IMPROVING THERMAL AND FLAME RETARDANT PROPERTIES OF SORBITOL BASED BIOEPOXY BY PHOSPHORUS-BASED FLAME RETARDANTS

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Main message: The range of phosphorus-containing flame retardants (PFRs) is extremely wide since P exists in several oxidation states. The effect of some additive PFRs with different oxidation states: aluminum diethyl phosphinate (+1), phosphonate polyol (+3), ethyl ethylene glycol phosphate and ammonium polyphosphate (+5), on the thermal and FR properties of a bio-epoxy resin have been assessed. Also, the cooperative effect of melamine cyanurate (MC) with APP and AlPi has been discussed.

Keywords: Bio-epoxy, flame retardancy, phosphinate, phosphonate, phosphate

Introduction

Epoxy resins represent one of the most important thermosetting polymers because of their remarkable properties. Recently, biobased epoxy resin systems have got increasing attention due to their environmental benefits in addition to the variety of their natural resources [1]. The highly functional sorbitol glycidyl ethers are widely used as epoxy monomers. In general, they enhance cross-linking densities paralleled by an improved performance [2].

Many attempts have been made to improve the flame retardancy of epoxy resins while simultaneously maintaining the outstanding properties of end products [1, 3]. The use of phosphorus-containing compounds as flame retardants for epoxy resins has been studied extensively. These compounds can work in the gas phase or in the condensed phase, depending on the flame-retardant composition and the different interactions within the other components of the epoxy resin system [4].

Experimental

The flammability of the samples was characterized by limiting oxygen index measurement (LOI), UL-94 flammability test, and mass loss type cone calorimeter. Differential Scanning Calorimetry (DSC) tests were carried out in order to determine the glass transition temperature (T_g). Thermogravimetric Analysis (TGA) was used to identify the different phase mechanism of flame retardants. The morphology of the residues obtained after cone calorimeter measurements was characterized by Scanning electron microscopic (SEM) micrographs.

Results and Discussion

The self-extinguishing behavior was displayed in EP/FR blends at 3% P-content when AlPi, APP, and alkyl phosphate flame retardants were used. Phosphonate polyol-containing samples showed the lowest T_g values and the lowest thermal stability among the investigated samples. However, in case of APP and AlPi blends, the good flame retardancy was combined with relatively good Tg due to their rigid particles which can maintain their morphology in the cross-linked epoxy matrix.

The development of charring effect by increasing oxidation state was confirmed by increasing char yield and decreasing peak of heat release rates (pHRR) in the same order. Alkyl phosphate showed a potential activity in the gas phase due to the low stability of phosphorus ester bonds present in its molecules, which on the other hand competes with its activity in the condensed phase. Also, the charring effect is not very significant in case of the used phosphonate polyol due to the low P-content and the long aliphatic chains in its structure.

Even though UL-94 rates were declines when MC was used with AlPi or APP, it helps to decrease TTI, pHRR, and FIGRA values significantly, meaning that the incorporation of MC reduces the propensity of quickly growing fire.

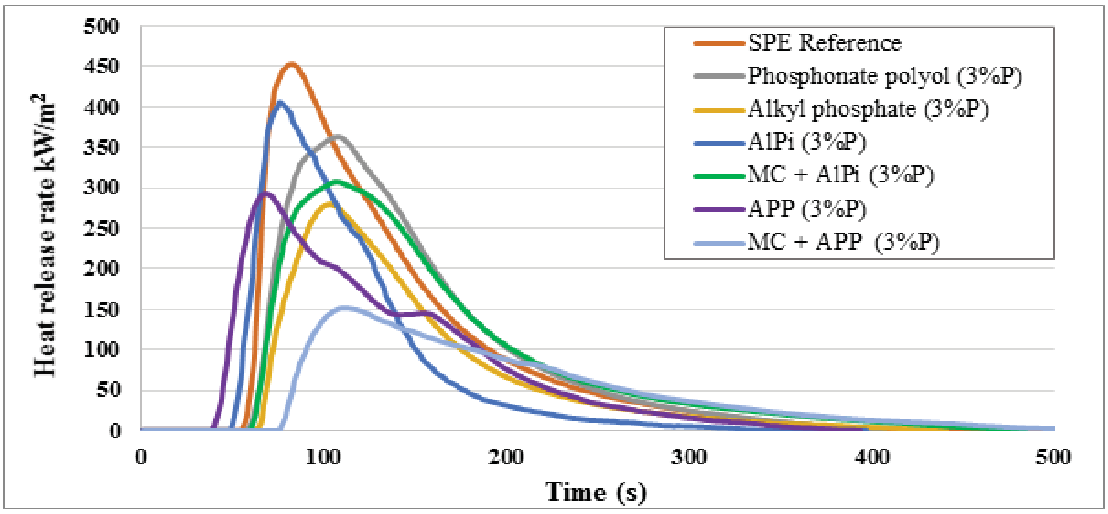

FIGURE 1. Heat release rate (HRR) for a heat flux of 25 kW/m^2 of SPE reference sample and its blends with 3%P content FRs.

TABLE 1. T_g, LOI, and UL-94 results of the reference sample and flame retarded formulations.

Sample	**T_g [°C]**	**LOI [%]**	**UL-94 rate**
SPE reference (0%P)	121	22	HB (20 mm/min)
Phosphonate polyol (3%P)	48	29	V-1
Alkyl phosphate (3%P)	78	27	V-0
AlPi (3%P)	32	32	V-0
AlPi (3%P) + MC	97	31	V-1
APP (3%P)	107	32	V-0
APP (3%P) + MC	100	35	V-0

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