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.

Keywords: vinyl ester, phenolic resole, curing, blend, flame retardance

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 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 sulphate [14] and silicone-based additives [15]. However, use of additives can lead to significant changes in resin viscosity, curing behaviour, 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 Figure 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.

(Fig. 1 here)

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 N₂ 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 impregnated with the resin/resin mixture (prepared as explained in above section), all eight layers were stacked together to form a consolidated wet laminate, which was then vacuum bagged and cured using the conditions established for cast resins.

2.5. **Analysis, characterization and testing**

Thermal and thermo-oxidative stabilities of cured resins and their blends were assessed by thermogravimetric analysis (TGA) on a TA Instruments SDT 2960 over the temperature range 25–
800 °C using 15 ± 1 mg samples heated at a constant rate of 10 °C/min in air flowing at 100 ± 5 ml/min.

Dynamic mechanical thermal analysis (DMTA) on cast resins was carried out on a TA instruments Q800 with a single cantilever clamp and multi-frequency set up (0.1 % strain and 1 Hz frequency) over the temperature range 25–350 °C at 5 °C/min heating rate. From these experiments, storage moduli were evaluated along with glass transition temperatures (from maxima in plots of tan δ vs. T).

2.6. Assessment of flame retardance

A cone calorimeter (Fire Testing Technology Ltd. UK) was used to assess the flammability parameters of cured resin plaques. For the plaques, the circular samples measuring 55 mm in diameter with a nominal thickness of 3 mm were fire tested in the horizontal mode with an ignition source under a radiant heat flux of 50 kW/m². 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. This methodology differs from the recommended procedure of testing of standard square samples (100 mm × 100 mm). The effect of geometry (exposed surface area) of samples of similar thicknesses was studied in our previous work [30], where results showed that measured peak heat release rates (PHRR), total heat release (THR) and char yields (CY) of circular samples had similar relative trends to those observed using 100 mm × 100 mm samples; absolute values though differed. Smoke production results for round samples however, were found to be very different from those measured for standard specimens since this parameter is dependent on exposed specimen surface area. However, since in this work all samples are compared with control samples with the same geometrical dimensions, the methodology used can be considered appropriate.

The fire performance of the composite laminates was evaluated using a UL-94 flame-spread test. The UL-94 test was conducted according to ISO 1210 in both vertical and horizontal orientations, from the latter rate of burning for each sample was also recorded.

2.7. Assessment of mechanical performance of composites

The tensile tests of the composite samples (200 mm × 20 mm × ~3 mm) were conducted using a 50 kN load cell attached to a Universal Instron 3369 tensometer frame with 1 mm/min
crosshead speed. The gauge length of each specimen was 100 mm. Polymeric tabs were bonded at the end of specimens to improve the gripping and to ensure failure within the gauge region. The results are reported as initial modulus, tensile strength at failure and strain at failure, and are averages of three tests for each of the samples investigated.

The flexural moduli of the specimens (200 mm × 20 mm × ~3.0 mm) were measured in three-point bending mode using a 50 kN load cell attached to a Universal Instron 3369 tensometer. The specimens were tested in the displacement-controlled mode (i.e. crosshead speed of 1 mm/min). Results reported are an average of three tests for each of the samples investigated. The average flexural modulus (E) of the samples was calculated using the three point bending formula:

\[
E = \frac{FL^3}{4sh^3}
\]

in which, \(F\) is the applied load, \(s\) is the displacement, \(L\) is the span length, and \(b\) and \(h\) are the width and thickness of samples, respectively.

3. Results and discussion

3.1. Curing conditions for resin and resin-blend plaques

3.1.1. Pure resins

The curing reaction is always an exothermic reaction. In phenolic resins, however, prior to the curing exotherm, an endothermic peak is also observed, which arises from polycondensation reactions leading to production of both water and formaldehyde, which evaporate endothermically. Fig. 2 (a), (b), (c) and (d) show the DSC traces for VE-Ep, VE-Nov, Durez and Methylon together with pictures of 3 mm thick samples of the materials cast as plaques in 55 mm diameter aluminium trays, before and after curing. As can be seen from Fig. 2(a), curing of VE-Ep gives rise to two exothermic peaks, the first one starting at room temperature and with maxima of the two at 74 and 143 °C, respectively. VE-Nov on the other hand gives only one exotherm with a maximum at 80 °C. These exotherms represent curing reactions of the resins and the results indicate that both resins can be cured at room temperature and post curing at 80 °C, which is similar to the UP resin [21], however for complete curing of VE-Ep, additional post curing at 140 °C will be required. The DSC traces of both phenolic resins have been discussed in our previous publication [21]. On the basis of these experiments the curing conditions were selected and samples cured. Cured resin samples were
tested again by DSC and if the exotherm was observed again, curing conditions were modified or post-curing done until the exotherm completely disappeared. From these tests the following optimum curing regimes were selected:

- **VE-Ep:** room temperature (RT) for 24 h followed by 80 °C for 3 h and 140 °C for 3 h.
- **VE-Nov:** RT for 24 h, 80 °C for 3 h.
- **Durez:** 50 °C for 6 h, 80 °C for 12 h, 160 °C for 3 h and 180 °C for 2 h.
- **Methylon:** 100 °C for 8 h, 120 °C 6 h, 130 °C for 6 h, 150 °C for 2 h, 180 °C for 2 h, 220 °C for 3 h.

