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Blends of unsaturated polyester and phenolic resins for application as fire-resistant matrices in fibre-reinforced composites. Part 2: Effects of resin structure, compatibility and composition on fire performance

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ABSTRACT

The effects of co-curing blends of an unsaturated polyester (UP) with inherently fire-retardant and char-forming phenolic resoles (PH) on the thermal stability and fire retardancy of the resulting resins have been investigated. To overcome the challenge of UP/PH incompatibility, arising from their different chemical structures and curing mechanisms (radical *vs.* condensation), different phenolic resoles have been used: ethanol-soluble, epoxy-functionalized, and allyl-functionalized. A traditional water-based resole has also been used to give a reference non-compatible system. In Part 1 of this series of publications it was shown that the compatibility of the two resins increases with functionalization; the allyl-functionalized resole showing the best compatibility with UP. Limiting oxygen index measurements and cone calorimetry have shown that fire performance of the functionalized PH resins and their blends with UP is worse than that from the unfunctionalized PH resin, but still significantly better than that of the UP. To understand this behaviour, thermal analyses coupled with infrared spectroscopy of volatile degradation products have been used on all resins and their blends, based on which, mechanisms of their decomposition and interactions are proposed, and the effects of these on flammability are discussed.

1. Introduction

Fire, smoke and toxicity standards for glass fibre-reinforced polymeric composites (GRPs) based on unsaturated polyesters (UP) and used in marine and mass transit systems especially, are closely monitored. UP resins burn readily in air, their aromatic contents from species such as styrene and phthalic acid functionalities, cause significant smoke generation [1]. Typical halogenated flame-retardant formulations used for UP systems serve the purpose of reducing flammability but consequent increases in the corrosiveness, toxicity and the smoke content of the resultant combustion products are major disadvantages. Inorganic additives such as alumina trihydrate reduce flammability and smoke production, but for them to be effective, very high quantities (typically >50 wt%) are required, which cause processing problems and adversely affect the mechanical properties of laminates based on these resins [2–4]. Even chemically reactive type flame-retardant additives are usually required in concentrations >30 wt% to be effective enough to pass commercial flammability tests [2,3]. An environmentally friendly alternative is to blend the resin with another inherently flame-retardant and char-forming resin such as a phenolic [2,3,5] or melamine formaldehyde resin.

Polymer blending is designed to generate materials with optimized chemical, structural, mechanical, morphological or biological properties. Ideally, in a polymer blend the components are chosen such that the weaknesses of one polymer can, to a certain extent, be masked by the strengths of the other and vice versa [6]. Preparation of different ratios of blended polymers requires many combinations and each has to be individually characterized [7]. In a polymer blend two or more polymer chains having constitutionally or configurationally differing features are in intimate combination but not bonded to each other. Polymer blends will typically display the good properties of each polymer. UP resins can be blended with epoxy resins [8–10]; similarly phenolic resins can be blended easily with epoxies [11]. Blending of UP with phenolic resins, however, is a challenge owing to the different curing mechanisms of these two resins: resoles (phenolic resins bearing reactive methylol groups) cure by condensation reactions

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with the elimination of water (incompatible with UP) and novolacs (phenolic resins to which a formaldehyde derivative, e.g. hexamethylenetetramine, has to be added to effect cure) are cured, usually under pressure to prevent the release of volatiles, at temperatures of up to 180–200 °C [12]. UP resins, on the other hand, are cured by a free radical process after the addition of a crosslinking monomer such as styrene, usually at temperatures below 80 °C [13]. Nevertheless, interpenetrated cured structures have been formed from UP and some phenolic resoles by vigorous dispersive mechanical stirring followed by a multistage curing regime [13,14].

The main aims of this research are to reduce the flammability of UP by blending with compatibilized phenolic resoles (PH) [15], to study the effects of different PH on the flammability/fire retardancy of UP, and to understand the mechanisms of decomposition of different types of blends and how these impact upon fire peformance. Compatibilization strategies include the use of a common solvent, or the chemical functionalization of at least one of the components of the blend [13,15]. Four different commercially available PH resoles, PH1, PH2, PH3 and PH4 have been selected and blended with a UP. PH1 is water soluble; PH2, although having structure similar to that of PH1, is ethanol-soluble; PH3 is epoxy-functionalized; and PH4 is functionalized mainly with allyl groups. PH1 was chosen so that we could blend a traditional water-based resole with UP to give a reference, non-compatible system, whilst the three other resoles have been shown to have increased compatibility with UP in that PH2 employs a solvent (ethanol) with which both resins are compatible, PH3 is also isopropanol-based but in addition has the epoxy functionality, which may react during curing with any terminal carboxylic acid groups in the UP, and the allyl groups in PH4 have the potential to co-cure, free radically, with the carbon–carbon double bonds in the UP backbone and the styrene crosslinking monomer present in the UP. In Part I of this series of publications [13], the physical and chemical properties of cured UP/PH mixtures have been investigated, principally by differential scanning calorimetry (DSC), differential mechanical thermal analysis (DMTA), solid-state 13C NMR spectroscopy and scanning electron microscopy (SEM). The results have shown that the compatibility of UP with PH increases in the order PH4 > PH3 > PH2 > PH1. In this part we describe our studies of the effects of PH structure and blend compatibility on fire performance.

