Phase separation in styrenated polyester resin containing a poly(vinyl acetate) low-profile additive

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Scanning electron microscopy has been used to observe morphology in styrenated polyester resins containing poly(vinyl acetate) (PVA). Resins containing 8% PVA form composite spherical particles which occupy 35 vol% of the total material. It is concluded that these particles consist of resin sub-inclusions embedded in the continuous matrix of polyester resin. Increasing the PVA content to 16% results in a phase inversion: PVA forms the matrix, and the resin is present as spherical particles. These observations are interpreted with the aid of a ternary diagram.

INTRODUCTION

The modification of unsaturated polyesters by 'low-profile' thermoplastic additives has attracted considerable interest in recent years, as a means of improving the appearance of sheet-moulding and dough-moulding compounds. Initial work on these modifiers followed a largely empirical approach, but a number of subsequent papers have sought to explain the mechanism of shrinkage compensation[1-5]: a review by Atkins[6] summarizes the main theories, none of which can be regarded as completely satisfactory.

One of the most popular low-profile additives is poly(vinyl acetate) (PVA). This paper discusses the structures formed on curing a particular polyester system modified with different amounts of PVA. Previous investigations of structure in cured low-profile resins have been reported by several authors. In two frequently-quoted papers[7,8] Pattison *et al.* discussed the structures formed from both compatible and phase separated resin systems. Adding 12% by wt. of PVA, which is initially completely soluble in the resin, resulted in the separation of beads between 0.2 and 1 μm in diameter which were covered by a coating. The authors concluded that the beads consisted of crosslinked resin, and that the coating contained a high proportion of low-profile additive. Atkins *et al.*[4], using scanning electron microscopy (SEM) and dynamic mechanical analysis (d.m.a.), also observed phase separation between polyester resin and PVA to give a bead-like structure. Peltzer *et al.*[9], following a SEM study of a wide range of low-profile additives, identified two distinct types of structure in the cured resins. Some additives, including PVA, were shown to exhibit a structure made up of agglomerates of 'fine pearls' of diameters between 1.5 and 3 μm, which were in turn made up of smaller particles between 0.1 and 0.2 μm in diameter. Such structure was contrasted with structures observed in systems modified with polyethylene, made up of large (20–50 μm) voids and smaller particle clusters. Other authors have used observations of structural details to support mechanistic theories[3,10].

EXPERIMENTAL

The polyester system used was supplied by Scott Bader and based on 1 mol. maleic anhydride, 1 mol. isophthalic acid, 1.5 mol. propylene glycol and 0.6 mol. diethylene glycol; 60 parts of this resin are mixed with 40 parts of styrene monomer. An initiator, consisting of equal parts by weight of benzoyl peroxide and an inert powder, was added as 1.3% by weight of the styrene–resin mixture. The commercial low-profile additive was Union Carbide LP-40A, which is known to be a styrene solution containing 40% by wt. of acrylic-modified poly(vinyl acetate).

The materials were thoroughly mixed at room temperature and cured in 30 g batches at 130°C for 4 h. A short-lived exotherm caused a temperature rise to 210°C over a period of about a minute, followed by cooling to 130°C over the next 5 min. The mixture was initially clear but began to turn cloudy during this period, whitening rapidly and uniformly throughout the specimen.

Samples measuring $46 \times 12 \times 2$ mm were milled from the cured material and subjected to dynamic mechanical testing, using Polymer Laboratories DMTA equipment in the bending mode, at a frequency of 3 Hz and heating rate of 4°C min^{-1}.

Fracture surfaces were obtained by impact and coated with a thin layer of Au/Pd alloy before examination by SEM.

