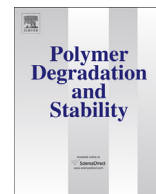




Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Novel flame retardant thermoset resin blends derived from a free-radically cured vinylbenzylated phenolic novolac and an unsaturated polyester for marine composites

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ARTICLE INFO

Article history:

Received 19 August 2015
 Received in revised form
 2 December 2015
 Accepted 12 January 2016
 Available online xxx

Keywords:

Vinylbenzylated
 Phenolic novolac
 Unsaturated polyester
 Blend
 Fire performance
 Thermal stability

ABSTRACT

A phenolic novolac resin has been chemically reacted with 4-vinylbenzyl chloride to introduce polymerizable vinyl benzyl groups. The modified novolac spontaneously polymerizes like styrene, is physically and chemically compatible with a typical unsaturated polyester (UP) resin, and can be free-radically cured (crosslinked) alone and in mixtures with UP using styrene as a reactive diluent. The cured vinylbenzylated novolac and co-cured blends of it with UP show superior flame retardance to cured UP alone and have potential applications as matrix resins in glass-reinforced composite laminates especially for marine structures.

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1. Introduction

Glass-fibre reinforced composite laminates utilising styrene-cured (free-radically crosslinked) unsaturated polyesters (UPs) as the resin matrix are today widely used in the manufacture of strong, light-weight panels for automobiles, trucks, boat hulls and aircraft interiors [1]. There is currently one major disadvantage to such materials however, especially when used in marine composites, and that is their flammability, which arises from the low thermal stability of the resin matrix and the fact that they decomposes to give a variety of flammable degradation products, such as styrene, aliphatic alcohols, aromatic and aliphatic anhydrides, and other hydrocarbon fragments, leaving very little protective char residue [2]. Hitherto, the problem of flammability in UPs has been addressed through the incorporation of flame-retardant additives [3,4], by building reactive flame-retardant

groups into the UP structure [3,5] or by replacing some or all of the styrene cross-linking monomer with a more flame-retardant monomer [3,6,7]. These strategies, however, can have deleterious effects on the physical and mechanical properties of the UP and/or can significantly increase material costs. In order to address this problem, we have been investigating a potentially more cost-effective method of flame retarding UPs by co-curing UP with char-forming, and hence more flame-retardant, resins such as phenolic resoles, furan resins and melamine-formaldehyde resins [8–13]. Surprisingly, the blending of UP with other resins has hitherto been used mainly to improve surface finish or to decrease mould shrinkage rather than to improve flame retardance [14,15]. Our work has demonstrated that whilst flame-retardance may easily be improved by this “blending” approach, it is important that the added resin is co-cured into the matrix if good flame-retardance is to be accompanied by acceptable physical and mechanical properties. Thus furan resins, which do not co-cure with UP, effectively plasticise the UP [12], and simple resoles, which also do not co-cure, lead to phase separated blends displaying two glass-transition temperatures [9]. Of the commercially available resoles so far studied, we have found only allyl-substituted resoles to be chemically incorporated into the styrene-cured UP matrix (via radical reactions involving the allyl

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groups) giving homogeneous blends with single glass transition temperatures (T_g s), good mechanical properties and acceptable flame retardance [9,10]. However, to achieve these properties, the blends have to be subject to a complex curing cycle involving several stages, at temperatures up to 190 °C in order to fully react free methylol and residual allyl groups, whereas unmodified UPs can be cured at temperatures no higher than 80 °C. Because of these last observations, we have most recently incorporated into styrene-cured UPs, a phenolic novolac resin (no free methylol groups) chemically modified at the phenolic-OH with methacrylate groups [13]. These groups are incorporated readily into the UP network via copolymerization with styrene and with the unsaturated maleate groups in the backbone of the UP over the normal RT–80 °C curing cycle for styrene-cured UP resins, giving homogeneous co-cured blends with single T_g s, good mechanical properties, and acceptable flame retardance. However, the flame retardance of these last blends are not as good (greater total heat release and peak heat release rate) than blends of similar composition based on blends of UP with allyl-functional resoles, probably owing to the ease with which the methacrylate groups depolymerize when heated.

In this paper we describe an alternative modification of novolac, this time with vinylbenzyl groups in an attempt to make a homogeneous, free-radically co-cured phenolic/UP blend with better flame retardance than those made using the methacrylate-functional novolac. The preparation of a flame retardant bearing vinylbenzyl groups was described in 1991 but this was based on a low molecular weight halogenated phenol and not on a phenolic resin [16].

2. Experimental

2.1. Materials

The following materials were obtained from the suppliers indicated and used as received:

Phenolic novolac: Durez 31459 (Sumitomo Bakelite Europe NV), molar mass *ca.* 2500.

