Development of vinyl ester resins with improved flame retardant properties for structural marine applications

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ABSTRACT

This work builds on our previous experience of blending and co-curing an unsaturated polyester resin with other relatively inexpensive, but more flame retardant resins such as chemically modified phenolic resins, and extends this technology to the almost equally flammable vinyl ester resins, commonly used in marine composites. It has been demonstrated that two commercial vinyl ester resins (Scott-Bader, UK), one epoxy based (Crystic VE 676) and the other novolac based (Crystic VE 673), may be blended with two different commercial low molecular weight phenolic resoles (Sumitomo Bakelite Europe NV), one unmodified (Durez 33156) and the other containing allyl groups (Methylon 75108) and the blends cured (crosslinked) to give blended resins with good flame retardance, in several respects better than that of the unblended vinyl ester resins. Compatibility of the vinyl esters with the Methylon resole is however better than with the Durez, which tends to give phase-separated blends, and thus blends having poor physical and mechanical properties. Moreover, the compatibility of the novolac-based VE with both Durez and Methylon is worse than blends of the unsaturated polyester with Methylon and Durez. This compatibility issue and derived flammability properties of different blends are discussed in terms of their chemical structures.

1. Introduction

Vinyl ester (VE) resins give high performance, fibre-reinforced composites at low cost and these composites possess superior material properties, compared to those from unsaturated polyesters (UP) [1]. Chemically, VE resins are addition products of various epoxide resins and unsaturated monocarboxylic acids, most commonly methacrylic or acrylic acid [2]. They have terminal reactive double bonds derived from the carboxylic acid used. These reactive groups can form a crosslinked network in the presence of a free-radical initiator, usually after the addition of a comonomer (typically styrene). In this respect VE resins are similar to UP resins as both systems contain carbon-carbon double bonds, which can copolymerize with styrene monomer. However, the physical properties of VE are, in general, superior to those UP owing to the fact that VE resins have reactive double bonds at the ends of short polyester chains, while UP resins have internal double bonds distributed along the chains. The terminal double bonds of VE are less sterically hindered and are inherently more reactive than the internal double bonds of a UP, hence providing better control over the degree of crosslinking of the resin [3].

Glass fibre reinforced VE resins, similar to UP resins are increasingly being used for military and commercial transport applications, e.g. in ship and boat construction, owing to good toughness, excellent resistance, good mechanical properties and minimal maintenance requirements [4–7]. Owing to superior physical and mechanical properties, VE resins are preferred to UP resins in marine applications. Surprisingly, despite their wide usage, not many studies of VE resins have been reported in the open literature [3], whereas UP resins have been extensively studied. All commercial passenger and cargo ships have to comply with the fire performance requirements contained in the IMO/HSC Code [8]. The fire tests acceptance criteria defined in the IMO/FTP code [9] advise that for areas of moderate and major fire hazard (e.g., machinery spaces and storerooms), the materials used should be 'Fire resisting', i.e., they should prevent fire and smoke propagation during a defined period of time. Moreover, for naval ships the fire threats from internal and external blasts and weapon-induced fire are much higher than for civilian ships, the fire performance requirements for the former are particularly stringent and consequently much research has been directed towards improving the fire performance of polymeric composites in such vessels [10]. It is with these types of requirement in mind that we have been investigating simple, effective and commercially viable ways of improving the flame retardance of VE and UP resins.

Conventionally, VE resins, like UP resins, are flame retarded with

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additives [11]: examples include organobromine and phosphorus compounds such as brominated vinyl ester, tricresyl phosphate, resorcinol diphenylphosphate, and inorganic materials such as aluminium trihydrate and nanoclays, often in synergistic combinations [12,13]. Other materials investigated as flame retardants for VE resins include layered copper hydroxyl dodecyl sulfate [14] and silicone-based additives [15]. However, use of additives can lead to significant changes in resin viscosity, curing behavior, smoke-production on burning, and on the thermal and mechanical properties of VE based materials [16–19]. An alternative approach to flame retarding a VE based material is to apply a fire-resistant intumescent coating; however, such coatings have been shown not to withstand the types of mechanical shock to which they might be subjected in a naval application [20].

In a recently completed project, we demonstrated that UP resins may be made significantly more flame retardant with no detrimental effect to mechanical properties, by blending and co-curing (crosslinking) these with other relatively inexpensive, but more flame retardant, resins such as chemically modified phenolic resins [21–25]. The work described here builds on this experience and extends this technology to the almost equally flammable VE resins, commonly used in marine composites. The aim is to see if the fire retardance of VE resin systems can be improved by the incorporation of char-forming resins, such as phenolic resoles, and to develop a knowledge base and capability with respect to vinyl ester resins that would complement the current knowledge and capability for UP resins.

