Mechanism of shrinkage control in polyester resins containing low-profile additives

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A commercial low-profile additive containing acid-terminated poly(vinyl acetate) (PVAc) was added, at concentrations of 0–16 wt%, to a solution of unsaturated polyester resin in styrene. The blends were cured under standard conditions. In all cases, the linear shrinkage during cure was 3.2 ± 0.2%, independent of PVAc content. In the absence of PVAc, addition of up to 60 wt% of $CaCO_3$ simply reduced the shrinkage of the resin in proportion to the volume fraction of filler. However, a combination of $CaCO_3$ with 16% PVAc gave a synergistic effect: the resulting shrinkage was substantially smaller than with $CaCO_3$ alone. On the basis of microscopy and other evidence, it is concluded that low-profile modifiers work by providing weak co-continuous regions in the resin, which can cavitate in response to tensile stresses arising from thermal- and cure-contraction in the presence of mechanical constraints. These constraints may be imposed internally, by mineral fillers or glass fibres, or externally, by forces acting on the surface of the resin. Optical microscopy provides evidence to support this interpretation.

(Keywords: polyester resin; poly(vinyl acetate); low-profile; shrinkage; fillers)

INTRODUCTION

Poly(vinyl acetate) is widely used as a 'low-profile' additive for unsaturated polyester resins, especially in sheet moulding compounds. This type of additive eliminates the surface distortion that would otherwise be present, produces a smooth surface free from fibre pattern marks, and overcomes the problems of warping and resin cracking that were frequently encountered in SMC before the introduction of 'low-profile' resins. The improvements brought about by shrinkage modifiers are graphically illustrated in the early paper by Bartkus and Kroekel[1].

A recent review discusses the current level of understanding of 'low-profile' behaviour[2]. Several theories have been advanced to explain the effect[3–11], but there is no general agreement on the subject. All of the theories to date are based upon the assumption that resin blends containing 'low-profile' additives show an intrinsic resistance to shrinkage during curing and subsequent cooling. If this assumption is correct, then it follows that the thermoplastic additive must interact with the surrounding resin, either alone or in combination with the styrene monomer, in some unusual way.

The present paper challenges this basic assumption, presenting experimental evidence to show that PVAc has a negligible effect on the shrinkage of polyester resin unless constraining mechanical forces are applied to the polymer.

EXPERIMENTAL

Materials

The unsaturated polyester resin used was a Scott Bader product, based on 1 mole each of maleic anhydride, isophthalic acid, propylene glycol, and diethylene glycol, and supplied as a solution containing 40 parts by weight of styrene monomer to 60 parts of resin. The thermoplastic additive was LP40, a 60/40 mixture of styrene with a vinyl acetate polymer that has been modified by the introduction of acrylic acid groups. The mineral filler was Tarmac Roadstone Calmote UF, a fine-ground limestone with a density of 2680 kg m^{-3}, in which the roughly equi-axed particles have diameters mainly in the range 1–10 μm, with a mean of 4 μm. A single batch of both polymer and filler was used throughout this study. Blending of all ingredients was carried out at room temperature, with manual stirring.

In the absence of the $CaCO_3$ filler, the blends are clear homogeneous solutions at this stage, with no sign of phase separation. Optical microscope examination of uncured and cured filled materials showed that the $CaCO_3$ was well dispersed. After adding 0.65% (based on total polymer) of benzoyl peroxide, the solutions were degassed, poured into moulds, and cured in an air circulating oven for 4 h.

Shrinkage testing

Two measures of shrinkage were used in this study. The first was the change in density at room temperature between the uncured liquid and the cured solid. The second followed the ASTM standard for measurement of linear shrinkage (ASTM D2566-86), but with smaller specimen dimensions: the casting trough was 80 mm long with an internal radius of 11 mm. In both series of tests, results reported below are mean values from 10 repeat specimens which were cured simultaneously.

The density of the liquid resin was determined at 25°C using a density bottle in the form of a 50 cm^3 'weight per gallon cup', as used in the industry. The resin was then cast into shallow circular aluminium pans with a diameter of 30 mm and a depth of 3 mm, degassed, and cured. The density of the cured material, also at 25°C,

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was obtained by an immersion method using distilled water.

