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New formulations for unsaturated polyester resins and their interactions with low-profile agents and glass fibres

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Special anhydrides, such as hexahydrophthalic, methyl-hexahydrophthalic, nadic, methyl-nadic and methyl-tetrahydroxyphthalic, have been polycondensed with glycols such as propylene and di-propylene, to obtain new formulations for unsaturated polyesters. The properties of these resins, such as tensile behaviour and ultraviolet resistance, neat or mixed with anti-shrinkage additives have been examined and compared to standard polyester resins. Particular attention was paid to the study of the influence of low-profile agents on the resulting phase structures of cured systems. Moreover, the role played by the different phases on the fibre/matrix addition in composite materials reinforced with coated glass fibres was also investigated.

1. Introduction

Unsaturated polyester resin (UPE) is one of the most important polymers for composite materials in the automotive, building and furniture industrials. Thermoset polyesters offer advantages such as light weight, high strength and excellent mechanical properties [1]. They are generally prepared by the condensation reaction of dicarboxylic acids or anhydrides with glycols and are cross-linked by organic peroxides or by irradiation in the presence of a reactive monomer (e.g. styrene). A broad range of properties can be obtained by suitable choice of starting monomers. The curing reaction is a free-radical chain-growth copolymerization between the styrene monomer and the unsaturated polyester molecules. During the curing, the resin tends to shrink away from the mould walls due to polymerization. In fact, the shrinkage force produces internal stresses which lead to surface and structural flaws.

The commercially available resins are made from maleic, phthalic and/or isophthalic anhydrides and propylene glycol. Unfortunately, the materials so prepared, suffer a number of deficiencies, namely brittleness, poor resistance to solvents and to long-term outdoor exposure. This last problem is particularly relevant when these materials are used in building and furniture applications.

Together with fillers, reinforcement and additives, they are usually available as compounds for compression moulding (sheet moulding compound, SMC), injection moulding (bulk moulding compound, BMC), resin transfer moulding and pultrusion. The addition of some thermoplastics to the polyester resin was found to compensate for and even eliminate the shrinkage problem [2, 3]. These thermoplastic materials are called “low-shrink” or “low-profile” additives (LPA).

In a previous paper [4] we have investigated the influence of the presence of some low-profile agents on the resulting phase structure and thermal behaviour of different polyester resin formulations reinforced, or not, with glass fibres coated by silane coupling agents. It was demonstrated that the polar-type LPA can stick to the surface of glass fibres during the curing reaction when the separation process occurs, thus allowing also a better compatibility at the fibre/matrix interface.

The aim of this work was to investigate the properties of new formulations of unsaturated polyester resins obtained by using alternative anhydrides combined with mono- or diglycols, evaluating the interactions carried out with different low-profile additives and glass fibres as functions both of anhydride and glycolic components in cured systems. The mechanical properties and the phase structuring of these resins to those of standard polyester resin, such as phthalic anhydride, were compared. Finally, the influence of such formulations on the fibre/matrix interfacial adhesion of cured systems was also investigated.

2. Experimental procedure

2.1. Materials

All the materials used in this study were supplied by LONZA S.p.A.

Polyester resins were obtained by the polycondensation reaction between propylene glycol or dipropylene

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glycol with maleic anhydride and the special anhydrides used are shown in Table I.

The polyester polymer was synthesized according to the general formula: propylene glycol 1.0 mol; maleic anhydride 0.8 mol; special anhydride 0.2 mol. Reaction parameters such as glycol excess, temperature and final acid value, were optimized in order to obtain polymers with a similar molecular weight for every kind of anhydride. The resulting polymers were then dissolved in styrene monomer and inhibitors were added in order to reach the following specifications: viscosity at 25 °C, 1000–1100 mPa s; styrene content, 32%–33%; gel time, 25–30 min; delta, 8–10 min.

The following curing cycle was adopted for all products: catalysis, 0.4% Co naphthenate 6% and 1.5% MEKP; curing, 24 h at 25 °C; post-curing, 3 h at 100 °C. Given that the anhydrides have similar molecular weights and that polymers have been synthesized with about the same average molecular weight, it is reasonable to assume that all differences in chemical and mechanical behaviour can only be ascribed to the anhydride properties.

Four different low-profile additives were used: two commercials, polystyrene (PS) and polyvinylacetate (PVAc) dissolved in liquid styrene (20% wt/wt). The other two were hybrid saturated aliphatic polyester-isocyanide extended (LPU1) and an hybrid unsaturated aromatic polyester–isocyanide extended (LPU2). The reinforced polyesters were prepared by adding a 30 wt/wt glass fibres sized by appropriate silane coupling agents.

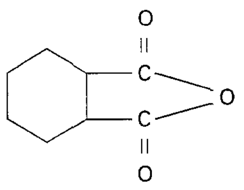
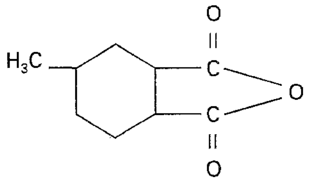
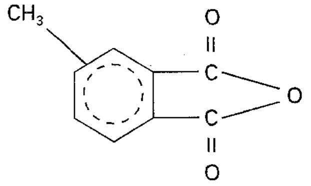
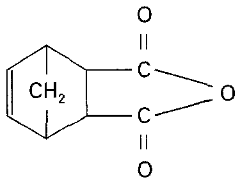
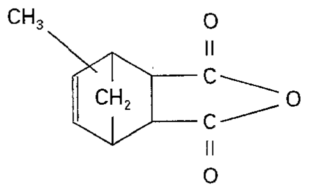
2.2. Techniques

The morphological studies, fractographic analysis and fibres/matrix adhesion were investigated using a Philips 501 model scanning electron microscope (SEM). The specimens, previously fractured in liquid nitrogen, were coated by a Polaron sputtering apparatus with an Au–Pd films to metallize the sample surfaces.

All the measurements were carried out under nitrogen gas.

The mechanical behaviour of the samples was investigated according to ASTM D638 tests by using an Instron Machine. The UV resistance was assessed by using a UV-CON Atlas Apparatus with a mercury lamp at 313 nm UVB.

TABLE I List of special anhydrides

Anhydride	Code	
Hexahydrophthalic anhydride	HHPA	
Methyl-hexahydrophthalic anhydride	Me-HHPA	
Methyl-tetrahydrophthalic anhydride	Me-THPA	
Endomethylenetetrahydrophthalic anhydride	nadic	
Methyl-endomethylenetetrahydrophthalic anhydride	Me-nadic	

3. Results and discussion

3.1. Special anhydrides-based polyesters, neat and glass fibres-reinforced

All polyester formulations prepared with the special anhydrides were characterized in terms of mechanical behaviour in comparison to phthalic anhydride (PA) based resin which we assumed as standard. In order to facilitate comprehension of resin properties, we fixed the value of the standard at 100.

The tensile strength, elongation at break and tensile modulus for all examined unreinforced samples in Fig. 1a–c, are reported, respectively. From these figures it emerges that tensile strength and elongation to break of resin based on Me-THPA and Me-nadic anhydrides present values very near to PA standard resin, while the value calculated for HHPA, Me-HHPA and nadic anhydrides are lower by 10%–20%. No substantial differences in the values of the tensile modulus were observed.