(Fig. 2 here)

It can be seen from Fig. 2 that the uncured VE samples are clear without any bubbles and that after curing both plaques are flat and uniform, without voids. Although the cured Durez and Methylon samples are similarly clear and uniform both before and after curing, plaques of both samples after curing are slightly bowed owing to differential mould shrinkage. Significant darkening of the phenolic samples (especially of the Durez) takes place during curing owing probably to some chemical degradation and rearrangement leading to increased conjugated unsaturation and hence light absorption.

### 3.1.2. Resin blends

The DSC traces for the 70 wt% VE: 30 wt% phenolic and 50 wt% VE: 50 wt% phenolic blends and pictures of plaques cast and cured from them are given in Fig. 3, (a) – (h). On the basis of these experiments the following curing regimes were selected:

- **VE-Ep/Durez 70:30 wt%:** 80 °C 10 h, 100 °C 6 h, 130 °C 1 h, 160 °C 1 h, 180 °C 2 h
- **VE-Ep /Durez 50:50 wt%:** 80 °C 24 h, 100 °C 1 h, 130 °C 1 h, 160 °C 1 h, 180 °C 2 h; one specimen was further postcured at 230 °C for 3 h
- **VE-Nov/Durez 70:30 wt%:** 80 °C 2 h, 130 °C 1 h, 160 °C 1 h, 180 °C 2 h
- **VE-Nov /Durez 50:50 wt%:** 80 °C 24 h, 100 °C 1 h, 130 °C 1 h, 160 °C 1 h, 180 °C 2 h
- **VE-Ep/Methylon 70:30 wt%:** 80 °C 2 h, 100 °C 6 h, 150 °C 6 h, 180 °C 3 h
- **VE-Ep/Methylon 50:50 wt%:** RT 24 h, 80 °C 6 h, 110 °C 6 h, 140 °C 6 h, 180 °C 3 h
- **VE-Nov /Methylon 70:30 wt%:** 80 °C 2 h, 100 °C 6 h, 150 °C 6 h, 180 °C 3 h
- **VE-Nov /Methylon 50:50 wt%:** RT 24 h, 80 °C 6 h, 110 °C 6 h, 140 °C 6 h, 180 °C 3 h
In the cases of the uncured and cured VE-Ep/Durez blends, the photographs of uncured resin plaques (Fig. 3 (a and b)) show that while the resins are not completely phase separated, these samples are not as homogeneous and clear as those of the individual resins (Fig. 2). There are some bubbles entrained within the cured samples. Colour change in 50:50 wt% blend can also be seen in Fig. 2(b), which may be due to some degradation resulting from curing at 230 °C. However, the photographs of VE-Nov show clear evidence of phase separation in the 70:30 wt% blend ((Fig. 3 (c)), which is worse in the 50:50 wt% blend (Fig. 3 (d)), in which a large globule of phenolic resin suspended in the VE can be seen. This is surprising as VE-Nov was expected to be more compatible than VE-Ep with the phenolic resin owing to the presence of the novolac moiety in the former.

For VE/Methylon blends, all uncured and cured mixtures appear from their photographs to be homogeneous (except VE-Nov/Methylon 70:30wt% in which some phase separation can be seen) and free from bubbles (Fig. 3 (e) – (h)). It can also be seen that in the DSC traces of all of the cured VE/Methylon blends (Fig. 3 (e) – (h)) there is a residual exotherm at around 220 °C; this exotherm can be removed, however, by subjecting the samples to a further post-cure at 220 °C for 3 h after which any further DSC run gives a flat trace indicating complete cure. However, curing at such a high temperature would result in degradation, as seen in case of VE-Ep/Durez 50:50 wt% blend in Fig. 2(b), hence curing at this temperature was avoided.

Comparing the DSC and curing profiles for the VE/resole blends with those of UP/resole blends of similar composition blends, reported in reference [21], shows that while UP/Durez was not very compatible, there were no visible signs of phase separation or inhomogeneity as there are with the VE/Durez blends. The compatibilities of UP/Durez and UP/Methylon blends have been discussed in detail in our previous publication [21].