Linear shrinkage was measured by casting the resin into copper troughs of semicircular cross-section with flat ends. The troughs were treated with Frecote 44 release agent before use. Cured resin specimens were removed from the troughs after cooling to room temperature, and their lengths were determined using a caliper gauge. Shrinkage $\Delta l/l$ was calculated as the difference in length between trough and cured sample at 23°C, divided by the length of the trough l. A limited number of experiments was also carried out using glass troughs, but copper ones were preferred for reasons discussed below.

Curing of both types of specimen was carried out in an air circulating oven at 120°C for 4 h. Embedded thermocouples showed that the material in the troughs reached the temperature of the preheated oven over a period of about 20 min. Peak temperature was reached approximately 15 s after the start of the rapid exotherm, and the samples cooled to 120°C over the following 10 min.

Mechanical tests

In addition to the shrinkage measurements described above, tensile tests were carried out at 80°C on ASTM bar specimens machined from 3 mm sheets of the cured resins, at a crosshead speed of 5 mm/min.

Microscopy

Optical microscopy was used to determine the conditions under which cavitation occurred in the resin and its blends. External mechanical constraints were applied by curing the resin between clean glass microscope slides. Both standard flat slides and cavity slides were used; the cavity slides have a rounded depression $\approx$15 mm in diameter and 1 mm deep in one surface. After cooling to room temperature, specimens were examined in transmitted light.

RESULTS

Specimen distortion

Resin samples cured in glass troughs showed six or seven small but sharp fold marks on the underside of the cast bars, marking regions where shear failure had taken place in compression, at 45° to the length of the bar. This effect is clearly due to thermal expansion of the resin during the reaction exotherm, as it begins to gel. The resin is still soft, but no longer liquid: its T_g increases with the degree of cure. The coefficient of linear thermal expansion of glass is very small compared with that of the resin ($5 \times 10^{-6}\,K^{-1}$ compared with $75 \times 10^{-6}\,K^{-1}$), and the ends of the trough will therefore restrict resin expansion. This would be true even if the glass were at the same temperature as the resin. In practice, the sample is hotter, especially at its core. The low thermal conductivity of glass also ensures that the surface region of the sample remains well above its T_g, and therefore soft enough to respond to compressive forces, for a prolonged period.

This slight distortion of the bars is largely eliminated when curing is carried out in copper troughs. Copper conducts heat away from the curing resin much more efficiently than glass, so that temperatures at the under surface of the bar, where it is in contact with the trough, are reduced. Furthermore, as a consequence of better heat transfer, peak temperatures reached at the centre of the bars are also lower: embedded thermocouples gave peak temperatures of 182°C in resin samples cured in copper troughs, compared with 227°C in glass troughs. The higher coefficient of expansion of copper ($17 \times 10^{-6}\,K^{-1}$) also helps to reduce the problem.

Effects of PVAc

The effects of PVAc on shrinkage, as determined by the two methods described above, are shown in *Figure 1*. Density data were converted to linear shrinkage $\Delta l/l$ using the equation:

$$\Delta l/l = (1 + \Delta V/V)^{1/3} - 1 \qquad (1)$$

where V is volume. Both $\Delta l/l$ and $\Delta V/V$ are, of course, negative in these experiments. It is clear from the figure that both tests show linear shrinkage to be essentially independent of composition over the range 0–16 wt% PVAc. Density data give an average value of 3.42% for $\Delta l/l$, whereas the direct linear shrinkage measurements from trough specimens give an average value of 3.17%.

The agreement between these two values is striking, because they measure shrinkage from different stages of the reaction. The baseline for the density results is the uncured resin at room temperature, whereas the baseline for the linear shrinkage measurements is the point during the curing reaction at which the resin is no longer sufficiently fluid to accommodate to the dimensions of the trough. A schematic diagram comparing the two tests is presented in *Figure 2*. The measurements of density include the effects of: a, the initial thermal expansion of the liquid resin; b, the whole of the contraction during curing of the resin; and c, thermal contraction to room temperature. By contrast, the linear shrinkage measurement contains no component of a, thermal expansion of the liquid resin, and only part of b, the cure contraction. Only in thermal contraction does it follow the density test closely, and even here there is a small discrepancy introduced by thermal contraction of the copper trough from the unspecified temperature at which the resin gels.