Let us now consider the data obtained on glass fibres-reinforced samples. The glass fibres content used was around 30 wt/wt. The tensile strength, the elongation to break and the tensile modulus in Fig. 2a–c are shown, respectively. From the figures it can be noted that the tensile strength and modulus of all special anhydride-based resins are higher than the PA resin by 10%–30%. Particularly resins based on HHPA, Me-HHPA and nadic anhydrides have shown an improvement of mechanical properties higher than

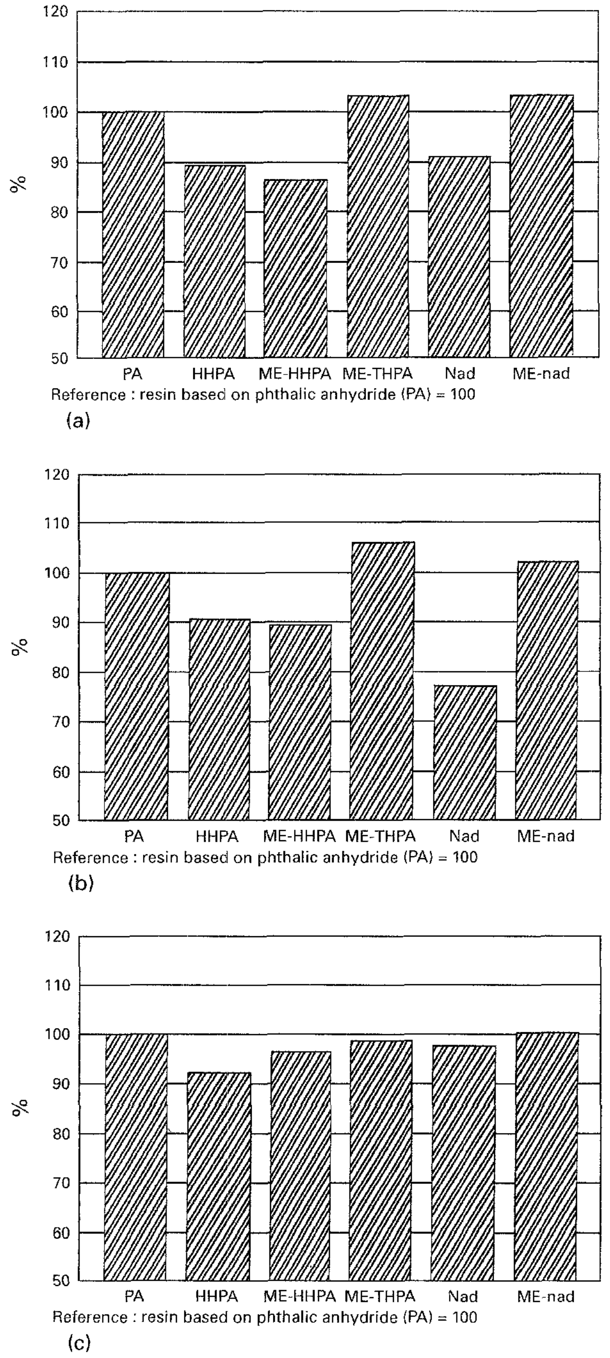


Figure 1 (a) Tensile strength evaluation on pure resin. (b) Elongation to break on pure resin. (c) Tensile modulus evaluation on pure resin. Anhydride content 0.2 mol.

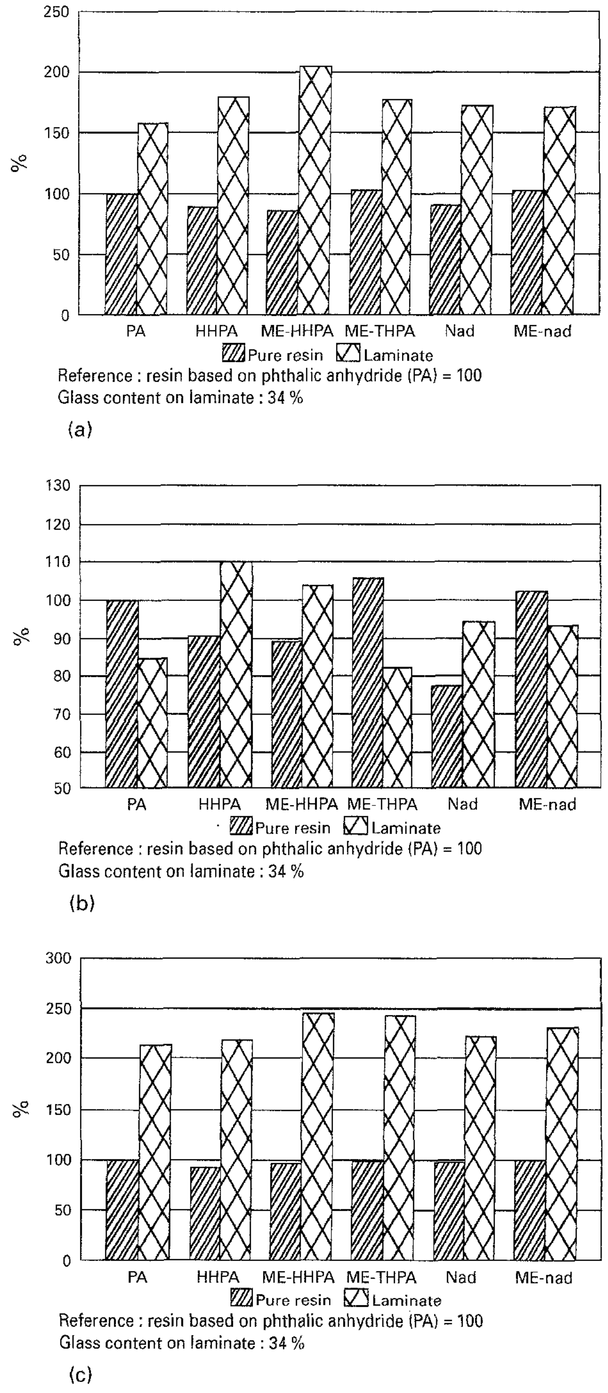


Figure 2 (a) Tensile strength: pure resin versus laminate. (b) Elongation to break: pure resin versus laminate. (c) Tensile modulus: pure resin versus laminate. Anhydride content 0.2 mol.

the other resins. Moreover, the elongation to break values are significantly increased moving from plain resin to glass fibre-reinforced.

Such behaviour could be ascribed to an improved fibre/matrix adhesion, probably due to a better interaction with coupling agents present on the glass-fibre surface. In order to evaluate this result described above, a study on the fracture surface of samples after the tensile tests by using SEM microscopy was carried out.

In Fig. 3 a–d the fracture surface of PA, HHPA, Me-HHPA and nadic based resins are shown, respectively. From these micrographs we can observe that the resins obtained with special anhydride formulations present a better matrix/fibre adhesion, being well wrapped in the polymeric matrices, while they are detached from the resin in the case of standard PA matrix.

3.2. UV resistance

It is well known that some plastic materials are sensible to the ageing by light especially in the field of ultraviolet wavelength. This phenomenon is mainly due to the presence of aromatic structures and to their aptitude to absorb radiation in the ultraviolet region.

Polyester resins belong to this class of plastic materials. The ageing is generally displayed as a yellowing of the surface of manufactured goods. It is possible to limit it by the addition of particular UV absorbs, such as benzophenones or benzotriazoles derivatives. An alternative could be the use of cycloaliphatic raw materials. So it is correct to suppose that resin made with anhydrides, as described in this work, can show better performances than PA, these being totally aromatic-free. In Fig. 4 we show the results of yellowing tests made on resins based on PA and special anhydrides. The value represents the variation of b coordinate after 4 h under UV exposure in a UV-CON test apparatus. We can observe a better performance of all products, in particular HHPA, Me-HHPA, nadic and Me-nadic.

The given Δb of a PA resin equal to 100, the yellowing variation of modified resin, is in most cases around or under 20%. This result confirms the above-mentioned hypothesis showing the possibility of using this new class of polymers where UV resistance is a specific requirement.