3.2. Characterization and testing of cured plaques

3.2.1. Compatibility study and mechanical properties by dynamic mechanical thermal analysis (DMTA)

Plots of tan δ vs. temperature for the pure resins and for blended samples are given in Fig. 4, and data derived from these plots are given in Table 1. Also included are plots and data for corresponding UP/Phenolic resin blends.
Plots of tan δ vs T for the VE-Ep/Durez and VE-Nov/Durez blends (Fig. 4(a and b)) show two clear maxima indicative of two glass transition temperatures ($T_g$) and therefore of phase separation within the blends. The second peak is more prominent in VE-Nov/Durez blends, indicating worse compatibility, which is as expected from visual observation discussed earlier. In both 50:50 wt% blends while two peaks are observed, these are closer to each other than those observed in 70:30 wt% blends, indicating lesser phase separation in the former. Similar two peaks were seen in case of UP/Durez blends, reported previously [21] and also shown here in Figure 4(c). Blends of VE with Methylon on the other hand all appear to be homogeneous single phase materials, i.e. compatible blends, with single $T_g$s in all cases. These observations on compatibility are broadly in line with those obtained from the photographic evidence (Fig. 3). $T_g$s of all the cured resins and resin blends are gathered in Table 1 for comparison.

The reasons for the lower compatibilities of the VE-Durez blends compared with those of the VE-Methylon blends are not clear but may be a consequence of the presence of the aliphatic allyl groups in the Methylon aiding compatibility with the largely aliphatic VE resins, whereas the such groups are absent in Durez. Another feature of the VE-Durez blends is the apparent lower degrees of cure compared with the VE-Methylon blends. It is possible that free radical curing of the acrylic groups in VE is inhibited/retarded to some extent by the phenolic groups in the Durez. Such groups occur also in Methylon of course, but Methylon also possesses allyl groups capable of co-crosslinking with VE (as they do with UP [21]), mitigating to some degree any effects of inhibition/retardation on extents of curing. This co-crosslinking of the Methylon resole with VE probably involves radical attack on the Methylon (either addition to the double bond of the allyl group and/or hydrogen atom abstraction from the allyl group, see Fig. 5) leading to transfer of radical activity upon which the Methylon can take part in radical chain extension and crosslinking with the reactive diluent (styrene) and the acrylic groups of the VE. Similar chemical incorporation of allyl groups in cured UP has been demonstrated by solid-state C13 NMR [21].

On comparing these results with UP and UP/phenolic blends, it can be seen that both VE resins have higher $T_g$s (116 and 157 °C) than UP (92 °C). UP/Durez also showed phase separation
but not as noticeable as in VE/Durez and in particular VE-Nov/Durez blends. UP/Methylon and VE/Methylon blends however, are similarly compatible.

### 3.3.2. Thermal and thermo-oxidative stabilities of cured resins and resin blends

Thermal and thermo-oxidative stabilities of cured resins and resin blends were assessed by thermogravimetric analysis of ca. 15 mg samples under nitrogen and air atmospheres, respectively, at a heating rate of 10 °C / min between RT and 900 °C. The TGA traces for the various cured resins and resin blends recorded under nitrogen and air atmosphere are shown in Fig. 6 (a) – (h) with salient data from these traces listed in Table 2, in which the onset of decomposition temperature is represented as $T_{10\%}$, the temperature at which 10% mass loss occurs, $T_{50\%}$ is the temperature at which 50% mass loss occurs, and residual mass at 850 °C represents the char residue. Residual mass at 550 °C is also given, this temperature has been chosen because both VE resins undergo complete degradation at this temperature and any additional residue at this temperature for the blended resins would indicate increased thermal stability, and hence lower flammability, of the blends.

(Fig. 6 here)

(Table 2 here)

It can be seen from Table 2 that both VE resins have onset of decomposition temperatures around 380 °C in N$_2$, with VE-Ep and VE-Nov undergoing complete decomposition around 520 and 550 °C, respectively (Fig. 6(a,c)), leaving 3.3 and 16.2% char, respectively. In air, the TGA curves of both resins show two stages of decomposition, the second stage representing oxidation of the char, leaving no char residue above 523 and 558 °C, respectively. These results indicate that VE-Nov should be slightly less flammable than VE-Ep, which is expected to be similar or slightly more flammable than UP.

Durez, while starting to lose mass at ~300 °C, has a much higher thermal stability in terms of retention of mass at any particular temperature than any other resin. Its charring tendency is evident from 51.8% char residue in N$_2$, and even in air retaining mass until 766 °C. On the other hand, Methylon has a $T_{10\%}$ of 424 °C, indicating that it should have higher time-to-ignition in fire tests, but has lesser charring tendency than the Durez resin (36.2% char residue compared to 51.8% in Durez). In air all mass is lost at 635 °C. The lesser thermal stability and charring tendency of the Methylon can be explained as arising from the additional aliphatic organic content of Methylon (allyl groups) compared with Durez, which contains no such groups.
As expected, the resin blends in nitrogen give char yields intermediate between those of the base VE and phenolic resins. However, in all but the VE-Nov/Durez 70:30 and 50:50 wt% blends, the char yields are greater than those that would be expected assuming the blends to behave as simple mixtures of the resin components, i.e. that a blend would have a char yield which is the weighted average of the char yields for the component resins. The reason for this may be that in those cases in which the resins in the blend are truly or nearly compatible, both components in the matrix are properly cured and the phenolic component provides a thermally protective effect around the VE component. However, in cases in which compatibility is poor (and the VE-Nov/Durez blends fall into this category), curing is less efficient and such a protective effect is not established. It is to be noted that the initial thermal stabilities of the cured Durez and Durez resin blends are less than those of the corresponding Methylon based materials, suggesting that the Durez-based materials may not be as efficiently cured as the Methylon-based materials. However, the Durez-based materials show a greater thermal stability at higher temperatures, probably reflecting the lower aliphatic content of these compared with the allyl-functionalized Methylon-based materials, as mentioned above.