4-Vinylbenzyl chloride, 90% (Sigma–Aldrich)

Potassium carbonate, anhydrous, $\geq 99\%$ (Sigma–Aldrich)

p-Benzoquinone (Sigma–Aldrich)

Methyl ethyl ketone (Fisher Scientific)

Diethyl ether (Fisher Scientific)

Unsaturated polyester: Crystic 2.406 PA (Scott-Bader), an unsaturated, phthalic anhydride based resin containing *ca.* 35–40 wt% styrene as a reactive solvent, pre-accelerated with 0.2 wt% cobalt octoate.

Catalyst M (Scott-Bader): a free-radical initiator consisting of a solution of MEK peroxide in MEK.

2.2. Synthesis of vinylbenzylated novolac (VB-novolac)

The synthesis of the VB-novolac was carried out according to the reaction scheme shown in Fig. 1, i.e. the phenolic groups in the novolac are reacted with 4-vinylbenzyl chloride (VBC) in the presence of weak base to remove the HCl produced by the condensation reaction.

Novolac (508.8 g, equivalent to 4.8 mol of phenolic rings) was dissolved in 1400 ml of methyl ethyl ketone (MEK) in a 1 L three-neck round bottom flask, purged with nitrogen and equipped with condenser, thermometer and mechanical stirrer. Anhydrous K_2CO_3 (729.3 g, 5.28 mol) was then added to the novolac solution with stirring upon which the solution became orange. To this

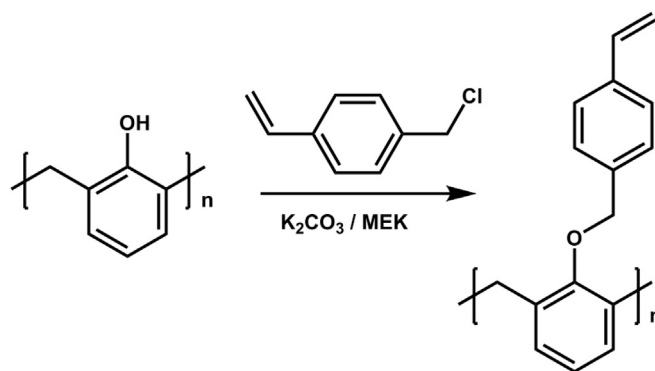


Fig. 1. Reaction of phenolic novolac with 4-vinylbenzyl chloride to give VB-novolac.

solution, *p*-benzoquinone (70 ppm) was added (to prevent polymerization of vinylbenzyl chloride), followed by anhydrous sodium iodide (0.8 g, 0.0053 mol). Following this, vinylbenzyl chloride (805.3 g, 5.28 mol) was added slowly, drop-wise at a rate of 1 drop/sec over a period of about 1 h. At the same time, the temperature of the reaction vessel was slowly raised to 80 °C, at which point another 30 ppm of *p*-benzoquinone was added and heating at 80 °C continued for another 6 h. Small samples were removed from the reaction vessel at hourly intervals for analysis by size exclusion chromatography (SEC) to monitor the progress of the vinylbenzylation. For the final hour of the 6 h heating period, SEC indicated no significant increase in molar mass of the resin so at the end of this period the reaction mixture was allowed to cool to room temperature.

MEK was then distilled from the reaction vessel by connecting it to distillation column, reducing the pressure to 1000 mbar and heating to 50 °C. After about 500 ml of the MEK had been removed, 1000 ml of deionised water was added with stirring, followed by 500 ml of diethyl ether. The VB-novolac resin mixture (the organic phase) was then separated from the more dense, yellow aqueous phase using a separation funnel and washed several times with deionised water before a final separation.

The recovered solution of VB-novolac resin in MEK/diethylether was then dried over anhydrous magnesium sulphate and transferred to a round bottom flask fitted with a distillation column, and the MEK/diethyl ether removed by distillation at 30 °C under a reduced pressure of 1000 mbar. The final VB-novolac was obtained as a viscous yellow liquid.

Yield: 779.3 g (47.7% of theoretical, assuming complete vinylbenzylation). Number-average molar mass by SEC: 3240. The resin was further characterized by IR spectroscopy to confirm that vinylbenzylation of the novolac had indeed occurred (see Section 3.1).

2.3. Preparation of cured plaques of UP/VB-Novolac blends

Plaques of UP, VB-novolac and UP/VB-Novolac blends were prepared by vigorous hand mixing of UP and VB-Novolac resin in various proportions with the addition of 2 wt% Catalyst M (a free radical initiator), and pouring the resultant mixtures into small circular aluminium moulds of diameter 5.5 cm and depth 3 mm. The method has been described in detail previously [9,13]. These plaques were then allowed to cure at RT for 12 h and then post-cured at various temperatures from 90 °C to 150 °C, depending on composition, for periods of up to 12 h, the exact cure procedure being decided on the basis of DSC experiments in which the temperature range over which curing exotherms occurred were monitored (see Section 3.3). In some of the samples, additional

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