3.3. SEM analysis of fractured surfaces of polyester/low-profile systems

The first stage of scanning electron microscopy investigations was developed in order to understand the resulting morphology of cured systems containing polyesters of different formulations obtained by using special anhydrides and doped with low-profile agents. As is known, when the curing reaction starts,

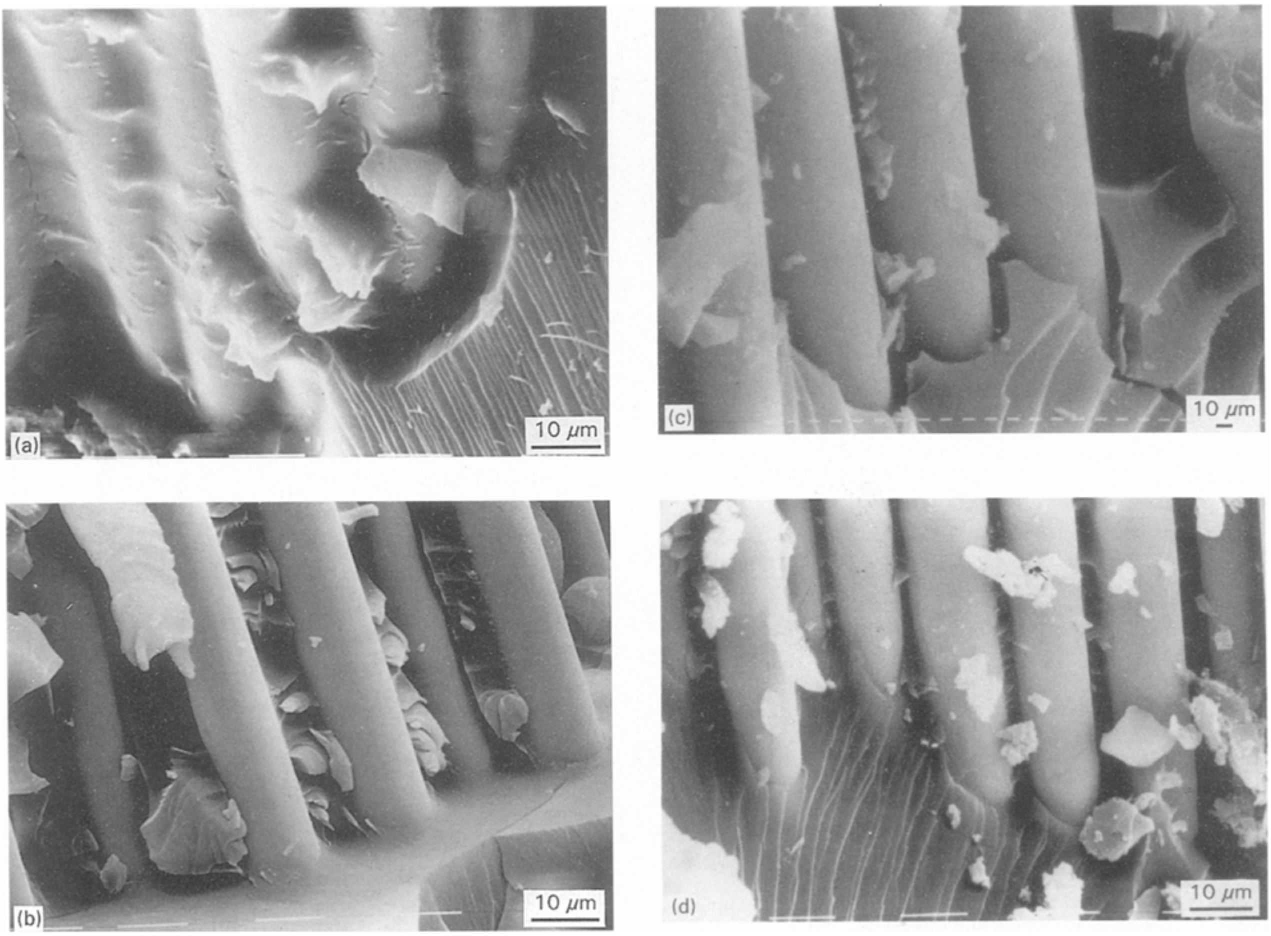


Figure 3 Scanning electron micrographs of fractured surfaces of polyester resins. (a) PA, (b) HHPA, (c) Me-HHPA, (d) nadic.

a separation process of the low-profile agents occurs, giving rise to a microstructure where, in a homogeneous matrix, well-defined domains of thermoplastic additive (LP) are uniformly distributed [4, 5].

The scanning electron micrographs of fracture surfaces, obtained at room temperature, of cured plain polyester of all examined formulations, present a homogeneous surface and preferential cracking lines are absent (see example in Fig. 5). The micrographs of fractured surfaces of some samples containing a low-profile additive, polystyrene (PS), are shown in Fig. 6 (a) PA, (b) HHPA, (c) nadic. The thermoplastic additive, for all the samples, is present as spherical domains of 10–100 μm. The most polystyrene particles have been ejected from the surfaces of polyester, indicating poor adhesion between low-profile agent and polyester resin. Nevertheless, the presence of numerous crack-stopping lines coming from the holes indicates that the PS phase hinders the fracture propagation, rendering the material less brittle than the starting polyester. In addition, it is commonly known that the polystyrene provides a good shrinkage control in polyester moulding. After all, no particular influence on the morphology in the case of PS low-profile additive can be attributable to the polyester formulations that can be obtained by varying the anhydride kind.

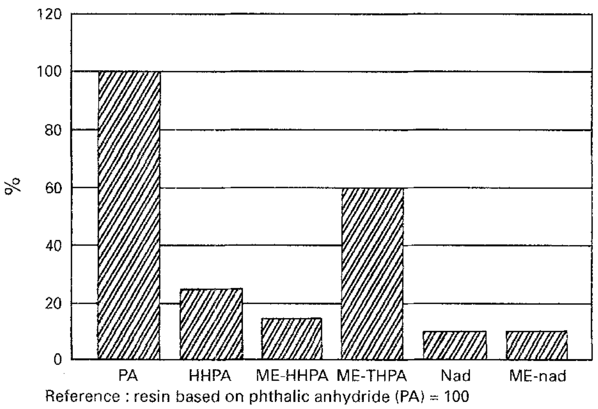


Figure 4 Yellowing after ultraviolet exposure. Δb on pure resin.

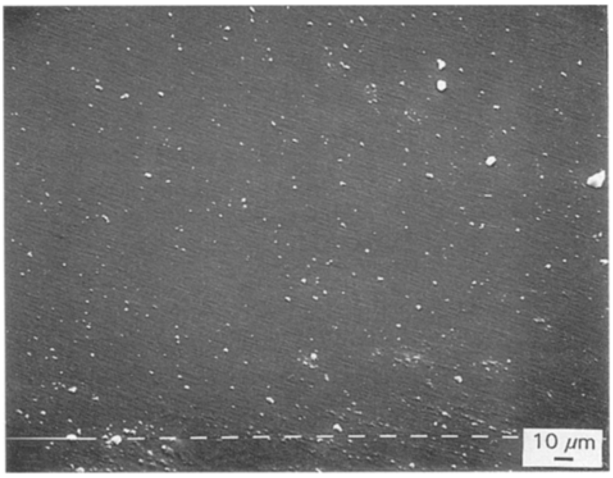


Figure 5 Scanning electron micrographs of fractured surfaces of polyester resin PA.

The micrographs of fractured surfaces of some samples compounded with polyvinyl acetate (PVAc) are shown in Fig. 7 (a) PA, (b) Me-HHPA, (c) Me-nadic. The PVAc forms smaller domains than those of PS low-profile additive for all formulations examined (4–5μm). The presence of the PVAc particles, after the fracture process, testifies to a strong adhesion to the polyester matrices. Also, in this case, no relevant differences were found between the various anhydrides in terms of dispersion and adhesion.

