPa s; density at 20 °C: 0.944 g/cm^3; curing time: 2 days at 25 °C) supplied by P+M Polimer Kémia Kft., Hungary. Schemes 1 and 2 show the main components of Eporezit AH-16 and Eporezit T-58.

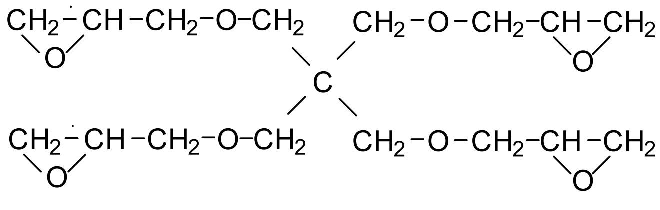
A newly synthesized phosphorus-containing reactive amine, TEDAP (amine number: 510–530 mg KOH/g; viscosity at 20 °C: 400 mPa s; curing time: 7 days at 25 °C, 4 h at 80 °C) (Scheme 3) was used as flame retardant [7].

2.2. Methods

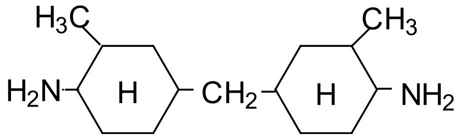
Preparation of epoxy resin samples: the epoxy and curing agent amine components were mixed at room temperature in a glass beaker in order to obtain a homogenous mixture. A silicone mould 120 mm long, 15 mm wide and 3 mm thick was used for preparing the cured samples.

The fire resistance was characterized by Limiting Oxygen Index measurement (LOI, according to ASTMD 2863), UL-94 test (according to ASTM 1356-90 and ANSI//ASTM D-635/77), Mass Loss Calorimeter (according to ISO 13927, Fire Testing Technology, heat flux of 50 kW/m^2), and Glow Wire Flammability Index test (GWFI, PTL DR. GRABENHORST, D-8652 Stadtsteinach, T03.34 type apparatus, according to IEC 60695-2-12).

The thermal treatment of the cured epoxy resin samples was done in the furnace of a TA Instruments AR2000 type rheometer. The temperature program consisted of a linear part with a heating rate of 10 °C/min from room temperature to the appropriate temperature (in the temperature range of 200–400 °C) and a subsequent 10 min isotherm part at the final temperature.



Scheme 1. Main component of Eporezit AH-16.



Scheme 2. Main component of Eporezit T-58.

The attenuated total reflection infrared (ATR-IR) spectroscopic measurement of the epoxy resin samples after thermal treatment was done on a Labram type ATR-IR apparatus (Jobin Yvon, France). The IR spectra were processed using LabSpec 4.02 software.

The gases evolved during thermal degradation of the epoxy resin were analysed using coupled techniques:

TG/DTA–MS: A TA Instruments SDT 2960 apparatus was coupled with Balzers Instruments Thermostar GSD 300 T3 type mass spectrometer (detector: Quadrupole CH-TRON, operating methods: SCAN, MID). The coupling element was a quartz transfer tube heated to 200 °C. First, mass spectra of the evolved gaseous mixtures were continuously scanned and collected between $m/z = 1–200$ (SCAN-mode), then 64 mass/charge numbers were selected and their ion currents were monitored in Multiple Ion Detection (MID) mode with the measuring time of 0.5 s for each channel. Samples with initial mass of 7–11 mg were heated in an open Pt crucible. The temperature program consisted of a linear part with a heating rate of 10 °C/min from 20 °C to 600 °C in air.

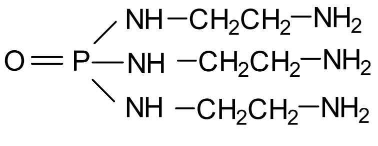
TG–FTIR: TGA 2050 type thermogravimetric analyzer was coupled to a Bio-Rad Excalibur Series FTS 3000 type FTIR spectrophotometer with external gas cell heated to 180 °C. The temperature program consisted of a linear part with a heating rate of 10 °C/min from 20 °C to 600 °C in air. Samples with initial mass of 42–110 mg were heated in open Pt crucible.

For performing an elemental analysis of the pyrolysis residues X-ray photoelectron spectroscopy (XPS) analysis was carried out on a Kratos XSAM 800 type spectrometer (15 kV, 15 mA) using 1253,6 eV energy characteristic X-ray of Mg K$\alpha_{1,2}$ radiation. It was focused on a spot having a diameter of ~2 mm. The general spectra were taken with an energy step of 0.5 eV steps up to 1250 eV, while the detailed spectra were taken in 0.1 eV steps.

3. Results

The flame retardancy of the AH-16–T-58 reference epoxy resin and the flame retarded AH-16–TEDAP system was compared in detail in the previous article of the authors [7]. In this paper, after a short summary of flame retardancy results, we compare the degradation mechanisms of the two systems and investigate the mode of action of the organophosphorous flame retardant.

The synthesized phosphorus-containing amine, TEDAP is suitable for substitution in place of the traditional epoxy resin curing agents additionally providing excellent flame retardancy: the epoxy resins flame retarded this way reach 960 °C GWFI value, 33 LOI value and V-0 UL-94 rating – compared to the 550 °C GWFI value, 21 LOI value and HB UL-94 rating of the reference epoxy



Scheme 3. Structure of the synthesized phosphorus-containing reactive amine, TEDAP.