DEVELOPMENT OF A FULLY WATERBORNE FLAME RETARDANT SUGAR-BASED EPOXY SYSTEM

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Main message: The recent industrial trends in production favor the replacement of organic solvents towards greener chemical processes, which can be accomplished by the utilization of aqueous systems. Fully waterborne epoxy system was prepared from waterborne sorbitol-based epoxy resin cured with a waterborne polyamine hardener. The flame-retardant property was accomplished by the application of different additive phosphorous flame retardants (FRs) with different phosphorous oxidation states: aluminum diethyl phosphinate (+1), phosphonate polyol (+3), ethyl ethylene glycol phosphate and ammonium polyphosphate (+5).

Keywords: Water borne epoxy system, flame retardancy, phosphinate, phosphonate, phosphate

Introduction

Epoxy resins have been widely used in adhesives, coatings, composites, marine and aerospace applications. Waterborne epoxy systems are widely used due to their good chemical resistance and exceptional adhesion [1]. The formation of the cured waterborne system has been studied widely [2]. In some applications of waterborne epoxy systems, waterborne epoxy curing agents can be used directly with solvent-based epoxy resins. However, these semi-solvent semi-aqueous systems has lower performance comparing to the all-water borne system [1].

Epoxy resins have inherent flammability like all other polymers. Halogen-free flame retardants (FRs), especially phosphorus-containing compounds have been developed due to low toxicity and high efficiency. They can act in the condensed phase or in the gas phase or in both, the mode of activity depends on the flame-retardant composition and the possible interactions during combustion within the other components of the polymer system [3].

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.

Results and Discussion

The results were very promising as all the investigated FRs accomplished the self-extinguishing V-0 rate according to UL-94 standard tests at 3% P-content, Alkyl phosphate and AlPi showed V-0 rate at 2% P, and APP containing samples reached V-0 rate even at 1% P. Limiting oxygen index (LOI) values were good for all flame retarded samples (the highest reached LOI value 62% for APP sample at 3% P).

Phosphonate polyol-containing samples showed the lowest thermal stability among the investigated samples due to the lower P-content and the higher content of hydroxyl groups leading to more water evaporation by dehydration reactions. Also, the charring effect is not very significant in case of the used phosphonate polyol due to the long aliphatic chains in its structure.

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.

According to HRR results, it can be determined that by increasing the phosphorus content, the THR and peak values of HRR are decreased, which shows a good correlation with LOI and UL-94 results. Moreover, in most cases, a significant shift in time of pHRR was observed.
When AlPi has been added, the THR and pHRR were relatively high, indicating an insufficient barrier effect of the formed char. In the case of SPE samples containing APP, the THR decreased by 43% and pHHR decreased dramatically by 56% at 3%P content compared to the reference epoxy matrix due to the very efficient solid phase mode of actions.

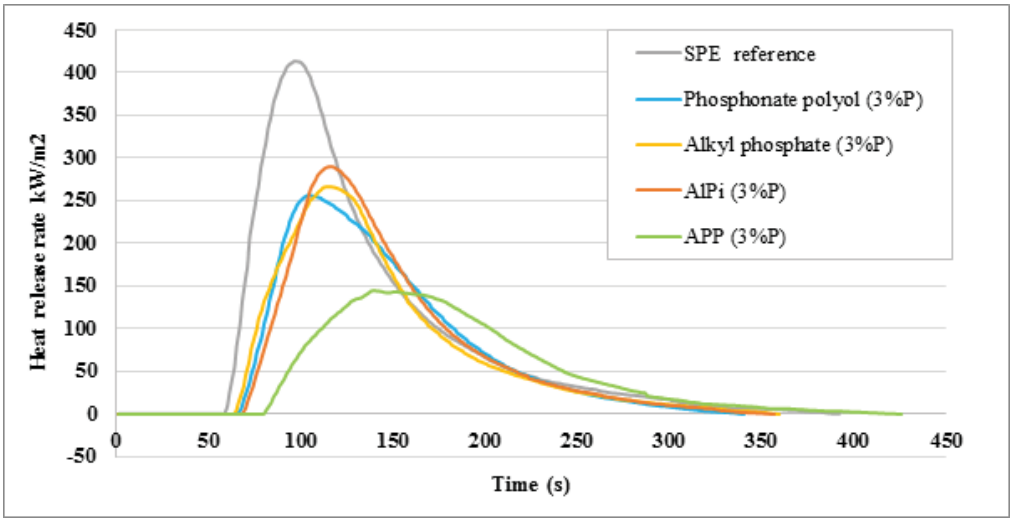

FIGURE 1. Heat release rate (HRR) for a heat flux of 25 kW/m^2 of SPE reference sample and its blends with 3%P content FRs.

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

Sample	LOI [%]	UL-94 rate
SPE reference (0%P)	22	HB (22.7 mm/min)
Phosphonate polyol (3%P)	34	V-0
Alkyl phosphate (3%P)	33	V-0
AlPi (3%P)	34	V-0
APP (3%P)	62	V-0

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