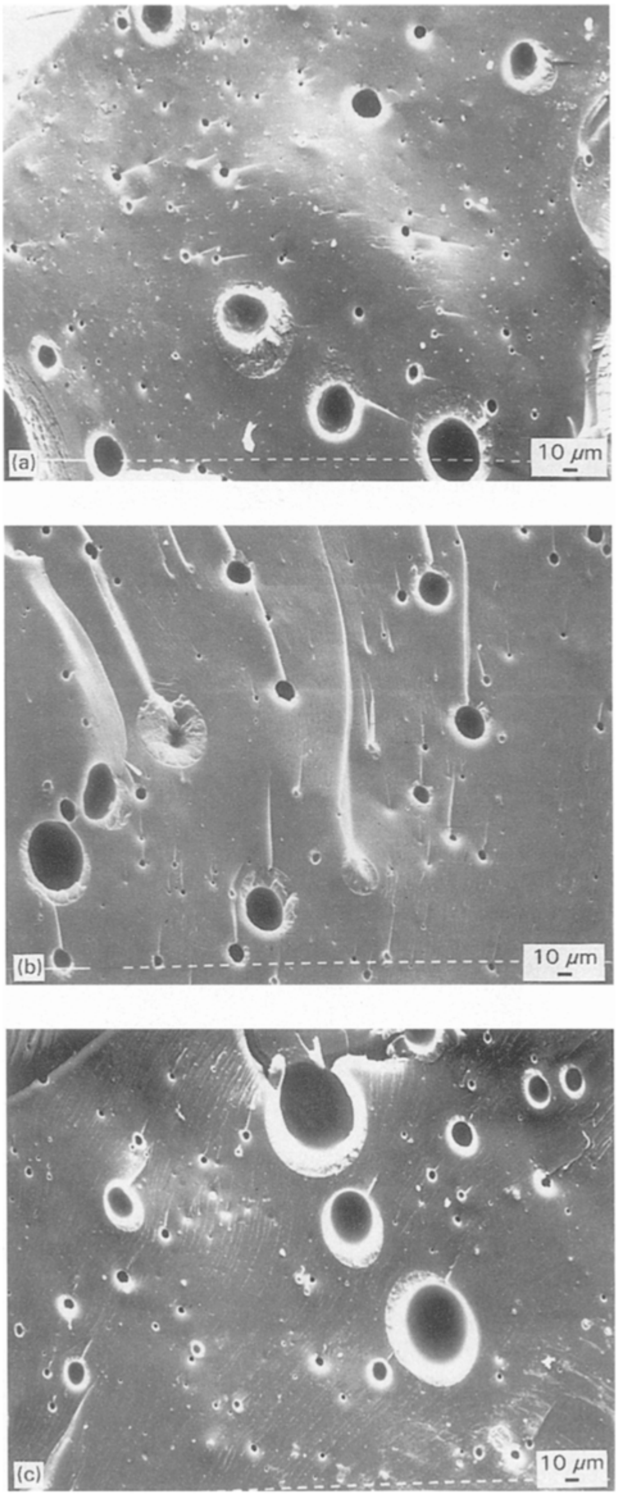


Figure 6 Scanning electron micrographs of fractured surfaces of polyester resins PS low-profile. (a) PA, (b) HHPA, (c) nadic.

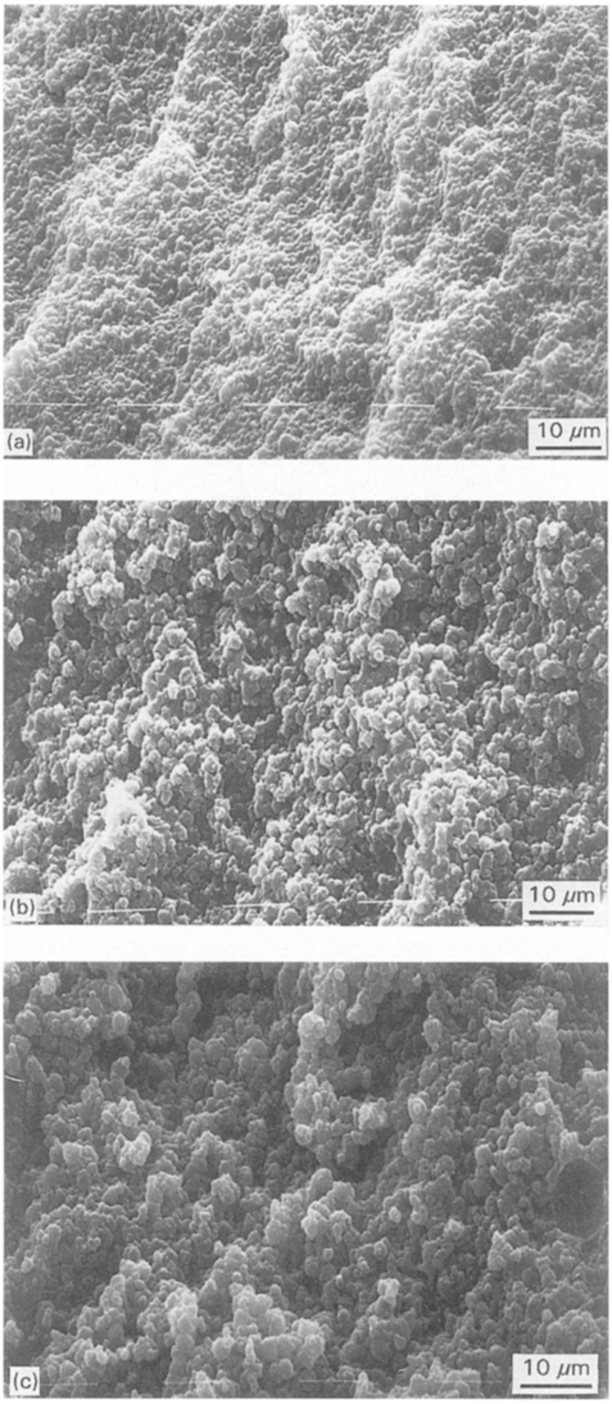


Figure 7 Scanning electron micrographs of fractured surfaces of polyester resins + PVAc low-profile. (a) PA, (b) Me-HHPA, (c) Me-nadic.