The homogeneous blending of two different polymeric materials is a challenge owing to the absence of a significant entropic advantage associated with the mixing of one macromolecule with another; only if there is a significant negative enthalpy of mixing, i.e. a specific positive interaction between the two components, such as dipole-dipole interactions or hydrogen bonding, is mixing readily achieved [26]. In the case of pairs of crosslinkable polymeric resins there is an additional requirement to complete the simultaneous curing of both resins i.e. over similar time-scales and at similar temperatures. This is even more of a challenge with UP or VE and conventional phenolic resins owing to the different curing mechanisms of these two resins: phenolics cure by condensation reactions with the elimination of water (incompatible with UP and VE) and formaldehyde at temperatures of up to 180–200 °C [27], whilst UP and VE resins cure with styrene by a free radical process at temperatures typically below 80 °C [28]. Thus, whilst mixtures of low molecular weight resin precursors may be miscible, once chain extension and crosslinking begins, immiscibility may develop leading to significant phase separation and resulting in brittle, non-homogeneous, blends. With crosslinkable polymers, however, gross phase separation may be prevented and domain sizes kept small if the two resins co-cure to form a semi- or fully interpenetrating polymer network [29]. Well interpenetrated networks can behave as homogeneous materials, displaying, for example, a single glass transition temperature (T_g). We have found such networks to be formed in the co-curing of certain phenolic resoles with unsaturated polyester resins [21].

2. Experimental

2.1. Materials

Two vinyl ester resins, one epoxy (bisphenol A) based (Crystic VE 676) and one phenolic novolac based (Crystic VE 673) were sourced from Scott Bader. Crystic VE 676, hereinafter referred to simply as VE-Ep, was selected because it is commonly used in the marine industry. Crystic VE 673, hereinafter referred to simply as VE-Nov, was selected because of the presence of the novolac structure as it was expected that this would be less flammable than VE-Ep and also that it would be more compatible with phenolic resins. The chemical structures of the two resins are shown in Fig. 1(a, b). A free-radical catalyst for curing the VE samples, cumyl hydroperoxide (Trigonox® 239) together with a redox

accelerator, cobalt octoate, were sourced from Akzo-Nobel.

Two phenolic resins were selected based on our experience of their blends with unsaturated polyester resins and possible compatibility with vinyl ester resins. The phenolic resins were an alcohol-soluble resole (Durez 33156, hereinafter referred to simply as Durez) and an allyl-functional resole (Methylon 75108, hereinafter referred to simply as Methylon). These resins were supplied by Sumitomo-Bakelite Europe NV. Structures of the VE-Ep, VE-Nov, Durez and Methylon are given in Fig. 1. For comparison, results of respective UP and UP-phenolic blends are also reported in this paper; these used an unsaturated, phthalic anhydride-based UP (Crystic® 2.406PA, Scott-Bader) containing 35–40 wt% styrene, pre-accelerated with cobalt octoate and cured with a methyl ethyl ketone peroxide-based radical catalyst (Catalyst M, Scott-Bader). The chemical structure of the UP is shown in Fig. 1(c).

2.2. Establishment of curing conditions

Resins are cured commercially at the lowest practicable temperature for a long period of time rather than at higher temperatures for shorter times in order to achieve maximum cross-linking, resulting in good mechanical properties. These curing conditions are established by running DSC experiments on small samples at very low heating rates (3–5 °C/min). A Q2000 differential scanning calorimeter (DSC) was used to monitor the curing of resins and resin blends. ~20 mg of an uncured resin or resin blend containing the appropriate amount(s) of curing agent(s) was placed in a standard aluminium pan fitted with a lid that had been pierced with a pin to introduce a small hole through which any volatiles could escape and then heated from 30 °C to 300 °C, at 5 °C/min under N_2 at a gas flow rate of 100 ml/min. From the onset and maximum temperatures of curing peaks, appropriate curing and post-curing temperatures were estimated. These temperatures were then used in the curing of small samples of resin for further experiments. DSC was then run again on the cured resin samples to check that they were fully cured (indicated by the absence of any further curing exotherm) or whether further post-curing was required.

2.3. Casting and curing of resin and resin blends

Circular plaques of cured VE resins were prepared by mixing the resin with initiator (2 wt% Trigonox) and catalyst (0.25 wt% cobalt octoate (12%)) with a mechanical stirrer in a 100 ml beaker and pouring these mixtures into shallow 55 mm diameter circular aluminium trays to a depth of 3 mm.

Samples of phenolic resins (Durez and Methylon) resins were directly transferred to 55 mm dia. moulds, again to depths of 3 mm.

Resin blends were prepared by mixing 70:30 and 50:50% w/w VE/phenolic 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). Initiator (2 wt% Trigonox) and catalyst (0.25 wt% cobalt octoate (12%)) were then added and the resulting mixtures were then transferred to 55 mm dia. moulds also (depth 3 mm). These resin mixtures were then cured in an air oven using temperature/time regimes previously optimised by DSC runs on milligram samples as outlined above.

2.4. Preparation of glass-reinforced composite samples

Composites measuring 300 mm × 300 mm × ca. 3 mm were prepared only from the VE resins and VE/Methylon blends, owing to the incompatibility observed with several of the blends of VE with Durez. After some preliminary experimentation, the amount of Trigonox catalyst used was reduced from 2 wt% to 1 wt% to increase gel times and the amount of the 12% cobalt octoate accelerator solution used similarly reduced (from 0.25 wt% to ca. 0.1 wt%).

Eight pieces of 300 mm × 300 mm woven E-glass fabric were used for composite laminate preparation. Each layer of fabric was