# Interaction between low-profile agents and glass fibres in polyester-based composites

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Scanning electron microscope and differential scanning calorimetry studies were used to study the morphology and thermal properties of cured systems constituted of different unsaturated polyester formulations, two conventional low-shrink additives and one suitably synthetized additive. The aim was to clarify the influence of these low-profile agents on the resulting phase structure and on the thermal behaviour of the systems. Moreover, the influence was investigated of low-profile agents on the fibre/matrix adhesion in composite materials reinforced with glass fibres coated by silane coupling agents.

## 1. Introduction

Unsaturated polyesters are widely used as thermoset matrices in composite materials with many applications in sectors such as the transportation and building industries. Generally, reinforced unsaturated polyester moulding compounds contain an unsaturated polyester dissolved in a reactive monomer (e.g. styrene) that acts as solvent and as curing agent. In the presence of a peroxide-type catalyst and an accelerator, the liquid resin is converted to a thermoset material through a curing reaction involving cross-links between the reactive monomer and the unsaturations present in the polyester chain [1]. For many uses, the resin is compounded with fibres (e.g. glass, carbon, kevlar) and fillers with different moulding techniques (SMC, BMC etc.) with the aim of improving the final properties. During the curing reaction, the polyesters shrink from 7 to 9% by volume. In order to reduce and even eliminate the shrinkage process [2, 3] some thermoplastic materials are blended to the liquid polyester. These thermoplastic materials, called 'low-profile' agents, give the polyester-based materials excellent surface quality, decreased internal cracks and voids, and optimum control of moulding dimensions [3, 4].

In this paper, results are reported concerning the properties of four different polyester formulations containing different low-profile additives, with the aim of clarifying their influence on the resulting phase structure and thermal behaviour of free-fibre polyester.

We have also investigated the role played by the low-profile agents on the fibre/matrix adhesion in composite materials constituted of an unsaturated polyester matrix reinforced with glass fibres coated by silane coupling agents.

## 2. Experimental procedure

### 2.1. Materials

The polyester resin formulations and the low-profile agents are reported in Table I. All the materials were supplied by Alusuisse (Italy).

For this study three different low-profile additives were chosen of which two were commercial: polyvinylacetate (PVAc) and polystyrene solved in liquid styrene (20 wt %) (PS). The third, the hybrid polyester–polyurethane (LPU), was suitably synthesized and is a saturated polyester-isocyaned extended. As curing agent, styrene ( $\sim$ 30 wt %) with the liquid polyester was used.

The catalyst (1 wt %) was the $t$-butyl perbenzoate, and the accelerator (0.3 wt %) the cobalt-ottoate. The content of low-profile agents was in the ratio 40/60 by weight with the liquid polyester/styrene mixture. The reinforced polyesters were prepared by adding a 30 wt % of glass fibres OCF–RO7Ex1–4000 TEX sized by appropriate silane coupling agents.

### 2.2. Techniques

The morphology of fracture surfaces and the fibre/matrix adhesion were investigated by Phillips 501 model scanning electron microscopy (SEM). The specimens, previously fractured in liquid nitrogen, were coated by a Polaron sputtering apparatus with an AU–Pd film to metallize the sample surfaces.

The thermal behaviour was studied by differential scanning calorimetry (DSC) (TA-3000 Mettler model). All measurements were carried out under nitrogen gas. The impact tests were performed by an instrumented pendulum according to the "Izod" ASTM method by using an impact speed of $1 \, \mathrm{m \, s^{-1}}$ at room temperature. The samples were obtained by compression moulding at 150 °C for 3 min.