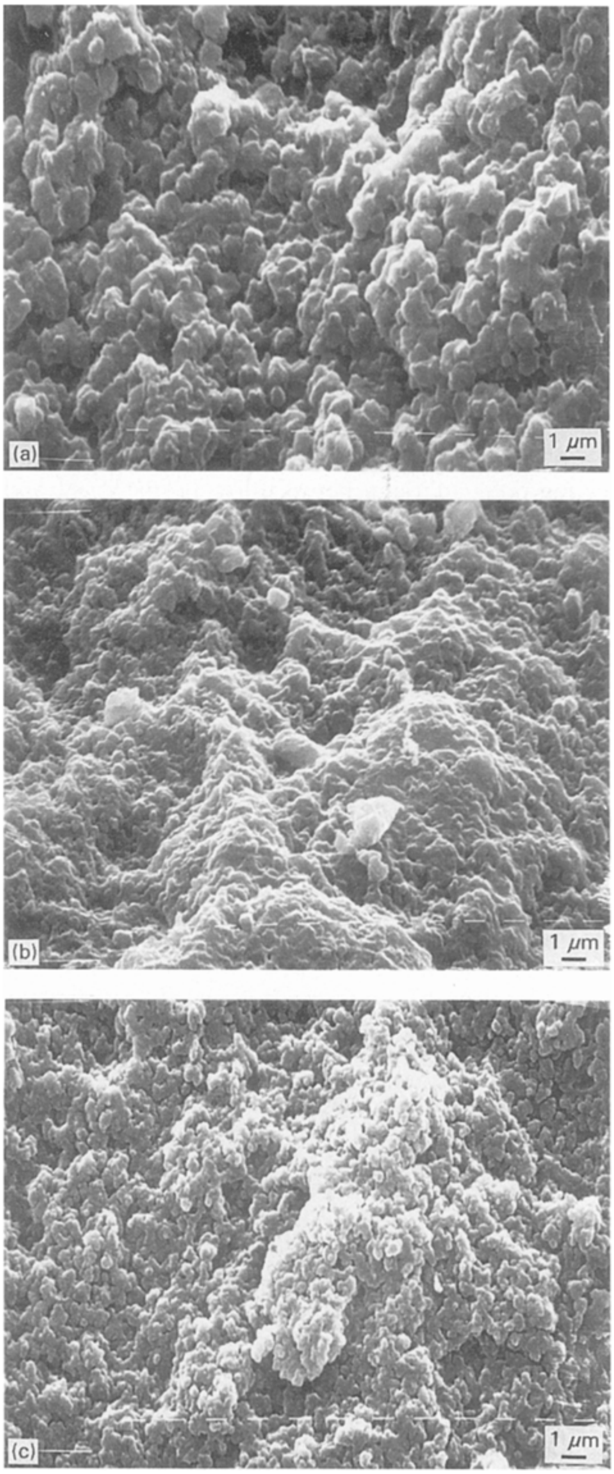


Figure 8 Scanning electron micrographs of fractured surfaces of polyester resins + LPU1 low-profile. (a) PA, (b) HHPA, (c) nadic.

Scanning electron micrographs of fractured polyester samples containing the last two low-profile agents considered (LPU1 and LPU2) are shown in Fig. 8 (a) PA, (b) HHPA, (c) nadic and Fig. 9 (a) PA, (b) Me-HHPA, (c) Me-HTPA, respectively. The differences between the two low-profile agents are due to the presence of some aromatic unsaturations in LPU2. The latter are used to improve the interactions with styrene monomer during the cross-linking reaction, in order to produce a better adhesion in the cured system between polyester matrices and antishrinkage additives. In fact, a higher adhesion between the two phases in the case of LPU2 agent (compare Figs 8 and 9) is very evident. The domains of low-profile additive are very difficult to recognize on the surface of polyester resins. Anyway, they are very small for both LPU1 and LPU2 (about 1 μm).

Finally, the special anhydrides seem to produce a fine dispersion of domains with respect to those of PA standard, especially in the case of LPU1 series (compare Fig. 8a with b and c).

In conclusion the findings show that the two hybrid polyester-isocyanide extended are more finely dispersed and better adhered to the polyester resins than the two commercial low-profile agents (PS and PVAc). Moreover, the presence of an amount of aromatic double bonds seems to improve even more the

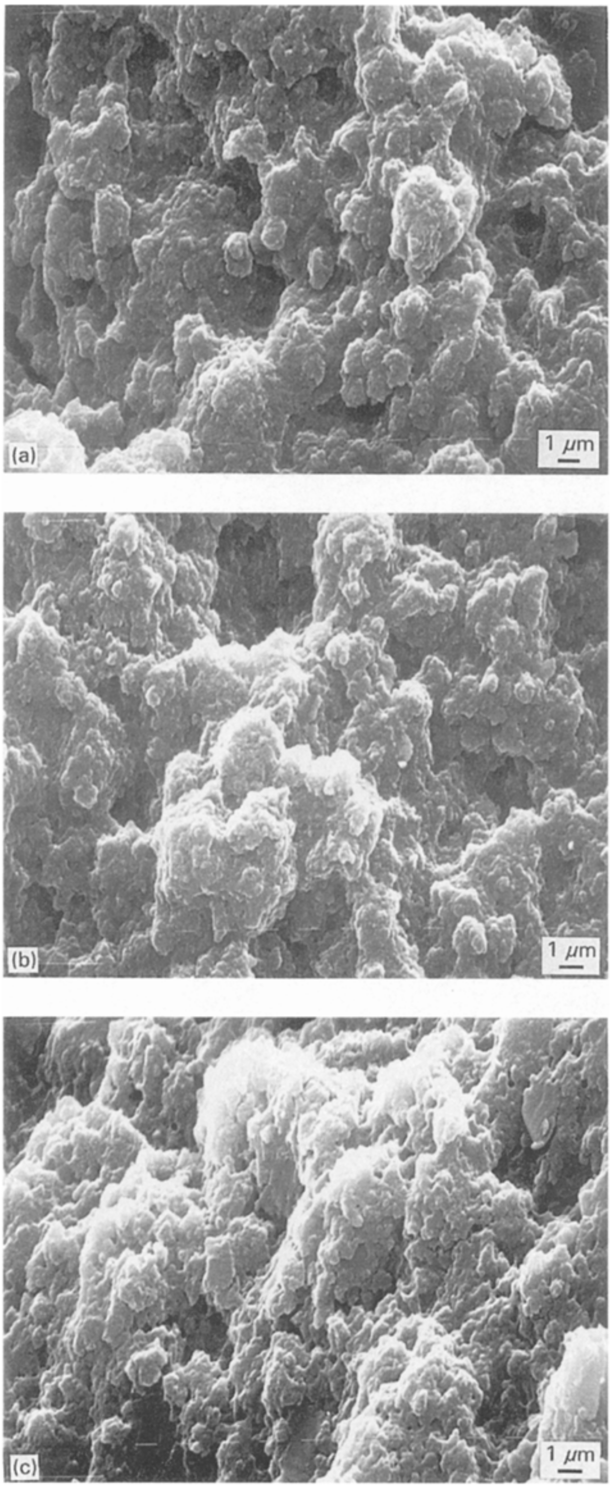


Figure 9 Scanning electron micrographs of fractured surfaces of polyester resins + LPU2 low-profile. (a) PA, (b) Me-HHPA, (c) Me-HTPA.

adhesion and dispersion, especially if the special anhydrides are used as matrices.

3.4. SEM analysis of fractured surfaces of glass fibres/polyester/low-profile agents systems

In this part of the work we investigated the influence of the presence of low-profile agents on the fibre/matrix adhesion of polyester resins based on special anhydrides and reinforced by glass fibres. As is known, the performances of polyester/glass fibre composites depend strictly on the resulting fibre/matrix interfacial adhesion. Generally, to obtain higher interfacial properties, some appropriate coupling agents (e.g. silane) are used to cover the fibres surface [6]. These agents develop their function during the curing process by participating with chemical bridges between polyester resin and coated glass fibres, so improving the fibre/matrix adhesion.

