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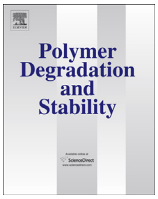

Blends of unsaturated polyester and phenolic resins for application as fire-resistant matrices in fibre-reinforced composites: Effects of added flame retardants

Baljinder K. Kandola*, Latha Krishnan, John R. Ebdon

Institute for Materials Research and Innovation (IMRI), University of Bolton, Deane Road, Bolton BL3 5AB, United Kingdom

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ABSTRACT

The flame retardance of co-cured blends of an unsaturated polyester with various phenolic resoles is improved by the addition of the phosphorus-containing flame retardants: resorcinol bis(diphenyl phosphate), bisphenol-A bis(diphenyl phosphate) and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide. Cone calorimetric studies indicate reductions in important parameters such as total heat released and peak heat release rate. However, although the improved flame retardancy is accompanied by increased char yields, smoke evolution is also increased indicating contributions from both condensed-phase and gas-phase mechanisms of flame retardance. Improvements in flame retardance are particularly marked in systems in which the unsaturated polyester is at least partly compatible with the phenolic resole; TGA studies indicate that this may be due to better retention of the flame retardant in the condensed phase in the more compatible systems.

1. Introduction

Unsaturated polyester (UP) resins, cured (crosslinked) with styrene, are widely used as the matrix resins in composites, especially those reinforced with glass fibre cloths or mats and now widely employed in the transport sector in applications such as car bodies, train cabs, boat hulls, seat frames and motor housings [1]. The main advantages of thermoset UP resins in such applications are their relatively low cost, good mechanical properties (when fibre-reinforced), and reasonable resistance to water, oils and other chemicals [2]. However, cured UP resins thermally degrade rapidly at temperatures above 300 °C to give volatile products (mainly styrene initially) that are easily ignited, and which burn readily with the evolution of considerable smoke [3]. For this reason, UP resins are generally compounded with halogen- and/or phosphorus-containing flame-retardant (FR) additives, often used at concentrations of 20% w/w or above to ensure efficacy but with consequent deleterious effects upon physical and mechanical properties [4,5]. Alternatively, the UP resin backbone may be chemically modified with FR groups, (a reactive strategy) [6], or be crosslinked using an FR monomer in partial replacement of the styrene [7,8], but either strategy significantly increases cost.

We have been investigating an alternative approach to improving the flame retardance of UP resins, namely by blending and co-curing them with inherently flame-retardant resins such as char-forming phenol-formaldehyde and melamine-formaldehyde resins [9–11]. This type of approach is well-established with high-performance thermosetting resins, e.g. the blending of epoxy with phenolic resins [12], but thus far, relatively little has been published ahead of our work on the blending of UPs with phenolics, owing to the inherent physical incompatibility of relatively hydrophobic UP resins with relatively hydrophilic formaldehyde-based resins, and to the fact that the former cure by a low-temperature (typically 40–80 °C) free-radical chain reaction whereas the latter cure via a high temperature (*ca.* 150 °C) polycondensation, often with an acid catalyst [13–16].

Despite the shortage of precedents and the seeming difficulties to be overcome, we have shown that UP resins may be successfully blended and co-cured with phenolic *resoles* (PH), i.e. phenolic resins made using an excess of formaldehyde and thus containing unreacted methylol groups, especially if a compatibilizing solvent, such as ethanol, is used in the initial blending process, or if the resoles have been chemically modified to contain hydrophobic and/or free-radically reactive groups, such as epoxy (UP/epoxy-PH blends) and allyl groups (UP/allyl-PH blends) [9,10]. The evidence of increased compatibility comes from SEM images of fracture surfaces, which show much less evidence of microscopic heterogeneity in the case of the more compatible systems, from DMTA

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* Corresponding author. Tel.: +44 1204903517.
E-mail address: b.kandola@bolton.ac.uk (B.K. Kandola).

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measurements of glass transition temperatures (T_g) with the most compatible system (UP/allyl-PH) showing only a single T_g, and, in the case of UP/allyl-PH blends, also from solid-state ^{13}C NMR spectra, which indicate significant copolymerization of allyl groups in allyl-PH with the styrene and the in-chain double bonds of the UP [10]. Moreover, these co-cured resin blends are significantly more flame retardant than unmodified UPs, burn with lower evolution of heat and the formation of more char, have physical and mechanical properties that in several respects are superior to those of unmodified UPs, and can satisfactorily be used to make glass-reinforced composite panels [10,11].

However, we have been surprised to find that unexpectedly it is the least compatible resin blends, i.e. those based on UP plus an unmodified resole (PH) and which give rise to co-cured products with poor physical and mechanical properties, that are the most flame retardant, whereas those based on epoxy-PH and allyl-PH resoles, which have better physical and mechanical properties, are less flame retardant [11]. We believe that the reasons for this lie in the greater extent of cure of the unmodified resole in blends with UP, providing a greater thermally protective effect for the latter.