The TGA traces for the various cured resins and resin blends recorded under air atmosphere also show that, as is to be expected, the thermo-oxidative stabilities of the cured resin blends are intermediate between those of the cured base resins. The poor compatibilities of the VE-Ep/Durez and VE-Nov/Durez resins are clear from the TGA curves in Fig. 6 (b and d), in which it can be seen that both components appear to be decomposing separately. In contrast, the TGA curves of the VE-Ep/Methylon and VE-Nov/Methylon blends are smooth, consistent with decomposition of a uniform, homogeneous material. The higher residual mass of all blends at 550 °C indicate their higher thermal stability and hence lesser flammability than either of VE resins.

3.3.3. Flammability study of cast resin plaques by cone calorimetry

Cone calorimetry was carried out on cured plaques of the resins and resin blends under a radiant heat flux of 50 kW/m². Plots of heat release rate (HRR) and mass loss vs. time for VE-Nov/Durez blends, VE-Nov/Methylon blends, VE-Ep/Durez blends and VE-Ep/Methylon blends are shown in Fig. 7 (a) – (d).

(Fig. 7 here)

In case of neat resins, both VE resins ignited around 42-46 s, similar to UP (40 s). Durez has a low time to ignition (TTI), whereas Methylon has the highest TTI. This trend is very similar to the
trend in $T_{\text{Onset}} (T_{10\%})$, seen in the TGA curves. The charring tendency and higher thermal stability of VE-Nov indicated its lower flammability than VE-Ep, and this is reflected here by lower peak heat release rate, PHRR, (914 kW/m$^2$), total heat release, THR, (99.2 MJ/m$^2$) and higher char residue (11%) of the VE-Nov compared to the values for VE-Ep (1275 kW/m$^2$, 110.0 MJ/m$^2$ and 1%, respectively). VE-Ep also seems to be slightly more flammable than the UP, producing more smoke (Table 3), which could be due to different styrene contents in two different resin types. The exact amounts of styrene in these resins is not known owing to this being commercially sensitive information. Of the phenolic resins, Durez has a lower TTI than Methylon (38 s vs. 68 s), and lower PHRR (445 vs. 728 kW/m$^2$), THR (41.6 vs. 59.4 MJ/m$^2$), and total smoke release (1392 vs. 2675 m$^3$/m$^2$), and produces a greater char residue (45 vs 32%).

Even though both VE/Durez blends displayed phase separation. as mentioned above, they were subjected to cone experiments. It should be noted, however, that this is an academic exercise for these samples since inhomogeneous blends are not suitable for use as matrix resins in laminates. From Fig. 7 (a) and (b), it can be seen that for the VE-Ep/Durez blends, TTI is similar to that for VE-Ep. PHRR, THR and smoke values (Table 3) are however reduced compared to those of VE-Ep, owing to the low flammability of Durez. In case of VE-Nov/Durez blends, TTI and PHRR are slightly higher, but THR and smoke values are considerably lower, compared to the corresponding values for VE-Nov. For greater clarity, the percentage changes in selected cone calorimetric parameters for all blends with respect to those of the constituent resins are given in Table 3. On comparing these results with respective UP/Durez blends it can be noticed that in VE/Durez blends there is no decrease in TTI, decrease in PHRR and THR is less, and increase in char residue also less in the latter compared to former. This could be due to more phase separation in VE/Durez and in particular VE-Nov/Durez blends, where each component be behaving separately and not as one entity.

(Table 3 here)

Fig. 8 (c) and (d) indicate that, as with VE-Ep/Durez or VE-Nov/Durez blends, trend for TTI for the blends of VE with Methylon is similar, i.e, noticeable increase in VE-Nov/Methylon than VE-Ep/Methylon. However, PHRR reduced only in VE-Ep/Methylon, but significant reduction in THR and smoke. This effect is more pronounced than the respective effect seen in UP/Methylon resins. On comparing these results with respective UP/Methylon blends it can be seen that both VE/Methylon behave similar to the former.