The electron micrographs of fractured surfaces corresponding to the samples doped with PS low-profile agent are shown in Fig. 10 (a) PA, (b) Me-HHPA,

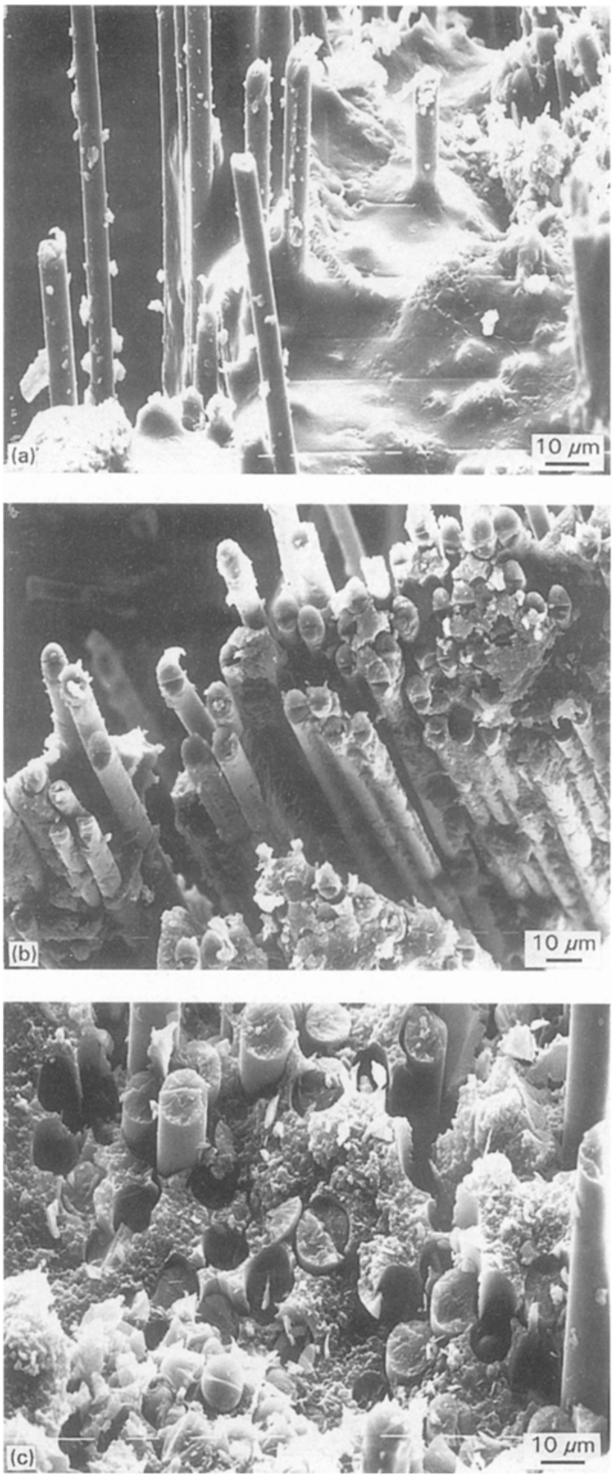


Figure 10 Scanning electron micrographs of fractured surfaces of polyester resins + PS low-profile + glass fibres. (a) PA, (b) Me-HHPA, (c) nadic.

(c) nadic. From the observations of such figures, a poor adhesion is observable: some fibres are pulled out and numerous voids are present, especially in the case of samples prepared by using special anhydrides such as nadic and Me-nadic. In contrast, some micrographs of composites obtained by using PVAc low-profile additive are shown in Fig. 11 (a) PA, (b) Me-HHPA, (c) nadic. From these figures, a good adhesion between fibres and matrices, in all the samples, is observed: no phenomena of debonding and pull-out are found; however, it should be noted that the fibres are clean and not covered by the resin. Moreover, no differences seem to be evident between PA and special anhydride-based polyester resins.

On examining the morphology resulting by using the two isocyanide extended low-profile agents (LPU1 and LPU2), we can deduce an improvement concerning the interfacial adhesion between fibres and low-profile agent/polyester resins systems (see Fig. 12 series LPU1, and Fig. 13, series LPU2). In fact, the electron micrographs reported in Fig. 12 (a) PA, (b) HHPA, (c) Me-nadic show a high degree of adhesion, no

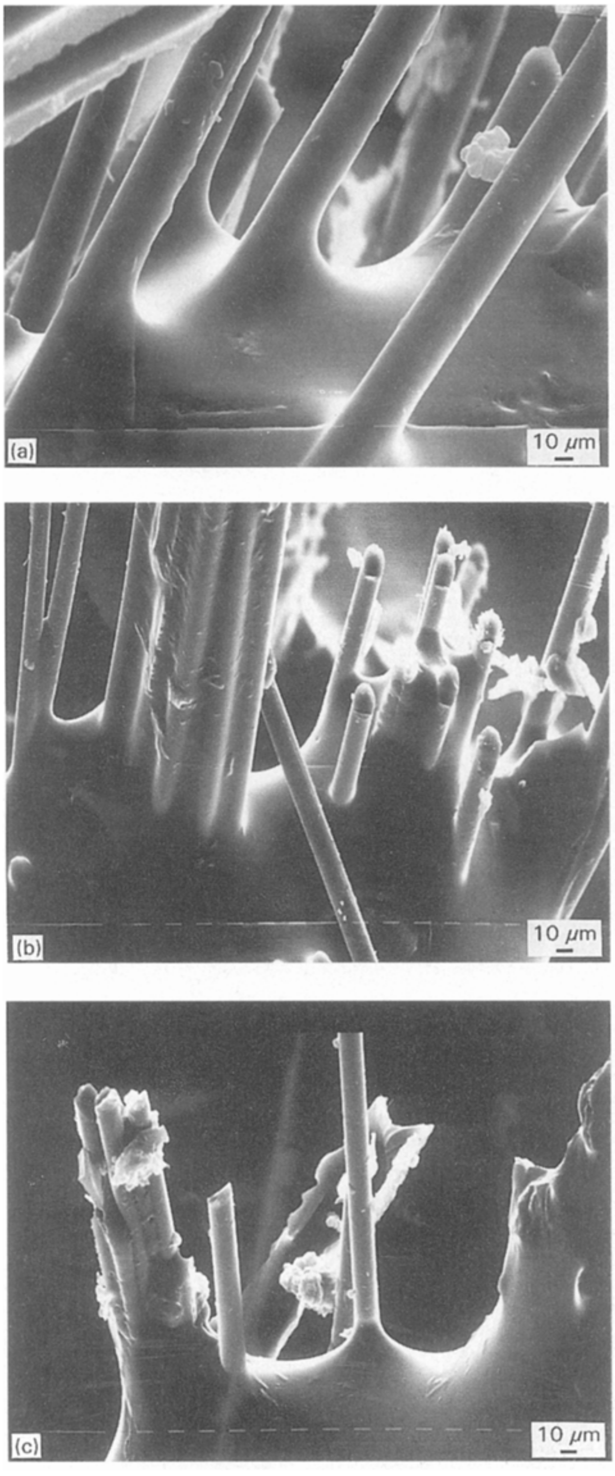


Figure 11 Scanning electron micrographs of fractured surfaces of polyester resins + PVAc low-profile + glass fibres. (a) PA, (b) Me-HHPA, (c) nadic.