In this paper we describe further studies of the flame retardance of UP/resole co-cured blends, concentrating upon the effects of additional flame retardants. The FRs we have chosen to study are resorcinol bis(diphenyl phosphate) (RDP), bisphenol-A bis(diphenyl phosphate) (BADP) and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO). RDP and BADP are well-established for use in polymer systems such as polycarbonate and polycarbonate blends [17,18], in which they are believed to act via both gas- and condensed phase mechanisms, whereas DOPO is a predominantly gas-phase flame retardant used mainly in epoxy resin-based materials [19].

2. Experimental

2.1. Materials

Crystic 2-406 PA, Scott-Bader: a pre-accelerated (cobalt octoate), phthalic anhydride-based unsaturated polyester (UP) resin containing 35–40% w/w styrene.

Catalyst M, Scott-Bader: a free-radical catalyst for UP curing consisting of methyl ethyl ketone peroxide dissolved in methyl ethyl ketone.

Durez 33156, Sumitomo-Bakelite NV: an ethanol-soluble resole containing 20–29% w/w ethanol, hereinafter referred to as “PH”.

Plyophen 223983, Sumitomo-Bakelite NV: an isopropanol-soluble, epoxy-functionalized resole containing 16–18% w/w isopropanol and <6% w/w water, hereinafter referred to as “epoxy-PH”.

Methylon 75108, Sumitomo-Bakelite NV: a solvent-free, allyl-functionalized resole, hereinafter referred to as “allyl-PH”.

Resorcinol bis(diphenyl phosphate) (RDP), Chemtura UK.

Bisphenol-A bis(diphenyl phosphate) (BADP), Chemtura UK.

9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), Tokyo Chemical Industry UK Ltd.

All of the above materials were used as received.

2.2. Casting and curing of resins and resin blends

2.2.1. UP resin

Samples of cured UP resin were prepared by mixing the resin with 2% w/w of catalyst M with a mechanical stirrer in a 100 ml beaker. The mixture was then poured into 5.5 cm diameter circular aluminium open moulds to a depth of 3 mm. The specimens were then allowed to cure at room temperature for 24 h and post-cured at 80 °C in an oven for 6 h.

2.2.2. PH resins

Samples of PH resins were directly transferred to 5.5 cm dia. moulds, again to depths of 3 mm, cured and then post cured for various times and at various temperatures up to 180 °C. In situations in which FR was added (i.e. RDP, BADP or DOPO), this was stirred into the resin until dissolved prior to transfer of the resin to the mould. For RDP and BADP, concentrations of 20% w/w FR/total resin (corresponding to 2.2% w/w and 1.8% w/w P/total resin, respectively) were employed, whereas for DOPO, the concentration was 10% w/w FR/total resin (corresponding to 1.6% w/w P/total resin).

2.2.3. Resin blends

Resin blends were prepared by mixing 70:30 and 50:50% w/w UP/resole for 10 min in a 100 ml beaker using a high-speed, overhead, electric stirrer fitted with a four-component blade (IKA RW16 at 900 rpm); additional FR was included where required. Catalyst M (2% w/w w.r.t. UP) was then added to the resin mixture and stirring continued for a further 10 min. The resulting mixtures were then transferred to 5.5 cm dia. moulds also (depth 3 mm), cured and then post cured by increasing the temperature again in stages to 180 °C.

2.2.4. Curing regimes

The precise curing regimes used for the various resin mixtures, with and without FR, are listed in Table 1.

These curing regimes were established by a process of trial and error so as to accommodate (a) initial evaporation of any solvent prior to significant cure (so as not to produce voids in the final cured product), (b) the relatively low temperature radical curing/co-curing stage for the UP, (c) the final higher temperature co-condensation of any residual methylol groups in the resole and, in so-doing, to obtain a rigid, visibly homogeneous product with optimised physical and mechanical properties [11]. It can be seen from Table 1 that for UP samples containing FRs, long cure times and high final post-cure temperatures (up to 160 °C in the case of UP with RDP) were required in order to obtain a satisfactory product, *i.e.* one that was rigid and non-tacky. All blends of UP with resoles also required long cure times and high final post-cure temperatures. However, for blends containing RDP and BADP, the final post cure temperatures were required to be no higher than those required in the absence of FRs (160 °C), whereas when DOPO was used as the FR, a final post-cure temperature of 180 °C was necessary. There was no apparent loss of FR through migration to the surface (blooming) during the curing of samples containing FR, indicating that the FRs were satisfactorily incorporated in the cured resins and resin mixtures.

The cured and co-cured resin samples were used in cone calorimetric experiments, and small portions of them were used also in TGA experiments.

2.3. Cone calorimetry

A cone calorimeter (Fire Testing Technology Ltd., UK) was used to assess flammability parameters for cured resins. Circular samples measuring 5.5 cm dia. with a nominal thickness of 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 surface and the edges of the samples were wrapped with aluminium foil to ensure that only the top surface 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 cone calorimetric behaviour of round and standard square (10 cm × 10 cm) samples was undertaken in order to understand

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