(Fig. 8 here)
The relative overall fire performance of different resins can be evaluated by plotting the total heat release against the fire growth rate values calculated by dividing PHRR by TTI $[31]$, as shown here in Fig. 9. Here only 70:30 blends have been plotted because only this blend ratio has a potential for commercial exploitation, as higher phenolic content can have adverse effect on mechanical properties of VE or UP resins. Fire safe materials should have low THR and PHRR/TTI values; i.e. such materials should fall close to the coordinates (0;0) on a 2-D plot. It can be seen that, as expected, VE and UP resins are the most flammable and, moreover, that both VE resins (and especially VE-Ep) are more flammable than UP. However, as with UP, blending VE resins with phenolic resoles leads to significant improvements in fire safety. Of particular note is the large improvement in the fire safety aspect of the VE-Ep/Methylon 70:30 blend relative to that of VE-Ep compared with the corresponding UP system. We believe that this is a consequence of the greater ease with which the allyl groups of the Methylon can co-crosslink with the terminal (i.e. readily accessible) double bonds in the acrylic end-groups in VE compared with the internal (i.e less accessible) double bonds of the maleate/fumarate groups in UP.

(Fig. 9 here)

3.4. Flammability and mechanical properties of glass fibre-reinforced composite laminates

Due to the incompatibility of both types of VE resins with Durez, composite laminates from these resins were not prepared. The properties of composite laminates from VE/Methylon blends have been studies and compared with respective composites from VE resins.

3.4.1 Flammability study of the composite laminates by UL-94

All VE and VE/Methylon blended samples failed during vertical UL-94 testing. Of particular importance in the application of glass-reinforced composite panels in marine applications is their resistance to horizontal flame spread. To assess the relative performance of VE/phenolic blend composites in this respect, UL 94 test in the horizontal orientation was conducted. In these tests, the sample was marked at 25, 75 and 125 mm from the end of the specimen. The sample was clamped in the horizontal position, and a flame was applied to the end of the specimen for 30 s. If the flame extinguished before reaching the first mark, the sample was ranked as self-extinguishing, otherwise the times to reach 75 mm ($t_{75}$) and 125 mm ($t_{125}$) from the first mark were recorded.
As can be seen from the results of these tests gathered in Table 4, VE-Nov has lower burning rate compared to VE-Ep, which is expected from earlier cone results. All resin blend composites self extinguished and performed exceptionally well in this test compared with composites based on just VE-Ep or VE-Nov.

3.4.2 Mechanical properties of the composite laminates

Tensile and flexural moduli were measured for all composite samples. The results are gathered in Table 5 and tensile stress/strain plots are shown in Figure 10. Since all composite laminates had different resin/fibre ratio, the modulus values were normalised to 40% fibre volume fraction (FVF) and the values are given in parentheses in Table 5. VE-Ep and VE-Nov composites have similar tensile moduli (normalised to 40% FVF) with the modulus in both cases decreasing on addition of Methylon. The blend ratio however has a marginal effect on modulus. Stress-at-failure for blend samples is also lower than for VE samples; the strain values at failure however are less affected by blending.

Both VE-Ep and VE-Nov composites have good flexural moduli, 15.6 and 17.5 GPa, respectively. Addition of Methylon causes a decrease in the modulus. The only exception is VE-Ep/Methylon 50:50 (wt%), for which the flexural modulus is higher than that of the 70:30 blend. This could be due to variation in sample caused perhaps by different wetting of the fabric, or differences in amounts of resin at the surfaces.

Overall these results indicate that mechanical properties of composite sample from blends are lower than those form pure VE resins, which is as expected because of the lower mechanical properties of phenolic resins. The values though are not too low to be used for structural applications.

4. Conclusions

It has been demonstrated that two commercial vinyl ester resins, 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, one unmodified (Durez 33156) and the other containing allyl groups (Methylon 75108) and the blends cured (crosslinked) to give solids with good flame retardance that in several respects is 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 properties. The greater compatibilities of the vinyl ester resins with the Methylon resole compared with the Durez resole are probably a consequence of the presence of the allyl groups in Methylon, which aid both compatibility and provide reactive sites capable of taking part in a free radical co-curing reaction with the vinyl ester and the styrene monomer contained within the VE as indicated above, leading to the formation of interpenetrating networks with high degrees of homogeneity.

Cured VE/Methylon blends have been used successfully as matrix resins in glass-fibre reinforced composites. These composites, whilst having mechanical properties slightly inferior to those of composites based on vinyl esters alone, nevertheless have better flame retardance, performing especially well in a horizontal UL 94 flame spread test in which they “self-extinguished”.

5. Acknowledgements

We thank DSTL for funding this work through their MAST scheme and Alan Groves and Emmajane Erskine of DSTL for helpful advice and guidance. We also thank Scott Bader and Sumitomo Bakelite Europe BV for gifts of resins.

6. References


[28] A. Zinke. The chemistry of phenolic resins and the processes leading to their formation. *J Appl Chem.* 1 (6), (1951) 257–266.


Captions for Figures and Tables

**Fig. 1.** Structural representation of (a) VE-Ep, (b) VE-Nov, (c) UP, (d) Durez and (e) Methylon. Circles highlight positions of double bonds involved in free radical crosslinking.

**Fig. 2.** DSC traces for uncured and cured samples of (a) VE-Ep, (b) VE-Nov, (c) Durez and Methylon with photographs of plaques of the materials before and after curing.