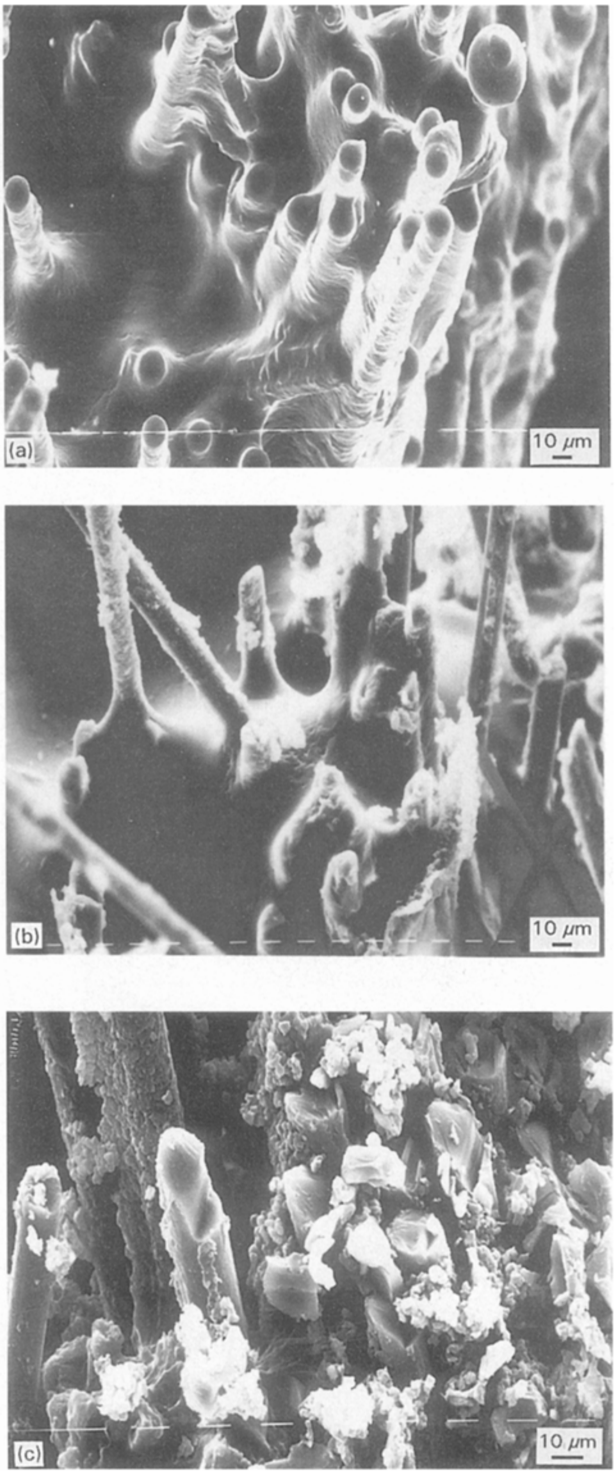


Figure 12 Scanning electron micrographs of fractured surfaces of polyester resins + LPU1 low-profile + glass fibres. (a) PA, (b) HHPA, (c) Me-nadic.

pull-out and debonding are observed and also the fibres are covered by the low-profile agent. However, the best performances are reached by using the aromatic unsaturated low-profile (LPU2) (see Fig. 13 (a) PA, (b) HHPA, (c) and (d) Me-HHPA: the fibres are completely covered by the low-profile agent and they all remain in the matrices; moreover a better performance seems to be attributable to the special anhydrides-based polyesters compared to PA standard resin.

3.5. Glycolic influence

Finally, we describe some preliminary results of the influence of the glycolic part of the resin on the resulting morphology of cured samples doped by low-profile agents. Our experiment was limited to a maleic anhydride-based polyester resin polycondensed with propylene glycol (resin PG) and the same resin with 60% wt/wt propylene glycol + 40% wt/wt dipropylene glycol (resin DPG). The low-profile additives used were polystyrene (PS), polyvinyl acetate (PVAc) and the hybrid saturated aliphatic polyester/isocyaned extended (LPU1).

The electron micrographs of fracture surfaces corresponding to the two polyester matrices containing the three low-profile agents are shown in Figs 14 and 15 (14a–c resin PG and 15a–c resin DPG respectively). From a comparison of the two series of photos the strong effect is evident on the resulting morphology of cured systems of the utilization of a different glycolic component: in fact, the resin DPG shows a finer dispersion of the low-profile domains, especially in the case of PVAc and LPU1 additives. In particular, the dimensions are very small (about 1 μm) compared to those of the same low-profile agents immersed in the resin PG (5–10 μm).

Help with understanding such differences in the resulting morphologies in cured polyester/low-profile systems can be obtained by calculating the solubility parameter, δ, of the components (glycol, styrene and low-profile agents). However, the use of solubility parameters has to be made with attention [7].

Table II shows the values of these parameters calculated at room temperature using the Small method [8]. The results show that DPG solubility parameter, δ, presents a value very near to that of styrene while the PG δ value is very high. Moreover, the DPG δ value is also nearer to those of our low-profile agents if compared with the PG δ value. This finding could confirm a better interaction of DPG both with styrene monomer and low-profile agents, affording the latter a finer dispersion during the

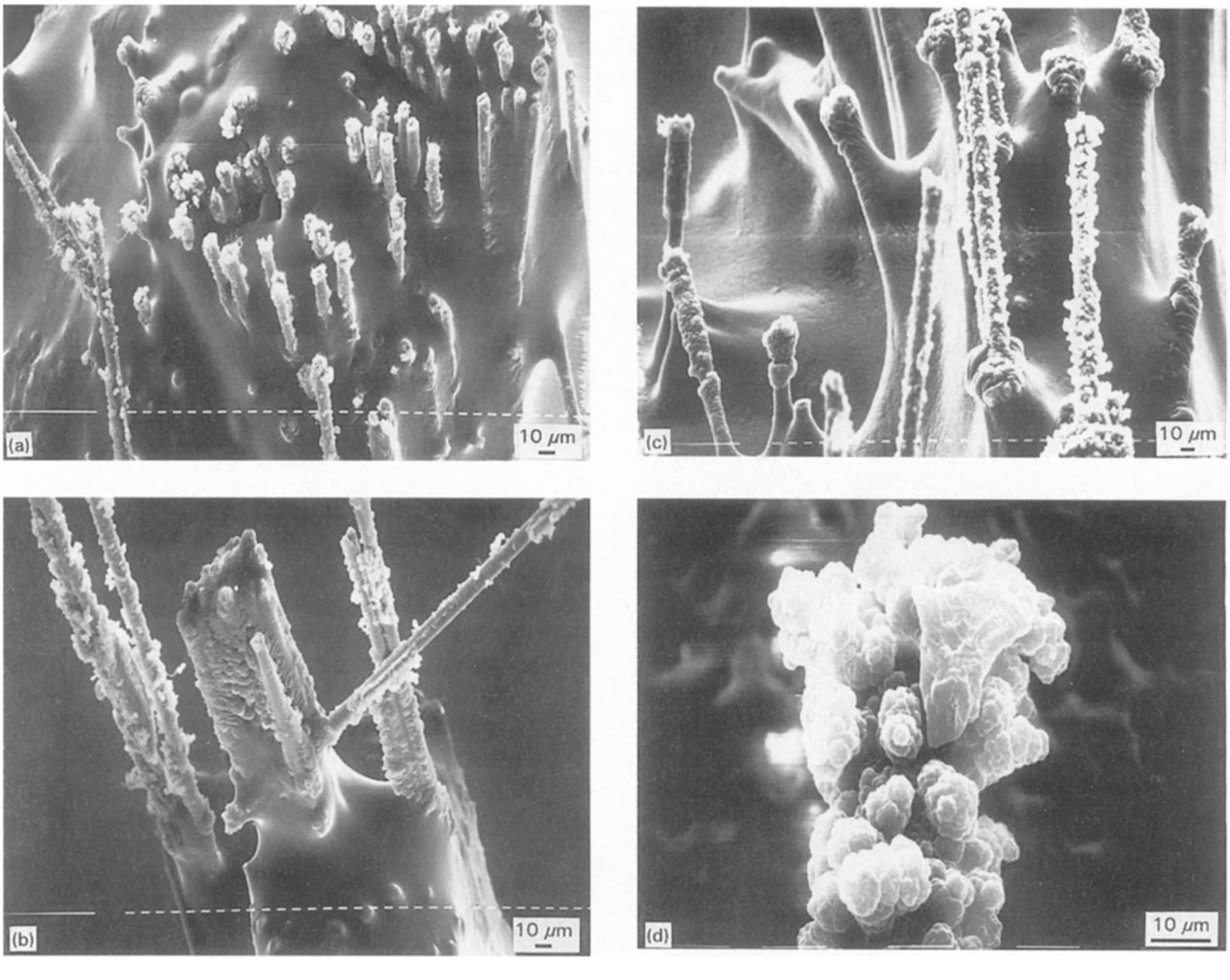


Figure 13 Scanning electron micrographs of fractured surfaces of polyester resins + LPU2 low-profile + glass fibres. (a) PA, (b) HHPA, (c) Me-HHPA, (d) Me-HTPA.