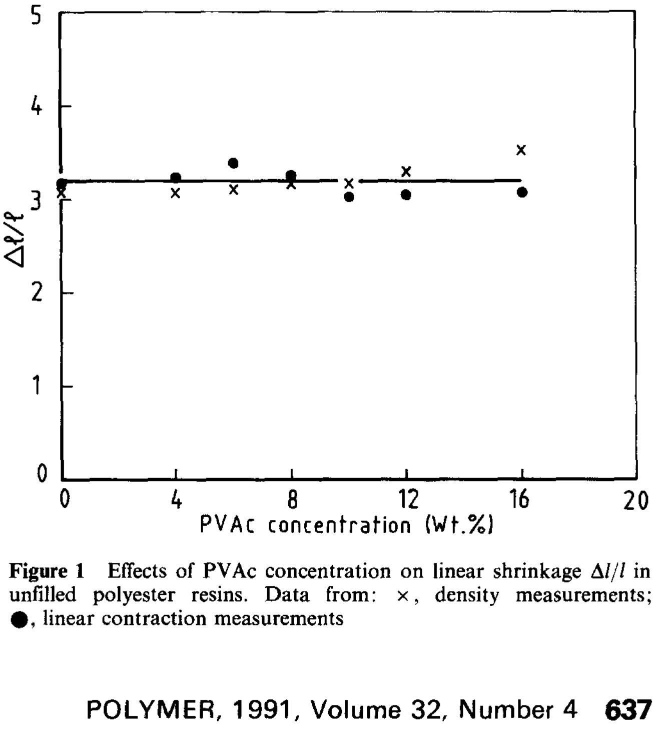

Figure 1 Effects of PVAc concentration on linear shrinkage $\Delta l/l$ in unfilled polyester resins. Data from: ×, density measurements; ●, linear contraction measurements

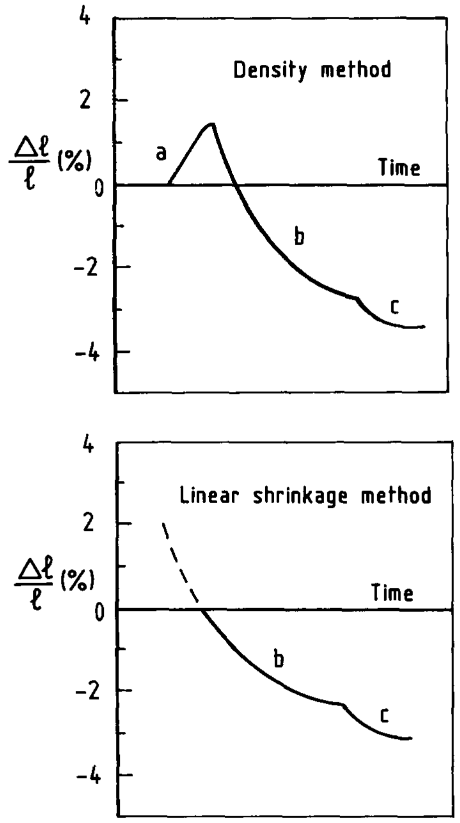

Figure 2 Schematic diagram showing dimensional changes with time, as they affect density and linear shrinkage. Note that in the latter case the reference state is defined after some cure contraction has taken place

We can estimate a reduction in measured shrinkage of between $\Delta l/l = 0.17\%$ (for $\Delta T = 100°C$) and 0.27% ($\Delta T = 160°C$) due to this effect. The overall conclusion is clear: the agreement shown in *Figure 1* between results obtained by the two different methods indicates that shrinkage before gelation approximately cancels out expansion of the liquid resin from room temperature.

Effects of mineral fillers

The effects of mineral fillers on volumetric shrinkage in blends containing different amounts of PVAc are illustrated in *Figure 3*. Addition of a mineral filler reduces shrinkage simply by diluting the resin, but it is clear that the reduction is much greater in the blends containing 16% PVAc.

The data are replotted in *Figure 4*. Shrinkage is normalized by dividing $(\Delta V/V)_C$, the observed shrinkage of the composite sample, by $(\Delta V/V)_R$, the shrinkage of the corresponding unfilled resin. In addition, weight fractions are converted to volume fractions, using measured densities for the resin blends, and the quoted value of 2680 kg m^{-3} for the $CaCO_3$. The densities of the cured resins decreased approximately linearly from 1260 kg m^{-3} at 0% PVAc to 1218 kg m^{-3} at 16% PVAc.

Figure 4 shows that within experimental error, the data for the unmodified resin and the blend containing 8% PVAc all lie on the line predicted by the rule of mixtures:

$$(\Delta V/V)_C = \phi_R(\Delta V/V)_R + \phi_F(\Delta V/V)_F = (1-\phi_F)(\Delta V/V)_R \tag{2}$$

where ϕ is volume fraction, and subscripts C, R and F respectively denote composite, resin (including any added PVAc) and filler. The volume change $(\Delta V/V)_F$ in the filler is taken as zero.