**Fig. 3.** DSC traces for uncured and cured samples of (a) VE-Ep/Durez 70:30 wt% (b) VE-Ep/Durez 50:50 wt%, (c) VE-Nov/Durez 70:30 wt%, (d) VE-Nov/Durez 50:50 wt%, (e) VE-Ep/Methylon 70:30 wt%, (f) VE-Ep/Methylon 50:50 wt%, (g) VE-Nov/Methylon 70:30 wt%, and (h) VE-Nov/Methylon 50:50 wt%, with photographs of plaques of the materials before and after curing.

**Fig. 4.** Plots of tan δ vs. T for cured samples of vinyl ester resins, phenolic resoles and their 70:30 and 50:50 blends with data for UP/phenolic blends for comparison.

**Fig. 5.** A probable mechanism for the co-crosslinking of VE resins with Methylon.

**Fig. 6.** Thermogravimetric traces (residual mass vs. T) recorded for (a, b) VE-Ep/Durez blends, (c, d) VE-Nov/Durez blends, (e, f) VE-Ep/Methylon blends and (g, h) VE-Nov/Methylon blends under (a, c, e, g) N₂ and (b, d, f, h) air atmospheres.

**Fig. 7.** Plots of HRR (a-c) and mass loss (d-f) vs. time for constituent resins and blends of (a, d) VE-Ep/Durez, (b, e) VE-Nov/Durez, (c, f) UP/Durez.

**Fig. 8.** Plots of HRR (a-c) and mass loss (d-f) vs. time for constituent resins and blends of (a, d) VE-Ep/Methylon, (b, e) VE-Nov/Methylon, (c, f) UP/Methylon.

**Fig. 9.** A2-D fire safety assessment grid for VE-Ep, VE-Nov, UP, Durez and Methylon resins and their blends, when exposed to 50 kW/m² heat flux.

**Fig. 10.** Stress/strain plots from tensile tests for composite samples based on (a) VE-Ep and (b) VE-Nov systems.
Table 1. Glass transition temperatures ($T_g$) for cured resins and resin blends

Table 2. Salient data extracted from TGA traces recorded under N$_2$ and air atmospheres for cured resins and resin blends

Table 3. Summary of cone calorimetric results for VE-Nov/phenolic, VE-Ep/phenolic blends and for the constituent resins.

Table 4. Results of UL 94 tests on VE-Ep and VE-Nov based composites

Table 5. Mechanical properties for VE-Ep and VE-Nov based composite samples
Fig.1. Structural representation of (a) VE-Ep, (b) VE-Nov, (c) UP, (d) Durez and (e) Methylon. Circles highlight positions of double bonds involved in free radical crosslinking.
Fig. 2. DSC traces for uncured and cured samples of (a) VE-Ep, (b) VE-Nov, (c) Durez and Methylon with photographs of plaques of the materials before and after curing.
Fig. 3. DSC traces for uncured and cured samples of (a) VE-Ep/Durez 70:30 wt%, (b) VE-Ep/Durez 50:50 wt%, (c) VE-Nov/Durez 70:30 wt%, (d) VE-Nov/Durez 50:50 wt%, (e) VE-Ep/Methylon 70:30 wt%, (f) VE-Ep/Methylon 50:50 wt%, (g) VE-Nov/Methylon 70:30 wt%, and (h) VE-Nov/Methylon 50:50 wt%, with photographs of plaques of the materials before and after curing.
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Fig. 8. Plots of HRR (a-c) and mass loss (d-f) vs. time for constituent resins and blends of (a, d) VE-Ep/Methylon, (b, e) VE-Nov/Methylon, (c, f) UP/Methylon.
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**Fig. 10.** Stress/strain plots from tensile tests for composite samples based on (a) VE-Ep and (b) VE-Nov.
Table 1.
Glass transition temperatures ($T_g$) for cured resins and resin blends

<table>
<thead>
<tr>
<th>Resin</th>
<th>$T_g$ / °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>VE-Ep</td>
<td>116</td>
</tr>
<tr>
<td>VE-Nov</td>
<td>157</td>
</tr>
<tr>
<td>UP</td>
<td>92</td>
</tr>
<tr>
<td>Durez (D)</td>
<td>277</td>
</tr>
<tr>
<td>Methylene (M)</td>
<td>295</td>
</tr>
<tr>
<td>VE-Ep/D 70:30 wt%</td>
<td>107, 264</td>
</tr>
<tr>
<td>VE-Ep/D 50:50 wt%</td>
<td>132, 259</td>
</tr>
<tr>
<td>VE-Nov/D 70:30 wt%</td>
<td>138, 231</td>
</tr>
<tr>
<td>VE-Nov/D 50:50 wt%</td>
<td>133, 198</td>
</tr>
<tr>
<td>UP/D 70:30 wt%</td>
<td>149, 235</td>
</tr>
<tr>
<td>UP/D 50:50 wt%</td>
<td>92, 197</td>
</tr>
<tr>
<td>VE-Ep/M 70:30 wt%</td>
<td>105</td>
</tr>
<tr>
<td>VE-Ep/M 50:50 wt%</td>
<td>113</td>
</tr>
<tr>
<td>VE-Nov/M 70:30 wt%</td>
<td>143</td>
</tr>
<tr>
<td>VE-Nov/M 50:50 wt%</td>
<td>139</td>
</tr>
<tr>
<td>UP/M 70:30 wt%</td>
<td>114</td>
</tr>
<tr>
<td>UP/M 50:50 wt%</td>
<td>119</td>
</tr>
</tbody>
</table>
Table 2.
Salient data extracted from TGA traces recorded under N\textsubscript{2} and air atmospheres for cured resins and resin blends