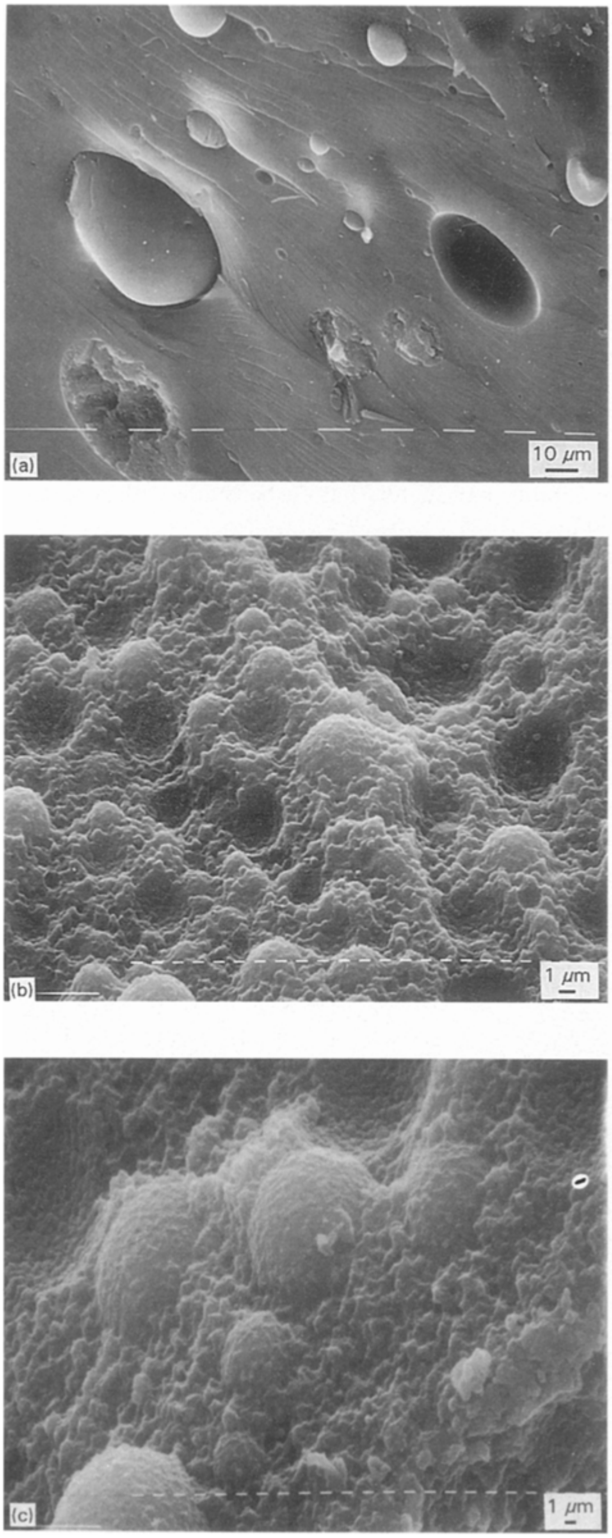


Figure 14 Scanning electron micrographs of fractured surfaces of polyester resins by using PG. (a) PS, (b) PVAc, (c) LPU1.

TABLE II Solubility parameters, δ, calculated by Small's method [8]

	δ (at 25° C (cal cm^{-3})$^{0.5}$
PG	12.6
DPG	10.0
Styrene	10.5
PS	9.2
PVAc	9.4
LPU1	9.6

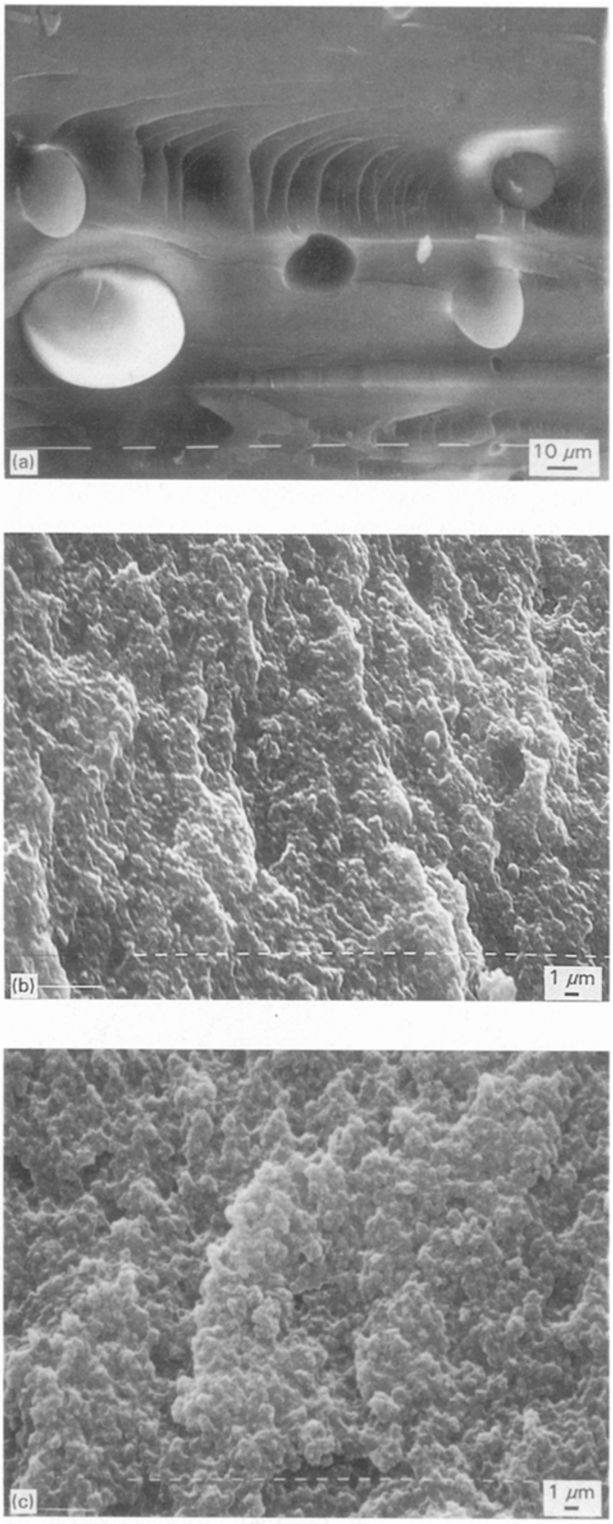


Figure 15 Scanning electron micrographs of fractured surfaces of polyester resins by using DPG. (a) PS, (b) PVAc, (c) LPU1.

curing reaction, giving rise to the morphologies described above.

4. Conclusions

1. The use of different anhydrides, from the conventional ones, in the formulation of unsaturated polyester resins, can produce improvement in their mechanical properties associated with a better resistance to ultraviolet radiations.

2. The presence of such anhydrides contributes to obtaining a finer and homogeneous dispersion of low-profile agents in the cured polyester resins, especially in the case of unsaturated aromatic polyester-isocyanide extended additives, allowing also a better fibre/matrix interfacial adhesion in composites reinforced by silane-coated glass fibres.

3. The alternative utilization of dipropylene glycol with respect to conventional propylene glycol seems to have a strong influence on the resulting morphology producing also a finer dispersion of low-profile agents such as PVAc and LPU1.

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