2. Experimental

2.1. Materials

The following materials were obtained from commercial sources:

Crystic® 2.406PA, Scott-Bader: an unsaturated, phthalic anhydride-based UP containing 35–40 wt% styrene, pre-accelerated with cobalt octoate.

Catalyst M, Scott-Bader: a methyl ethyl ketone peroxide-based radical catalyst for UP curing.

Durez 33166, Sumitomo-Bakelite Europe N.V: a water-based phenolic resole containing 25–30 wt% water (PH1).

Durez 33156, Sumitomo-Bakelite Europe N.V: an ethanol-based phenolic resole containing 20–29 wt% ethanol (PH2).

Plyophen 23983, Sumitomo-Bakelite Europe N.V: an isopropanol-based, epoxy-functionalized, phenolic resole containing 16–18 wt% isopropanol and <6 wt% water (PH3).

Methylon 75108, Sumitomo-Bakelite Europe N.V: a solvent-free, allyl-functionalized, phenolic resole (PH4).

The chemical structures of these products have been given before [13]; all were used as received.

2.2. Casting and curing of resins and resin mixtures

A sample of cured UP resin was prepared by mixing 60 g resin with 2 wt% of catalyst M with a mechanical stirrer in a 100 mL beaker. 11 g of this mixture was then poured into a 5.5 cm diameter circular aluminium open mould to a depth of 3 mm. The specimen was then allowed to cure at room temperature for 24 h and post-cured at 80 °C in an oven for 4 h. Samples of PH resins (Table 1) were directly transferred to 5.5 cm diameter circular moulds (11 g in each case), again to depths of 3 mm, cured and then post cured by increasing the temperature slowly up to 200 °C; detailed curing conditions are given in Part 1 of this series of papers [13].

The formulations of the major resin blends (Table 1) were prepared by mixing UP and each PH in 70/30 or 50/50 wt% ratios with a mechanical stirrer (IKA® RW 16 overhead electric, four bladed propeller stirrer) at high shear (900 rpm) in a 100 mL beaker. The required quantity of catalyst M (2 wt% with respect to UP) was added to the resin mixture which was stirred for a further 10 min. The resulting resin mixtures (11 g for each specimen) were transferred to aluminium moulds, cured at RT for 24 h and then post cured by increasing the temperature slowly up to 190 °C; detailed curing conditions are again given in Part 1 [13].

2.3. Flammability study

2.3.1. Limiting oxygen indices

The limiting oxygen indices (LOI) of all cured resins and their blends were measured according to a standard method (BS 2782) using a Fire Testing Technology (FTT) LOI instrument equipped with an oxygen analyzer. At least five specimens of dimensions 100 mm × 10 mm × *ca.* 3 mm were tested for each sample.

2.3.2. Cone calorimetry

A cone calorimeter (Fire Testing Technology Ltd, UK) was used to assess the flammability parameters of the UP-based systems studied in this work. Circular samples measuring 55 mm in diameter with a nominal thickness of *ca.* 3 mm were fire tested in the horizontal mode with an ignition source at an applied heat flux of 50 kW/m^2. Before testing, the bottom surfaces and the edges of the samples were wrapped with aluminium foil to ensure that only the top surfaces would be directly exposed to the heat source. A minimum of three tests were performed for each formulation.

Previously in our laboratories, a comparative study of the round and standard square samples (100 mm × 100 mm) was undertaken in order to understand the effect of geometry on flammability properties of polymeric materials [16]. Circular specimens with a four-fold reduction in area gave similar results for the peak heat release rates (PHRR), total heat release (THR) and effective heat of combustion (EHC). Smoke, CO and CO_2 production results were found to be different from those measured for standard specimens since these parameters are dependent on exposed specimen surface area. However, in the study reported here, these data were used for comparison purposes with respect to the control specimens hence there was no need for adjustments.

2.3.3. Thermogravimetry-FTIR study

Thermogravimetric analyses (TGA) of all cured resins and their blends were performed on an SDT 2960 simultaneous DTA (differential thermal anlaysis) – TGA instrument from room temperature to 800 °C using 15 ± 1 mg samples heated at a constant rate of 10 °C/min in both air and nitrogen flowing at 100 ± 5 mL/min. The experiments were performed in duplicate and showed good reproducibility. Averaged data is presented. During the experiments in nitrogen and some of the experiments in air, the SDT 2960 simultaneous thermogravimetric analyzer was linked to a Nicolet

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