<table>
<thead>
<tr>
<th>Resin</th>
<th>N\textsubscript{2} atmosphere</th>
<th>Air atmosphere</th>
<th>Char res. at 550 °C / wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_{10%}$ / °C</td>
<td>$T_{50%}$ / °C</td>
<td>Char res. / wt%</td>
</tr>
<tr>
<td>VE-Ep</td>
<td>380</td>
<td>418</td>
<td>5.0</td>
</tr>
<tr>
<td>VE-Nov</td>
<td>377</td>
<td>416</td>
<td>18.9</td>
</tr>
<tr>
<td>UP</td>
<td>325</td>
<td>380</td>
<td>4.4</td>
</tr>
<tr>
<td>Durez (D)</td>
<td>323</td>
<td>888</td>
<td>60.9</td>
</tr>
<tr>
<td>Methylon (M)</td>
<td>424</td>
<td>485</td>
<td>42.9</td>
</tr>
<tr>
<td>VE-Ep/D 70:30</td>
<td>311</td>
<td>428</td>
<td>24.6 (21.8)</td>
</tr>
<tr>
<td>VE-Ep/D 50:50</td>
<td>386</td>
<td>439</td>
<td>34.8 (33.0)</td>
</tr>
<tr>
<td>VE-Nov /D 70:30</td>
<td>259</td>
<td>422</td>
<td>29.2 (31.5)</td>
</tr>
<tr>
<td>VE-Nov /D 50:50</td>
<td>353</td>
<td>448</td>
<td>37.8 (39.9)</td>
</tr>
<tr>
<td>UP/D 70:30</td>
<td>338</td>
<td>402</td>
<td>21.1 (21.3)</td>
</tr>
<tr>
<td>UP/D 50:50</td>
<td>344</td>
<td>443</td>
<td>38.1 (32.6)</td>
</tr>
</tbody>
</table>

Note: Figures in parentheses are the char yields that might be expected for the resin blends assuming they behave as simple mixtures of the component resins.
Table 3.
Summary of cone calorimetric results for VE-Nov/phenolic, VE-Ep/phenolic blends and for the constituent resins.

<table>
<thead>
<tr>
<th>Sample</th>
<th>TTI / s</th>
<th>FO / s</th>
<th>PHRR / kW/m²</th>
<th>THR / MJ/m²</th>
<th>TSR / m²/m²</th>
<th>Residue / wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>VE-Ep</td>
<td>46</td>
<td>173</td>
<td>1275</td>
<td>110.0</td>
<td>5547</td>
<td>1</td>
</tr>
<tr>
<td>VE-Nov</td>
<td>42</td>
<td>212</td>
<td>914</td>
<td>99.2</td>
<td>4536</td>
<td>11</td>
</tr>
<tr>
<td>UP</td>
<td>40</td>
<td>178</td>
<td>1053</td>
<td>78.9</td>
<td>4090</td>
<td>1</td>
</tr>
<tr>
<td>Durez (D)</td>
<td>38</td>
<td>171</td>
<td>445</td>
<td>41.6</td>
<td>1392</td>
<td>45</td>
</tr>
<tr>
<td>Methylon (M)</td>
<td>68</td>
<td>216</td>
<td>728</td>
<td>59.4</td>
<td>2675</td>
<td>32</td>
</tr>
<tr>
<td>VE-Ep/D 70:30*</td>
<td>51 (+5)</td>
<td>163</td>
<td>937 (-26.5)</td>
<td>63.7 (-42.2)</td>
<td>3638 (-34.4)</td>
<td>14 (+13)</td>
</tr>
<tr>
<td>VE-Ep/D 50:50</td>
<td>47 (+1)</td>
<td>147</td>
<td>893 (-29.9)</td>
<td>56.5</td>
<td>2320</td>
<td>14 (+13)</td>
</tr>
<tr>
<td>VE-Nov/D 70:30*</td>
<td>59 (+17)</td>
<td>191</td>
<td>1025 (+12.1)</td>
<td>78.4</td>
<td>3124</td>
<td>18 (+7)</td>
</tr>
<tr>
<td>VE-Nov/D 50:50*</td>
<td>51 (+9)</td>
<td>161</td>
<td>1046 (+14.4)</td>
<td>63.7</td>
<td>2314</td>
<td>24 (+13)</td>
</tr>
<tr>
<td>UP/D 70:30</td>
<td>31 (-9)</td>
<td>178</td>
<td>630 (-40.2)</td>
<td>62.3</td>
<td>2307</td>
<td>24 (+23)</td>
</tr>
<tr>
<td>UP/D 50:50</td>
<td>31 (-9)</td>
<td>156</td>
<td>568 (-46.1)</td>
<td>48.4</td>
<td>1357</td>
<td>37 (+36)</td>
</tr>
<tr>
<td>VE-Ep/M 70:30</td>
<td>50 (+4)</td>
<td>151</td>
<td>1120 (-12.1)</td>
<td>65.2</td>
<td>3187</td>
<td>9 (+8)</td>
</tr>
<tr>
<td>VE-Ep/M 50:50</td>
<td>51 (+5)</td>
<td>199</td>
<td>1091 (-14.4)</td>
<td>72.1</td>
<td>3472</td>
<td>14 (+13)</td>
</tr>
<tr>
<td>VE-Nov/M 70:30</td>
<td>59 (+17)</td>
<td>160</td>
<td>1173 (-28.3)</td>
<td>70.5</td>
<td>3028</td>
<td>15 (+4)</td>
</tr>
<tr>
<td>VE-Nov / M 50 50</td>
<td>46 (+4)</td>
<td>167</td>
<td>1188 (-29.9)</td>
<td>68.2</td>
<td>3130</td>
<td>16 (+5)</td>
</tr>
<tr>
<td>UP/D 70:30</td>
<td>54 (+14)</td>
<td>179</td>
<td>955 (-9.3)</td>
<td>70.7</td>
<td>3819</td>
<td>11 (+10)</td>
</tr>
<tr>
<td>UP/D 50:50</td>
<td>57 (+17)</td>
<td>201</td>
<td>828 (-21.4)</td>
<td>61.0</td>
<td>3166</td>
<td>14 (+13)</td>
</tr>
</tbody>
</table>