By contrast, blends containing 16 wt% PVAc show much smaller degrees of shrinkage than those predicted by the rule of mixtures. Indeed, in blends containing 41 vol% $CaCO_3$, the results indicate a small amount of expansion. Results obtained from linear shrinkage tests show a similar trend, as illustrated in *Figure 5*. In this series of experiments, addition of 8% PVAc gave an increase in shrinkage, whereas a substantial reduction was obtained on adding 16% PVAc.

Microscopy

Microscopy studies were limited to unfilled resins. They showed cavitation in specific regions of resin blends, but no cavitation in the unmodified resin. Cavitation produced an intense local darkening of the microscope image. Elsewhere, two-phase structure could just be discerned in resins containing added PVAc. As noted in scanning electron microscope studies, the commercial

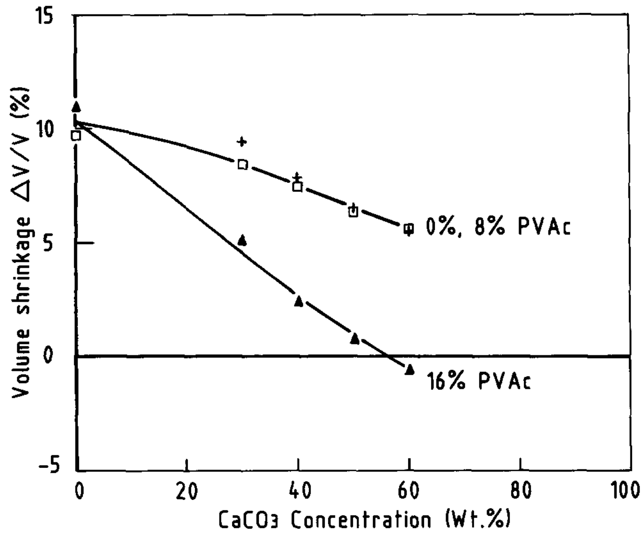

Figure 3 Effects of $CaCO_3$ filler on volumetric shrinkage determined by density measurements on resins containing: +, 0% PVAc; □, 8% PVAc; ▲, 16% PVAc

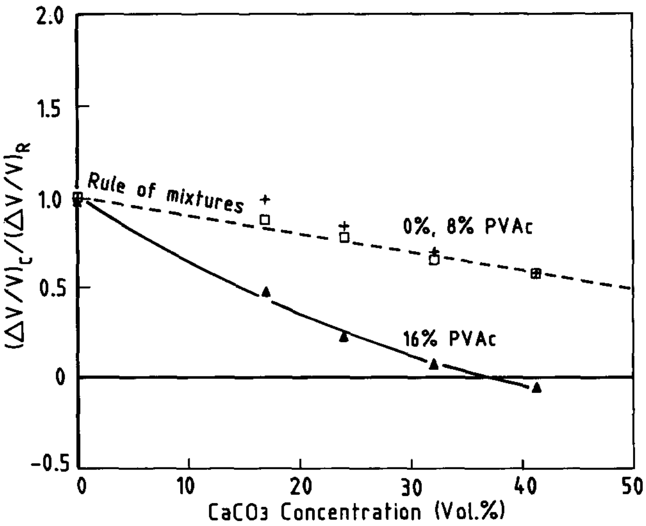

Figure 4 Data from *Figure 3* replotted as normalized shrinkage $(\Delta V/V)_C/(\Delta V/V)_R$ against volume fraction ϕ_F of $CaCO_3$. Dotted line shows predictions of equation (2)

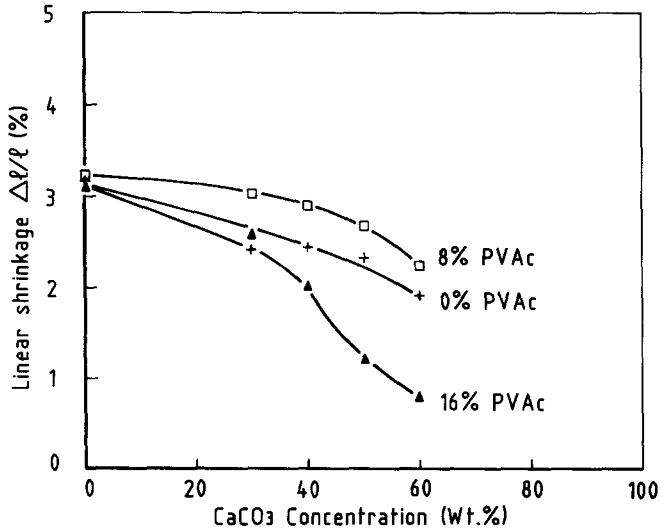

Figure 5 Effects of $CaCO_3$ content on linear shrinkage of blends containing: +, 0%; □, 8%; ▲, 16% PVAc