RESULTS

Figure 1(a) is a fracture surface of cured polyester containing 8% by wt. of PVA, which reveals the presence of composite particles, from 2 to 10 μm in diameter, each containing numerous sub-inclusions. The volume fraction of composite particles in this fracture surface, determined
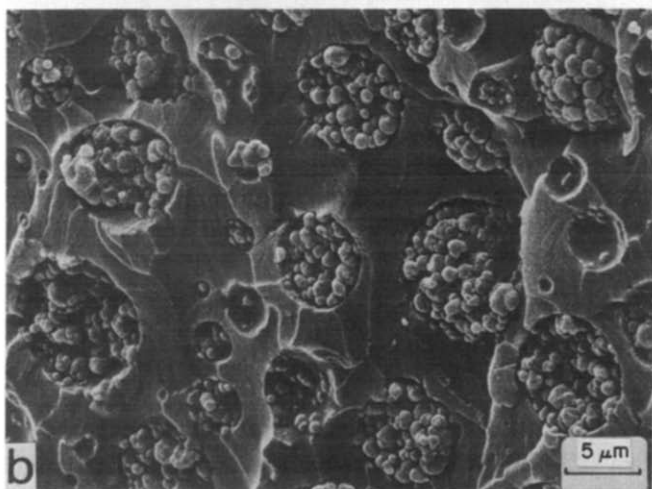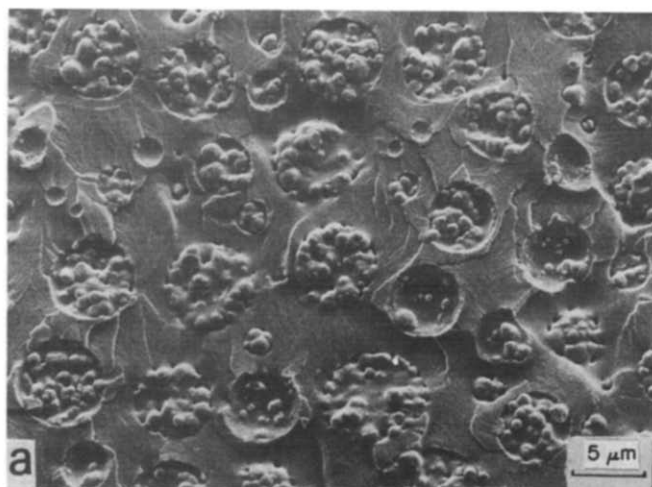
Figure 1 SEM of fracture surfaces of a cured polyester sample containing 8% by wt. of PVA. (a) Unetched; (b) etched in MEK for 20 min
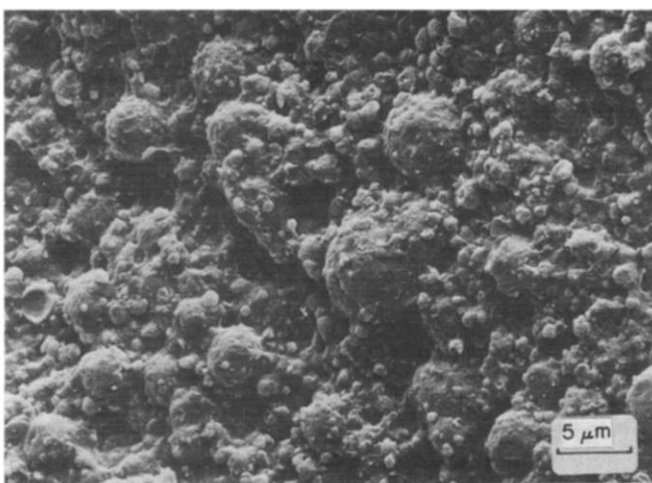
Figure 2 SEM of fracture surface of a cured polyester sample containing 16% by wt. of PVA (unetched)

from intercepts on a series of parallel lines drawn on the micrograph, was 0.35.

Figure 1(b) shows the effect of a 20 min etch at 23°C in methyl ethyl ketone (MEK) on another area of the fracture surface. A similar effect is achieved using ethyl acetate as the etch. Some of the material holding the sub-inclusions together has been dissolved away. From an examination of the micrographs it is estimated that this

soluble polymer represents about 20–25% by volume of the material in the composite particles, or 7–8% of the total volume of the cured resin, a figure that corresponds to the proportion of PVA present in the mix.