Notes: TTI = time to ignition, FO = time to flame out, PHRR = peak heat release rate, THR = total heat release, TSR = total smoke release. Numbers in parentheses and in italic font are differences in cone calorimetric parameters for VE-Ep/phenolic, VE-Nov/phenolic and UP/phenolic blends with respect to those of the constituent VE and UP resins expressed as percentages, except for TTI, where the difference is expressed in s. The reproducibility in cone parameters was ±5%. *These blends showed phase separation by DMTA and visual observation.
Table 4. Results of UL 94 tests on VE-Ep and VE-Nov based composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>(t_{75}) / s</th>
<th>(t_{125}) / s</th>
<th>Burning rate / mm/min</th>
<th>Self extinguishing?</th>
</tr>
</thead>
<tbody>
<tr>
<td>VE-Ep</td>
<td>212</td>
<td>425</td>
<td>14.1</td>
<td>No</td>
</tr>
<tr>
<td>VE-Ep/M 70:30</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Yes</td>
</tr>
<tr>
<td>VE-Ep/M 50:50</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Yes</td>
</tr>
<tr>
<td>VE-Nov</td>
<td>256</td>
<td>519</td>
<td>11.6</td>
<td>No</td>
</tr>
<tr>
<td>VE-Nov/M 70:50</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Yes</td>
</tr>
<tr>
<td>VE-Nov/M 50:50</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Note: \(t_{75}\) and \(t_{125}\) are the times for the flame to reach the 75 and 125 mm marks, respectively.
Table 5. Mechanical properties for VE-Ep and VE-Nov based composite samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>FVF / %</th>
<th>Tensile properties</th>
<th>Flexural modulus / GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Modulus / GPa</td>
<td>Stress-at-failure / MPa</td>
</tr>
<tr>
<td>VE-Ep</td>
<td>40.3</td>
<td>21.0 ± 0.9 (20.8)</td>
<td>310 ± 17</td>
</tr>
<tr>
<td>VE-Ep/M 70:30</td>
<td>42.9</td>
<td>16.6 ± 0.5 (16.5)</td>
<td>283 ± 1</td>
</tr>
<tr>
<td>VE-Ep/M 50:50</td>
<td>45.1</td>
<td>15.8 ± 0.3 (15.7)</td>
<td>329 ± 12</td>
</tr>
<tr>
<td>VE-Nov</td>
<td>33.2</td>
<td>18.4 ± 0.9 (22.2)</td>
<td>298 ± 1</td>
</tr>
<tr>
<td>VE-Nov/M 70:50</td>
<td>44.0</td>
<td>12.1 ± 0.2 (14.5)</td>
<td>294 ± 15</td>
</tr>
<tr>
<td>VE-Nov/M 50:50</td>
<td>35.0</td>
<td>12.8 ± 0.9 (15.5)</td>
<td>258 ± 12</td>
</tr>
</tbody>
</table>

Note: Values in parentheses are normalised to 40 % fibre volume fraction (FVF)