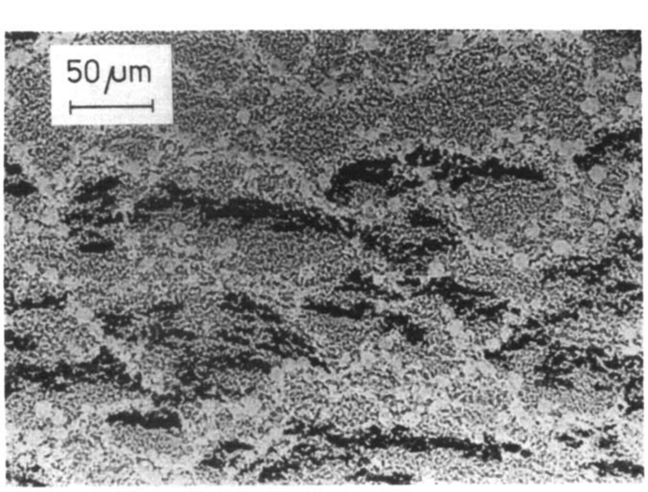

Figure 6 Optical micrograph of polyester blend containing 16% PVAc cured between microscope slides, showing localized cavitation near a lens-shaped area of resin, the rim of which is below, and parallel to, the bottom edge of the picture

modifier forms discrete particles at a concentration of 8%, and a co-continuous morphology at a concentration of 16%[12,13].

Figure 6 is a micrograph of a blend containing 16% PVAc, which was cured between a flat glass slide and one of the special slides containing a circular depression. Cavitation occurred in the polymer in a concentric ring about 1 mm wide, around the rim of the circular cavity. Outside this ring, there was no evidence of cavitation: in plain white light, there is just sufficient contrast to see the two-phase morphology of the blend. It was not possible to determine whether any cavitation occurred within the circular depression.

Tensile strength

A temperature of 80°C was chosen for tensile testing, as being representative of conditions under which shrinkage occurs: the resin is below its T_g, whilst the PVAc is above its T_g. *Figure 7* shows the relationship between tensile strength and composition. Addition of up to 8% PVAc has little effect on strength, but larger amounts of additive cause a rapid deterioration. This transition in behaviour is similar to that seen in toughness tests at 23°C on the same series of materials, and can be associated with the change from particulate to co-continuous morphology[13].

DISCUSSION

These results show that the shrinkage effect is not simply the result of interactions between resin, styrene, and thermoplastic additive, as proposed by earlier authors. Under the conditions employed in this study, the poly(vinyl acetate) modifier alone has no detectable influence on shrinkage. There is not even the reduction that might be expected from replacing up to 16 wt% of resin with PVAc, which has already undergone polymerization shrinkage from vinyl acetate monomer. This appears to be compensated by a volume decrease during demixing of the resin/PVAc solution.

The key result from this programme is that blends containing 16% PVAc show significant differences from the straight resin in the presence of $CaCO_3$ filler. This observation supports the view that external forces acting on the resin blend are responsible for 'low-profile' behaviour. In the case of filled materials, closely-spaced filler particles, which are well bonded to the resin, resist cure shrinkage, thereby setting up internal stresses in the polymer which can cause cavitation in the PVAc and shear deformation in the resin[14].

This mechanism of shrinkage control appears to operate effectively only when the PVAc concentration is sufficiently high to produce a co-continuous morphology. Electron microscope evidence for this type of morphology, and a discussion of the relationship between composition and morphology in styrene–polyester–PVAc blends are given in previous papers[12,13]. The presence of continuous PVAc regions weakens the structure, drastically reducing G_{IC} and K_{IC} (ref. 13) and causing a substantial drop in high-temperature tensile strength (*Figure 7*). These effects are a less desirable part of the mechanism that is responsible for 'low-profile' behaviour.