The addition of 16% by wt. of PVA leads to a completely different structure, as shown in *Figure 2*, which is at the same magnification as *Figure 1*. *Figures 3(a)* and *3(b)* show unetched and etched fracture surfaces respectively of this sample at a higher magnification. Etching appears to remove some of the connecting polymer matrix from between the spherical particles. The structure in this case consists of a very high volume fraction of spherical particles ranging in diameter from 0.5 to 10 μm.

Figure 4, taken from a poorly mixed sample of this modified polyester, shows that both types of structure, the composite particle and the uniform spherical particle structure, can be observed together.

Dynamic mechanical data presented in *Figure 5* show that the cured polyester and the PVA modifier are mutually incompatible. In an equivalent test unmodified polyester exhibited a tan δ peak at 110°C; PVA has a glass transition temperature of 45°C.

Samples of the commercial low-profile additive itself were polymerized by heating and found to undergo gross phase separation into two layers. The top layer was clear, readily soluble in ethyl acetate or MEK and appeared to
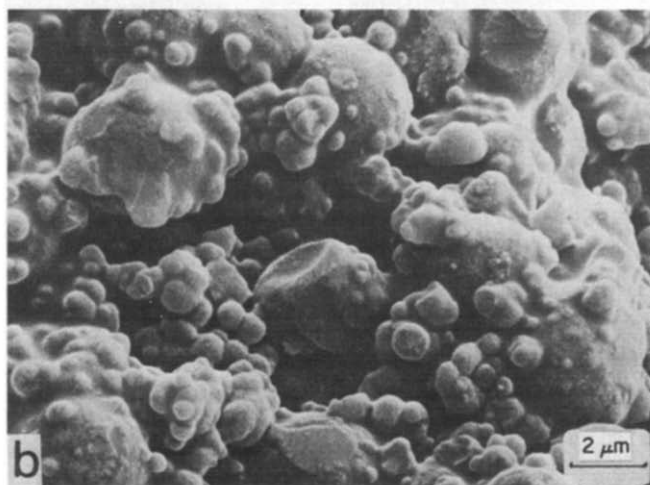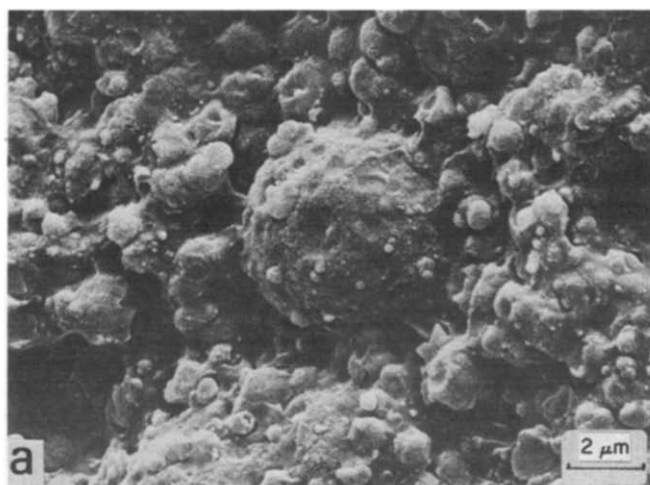
Figure 3 SEM of fracture surfaces of a cured polyester sample containing 16% by wt. of PVA. (a) Unetched; (b) etched in MEK for 20 min
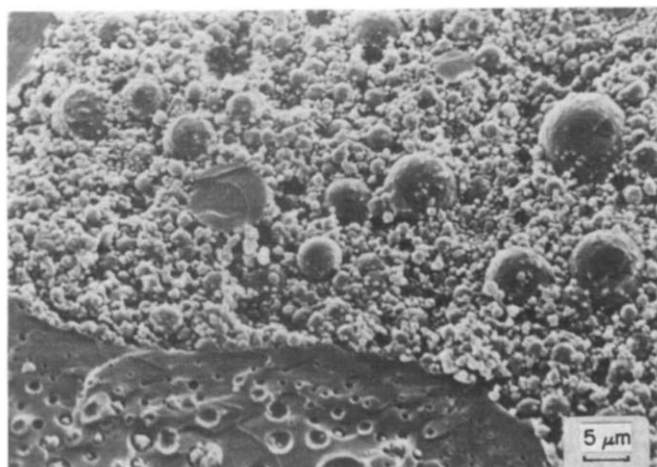
Figure 4 SEM of a poorly mixed cured polyester sample containing 8% by wt. of PVA (etched in MEK for 20 min)
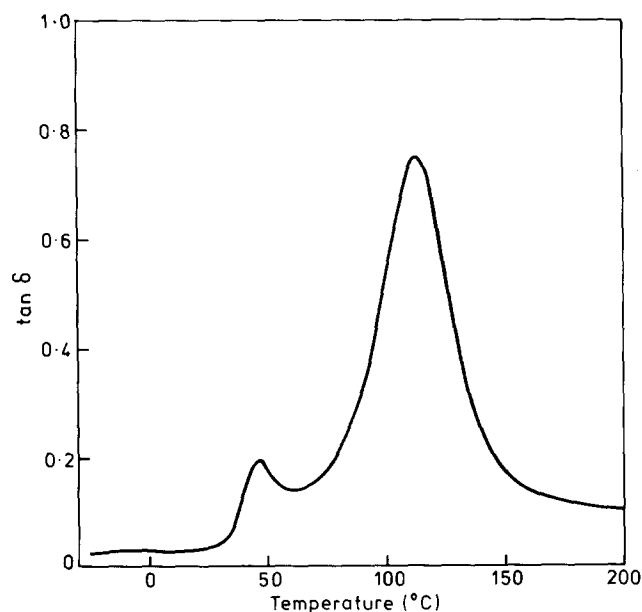

Figure 5 Dynamic mechanical analysis of a cured polyester sample containing 16% by wt. of PVA

consist essentially of polystyrene. The bottom layer was milky, soft and insoluble in these solvents. SEM examination revealed no defined morphology in either of these phases.

DISCUSSION

The solutions of PVA in styrene and polyester resin are initially transparent but become cloudy after a few minutes at 130°C, suggesting that the system begins as a single phase which separates into two or more phases as a result of the chemical changes taking place during cure. This kind of effect has been observed in a number of other polymerizing solutions, and its causes are well understood. Essentially, the increase in molecular weight of the polymerizing species reduces the entropic contribution to the free energy of mixing, so that the enthalpic contribution becomes dominant. Since mixing between polymers is usually endothermic, phase separation results.

A rigorous thermodynamic analysis is not possible in the present case, since the curing resin contains a large number of molecular species, the concentrations of which

are not known. Nevertheless, a qualitative model can be advanced to explain the effects observed. *Figure 6* is a schematic ternary diagram which serves as a basis for the discussion. The three components in the diagram are monomer, cured resin and PVA. Point A represents a single phase solution containing 8% PVA. As the monomer polymerizes, the composition of the system moves along the line ABC, undergoing phase separation at point B, to the left of the plait point, P. Between B and C the compositions and concentrations of the two phases are given by the appropriate tie-lines: the resin-rich phase constitutes the major component, and therefore forms the matrix. At a certain stage of polymerization, represented by point D, the resin matrix reaches a gel point, and mass transfer of polymer into or out of that phase ceases. Beyond that point, a straightforward application of the equilibrium phase diagram along the lines outlined above is no longer appropriate. Instead, attention must be directed towards the minor phase E which contains most of the PVA, and which has not yet reached a gel point. Since it is a minor phase formed under unstirred fluid conditions, composition E will be present as spherical droplets. Further polymerization takes the dispersed droplets along the line EF, with separation of a resin-rich phase G and a PVA-rich phase H. During the initial stages of this localized phase separation within the droplets, G represents the minor phase, and therefore forms the disperse phase within the droplet. However, continued