When a co-continuous structure of the type described above is subjected to tensile stress, it will cavitate relatively easily at low strains. Instead of generating large

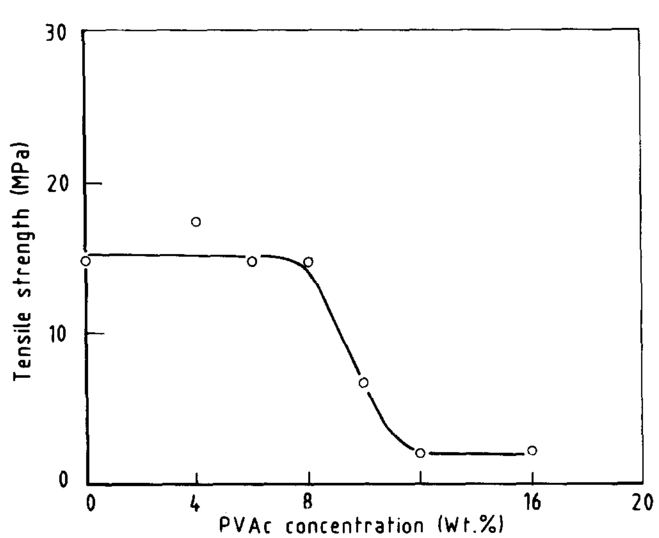

Figure 7 Effect of PVAc on the tensile strength of polyester resin at 80°C

internal stresses during cure contraction and subsequent cooling, the resin blend will generate cavities in the weak PVAc phase. The shape of the cavities will depend on the form of the stress field generated. In the microscopy study described above, tensile stresses act radially around the circular depression, which contains a comparatively large amount of resin, and therefore tends to pull material inwards as it cures and shrinks. Consequently, cavitation zones run circumferentially around the depression.

A similar pattern of cavitation was reported by Pattison, Hindersinn and Schwartz[5], who cured a solution containing styrene, polyester and PVAc on glass slides under cover slips on the hot stage of an optical microscope, and observed a loss of transparency during curing. Their micrographs show that the band of material under the cover slip, but within 200 μm of the edge, remained transparent while the specimen was at the cure temperature, and that the opaque region expanded to within 100 μm of the free edge when the resin was cooled to room temperature. However, they did not recognize the essential role of the cover slip in restraining contraction, thereby generating tensile stresses in the resin; nor did they discuss possible reasons why cavitation was localized in this way.

Like other authors, Pattison *et al.*[4,5] attempted to explain the low-profile effect purely in terms of the interactions between the resin matrix and the second phase which is formed as a result of introducing a thermoplastic additive. These explanations have involved boiling of styrene monomer within the thermoplastic phase[1]; thermal expansion of unreacted styrene[1,4,5,10]; thermal expansion of the thermoplastic component[3,6,9]; and migration of styrene from swollen thermoplastic phase after gelation of the resin phase[1].

The weakness of these theories is that they are seeking reasons why the thermoplastic additive and/or styrene monomer should of themselves prevent the resin from shrinking as it cures and subsequently cools. None of the explanations proposed can be regarded as convincing physically. These difficulties can be resolved quite simply by recognizing that the restraints on shrinkage are either external to the polymeric material, arising from embedded mineral filler particles, glass fibres, and other rigid adherent bodies such as glass microscope slides[4,5] and rheometer cones[11]; or internal stresses generated for well known reasons such as temperature differentials. Instead of asking why resins modified with thermoplastics do not shrink, we should address another question: how do single-phase and two-phase resins differ in their responses to tensile stresses which are generated through externally-imposed constraints on contraction?

This is a much easier question to answer in the case of PVAc. At lower concentrations (⩽8%) the modifier forms discrete particles, containing a high concentration of resin sub-inclusions. These particles are elastomeric above the T_g of PVAc at about 40°C, and the system is therefore effectively a rubber-toughened thermoset during the curing and cooling stages of manufacture. At higher concentrations of PVAc (⩾12%), both modifier and resin form continuous phases, strength is substantially reduced, and the blend acts as 'low-profile' resin.

CONCLUSIONS

This work has shown that addition of PVAc does not in itself cause a reduction in shrinkage of polyester resins during cure. Shrinkage control occurs only when tensile stresses are applied to the resin and initiate cavitation in the thermoplastic phase. The mechanism operates effectively only when resin and modifier phase separate to form a co-continuous structure, which is associated with a low strength in the blend.

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