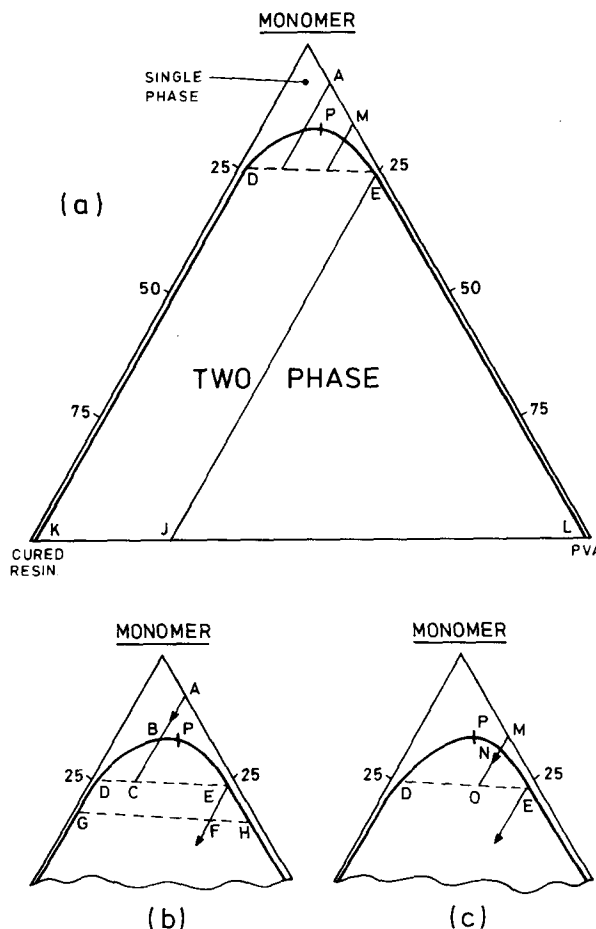

Figure 6 Schematic ternary phase diagram for the polyester – poly(vinyl acetate) system. (a) Complete diagram; (b) detail showing behaviour of resin containing 8% by wt. of PVA; (c) detail showing behaviour of resin containing 16% by wt. of PVA

reaction takes the sub-system along the line FJ, so that at the end of the polymerization the resin-rich sub-inclusions indicated by point K have grown to the stage at which they occupy about 75% of the volume of the droplets. Continuing phase separation and growth of the sub-inclusions by accretion is possible because the PVA-rich material within the droplets remains liquid, since it is above its glass transition temperature and uncrosslinked. The resin-rich matrix, on the other hand, gels at an early stage, as discussed above, and for that reason its PVA content is unlikely to fall below that of composition D, at which gelation occurs.

Point M in *Figure 6* represents a solution containing 16% PVA. Phase separation occurs at point N, and gelation begins when the composition is at point O. In this case the lever rule shows that the resin-rich phase D is the minor component, and will therefore form small droplets in a matrix rich in PVA. Continued polymerization results in growth of the resin droplets and formation of new ones to produce the structure shown in *Figure 3*, in which resin spheres of various sizes are embedded in an uncrosslinked matrix of PVA.

This discussion shows that a phase inversion is to be expected at a PVA concentration between 8 and 16%, corresponding to the midpoint of the tie-line DE. Similar effects have been reported previously for solutions of CTBN rubber in epoxy resin[11,12]. The structures formed are similar to those observed in high impact polystyrene, but the mechanisms responsible are different.

Internal morphology would be expected to affect both the mechanical properties of these systems and their performance as low-shrinkage formulations. The additive concentration levels explored here correspond to those used in commercial low-shrinkage resins, but the structures obtained and hence the resin performance will depend on the particular polyester–initiator formulation employed.

ACKNOWLEDGEMENTS

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