TABLE I Polyester resins and low-profile agents used

| Code | Propylene glycol | Dipropylene glycol | Maleic anydride | Phtalic anydride |
|---|---|---|---|---|
| Polyester resins | | | | |
| Maleic (A) | 1 | – | 1 | – |
| Maleic/iso (B) | 1 | – | 0.67 | 0.33 (ISO) |
| Maleic/orto (C) | 0.6 | 0.4 | 0.9 | 0.1 (ORTO) |
| Modified maleic (D) | 0.6 | 0.4 | 1 | – |
| Low-profile additives | | | | |
| Polystyrene (PS) | | | | |
| Polyvinyl acetate (PVAc) | | | | |
| Hybrid polyester – polyurethane (LPU) | | | | |

TABLE II Code and composition of polyester/low-profile samples used

| Composition | | Samples | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
| Polyester | A | 60 | 60 | – | – | – | – | – | – | 60 | – | – | – |
| | B | – | – | 60 | 60 | – | – | – | – | – | 60 | – | – |
| | C | – | – | – | – | 60 | 60 | – | – | – | – | 60 | – |
| | D | – | – | – | – | – | – | 60 | 60 | – | – | – | 60 |
| Low-profile | PS | 40 | – | 40 | – | 40 | – | 40 | – | – | – | – | – |
| | PVAc | – | 40 | – | 40 | – | 40 | – | 40 | – | – | – | – |
| | LPU | – | – | – | – | – | – | – | – | 40 | 40 | 40 | 40 |

# 3. Results and discussion

## 3.1. SEM analysis of fracture surfaces and thermal properties of polyester/ low-profile systems

During the first stage, the resulting morphology of a system constituted by low-profile dispersed in cured polyester resin was examined. The curing reaction was carried out at temperature and pressure comparable to the standard conditions of practical use. Generally, although the low-profile agents and polyester are incompatible, they can both be dissolved in styrene to form a pseudo-stable mixture. When the curing reaction starts, a separation process of low-profile agents occurs, giving rise to a microstructure where in a homogeneous polyester matrix, well-defined domains of thermoplastic additive are uniformly distributed.

This first stage of research was developed in order to understand the resulting morphology after the separation process of thermoplastic additives, as a function of the different polyester formulations. The compounds examined and the relative compositions of samples are shown in Table II.

The SEM micrographs of fracture surfaces, obtained at room temperature, of cured plain polyester resins of maleic and modified maleic are shown in Fig. 1a and b, respectively. The fracture surfaces appear extremely homogeneous and preferential cracking lines are absent.

The micrographs of fractured surfaces of samples compounded with polystyrene (PS) are shown in Figs 2–5. The thermoplastic additive after the curing reaction is present in spherical domains with dimensions of about 100 μm. It is evident that most polystyrene particles have been ejected from the surface of the polyester matrix, indicating poor adhesion between low-profile and polyester.

Nevertheless, the presence of numerous crack-stopping lines demonstrates that the polystyrene obstructs the fracture propagation, probably giving rise to a material less brittle than the starting polyester. Moreover, it is commonly known that the polystyrene provides a shrinkage control in polyester moulding, and is an optimum thermoplastic low-shrink additive [4].

The electron micrographs of fracture surfaces corresponding to the various polyester matrices containing poly (vinylacetate) (PVAc) as low-profile agent are shown in Figs 6–9. The PVAc seems to form smaller domains (~10 μm) than those of polystyrene, and its adhesion with polyester seems to be stronger. In fact the thermoplastic particles are not pulled out from the matrix and seem to be embedded in it. Moreover, the PVAc domains seem to be smaller and more finely dispersed in the two matrices with high maleic content (samples 2 and 8 in Table II; see Figs 6 and 9). SEM micrographs of fractured polyester samples containing as low-profile additive an hybrid polyester-polyurethane (LPU) are shown in Figs 10–13. The samples show a very fine dispersion of the LPU agent, the fracture surfaces being very smooth. A better dispersion seems to occur, even in this case, for the two matrices with higher maleic content (samples 9 and 12 in Table II).

In conclusion, the findings show that the hybrid polyester-polyurethane low profile is more finely dispersed than the two commercial low-profile agents (PS and PVAc). Moreover, LPU also gives better adhesion with the polyesters, especially with the two maleic based ones.

An attempt to understand the differences in the resulting morphologies in the cured polyester/low-profile systems can be obtained by calculating the
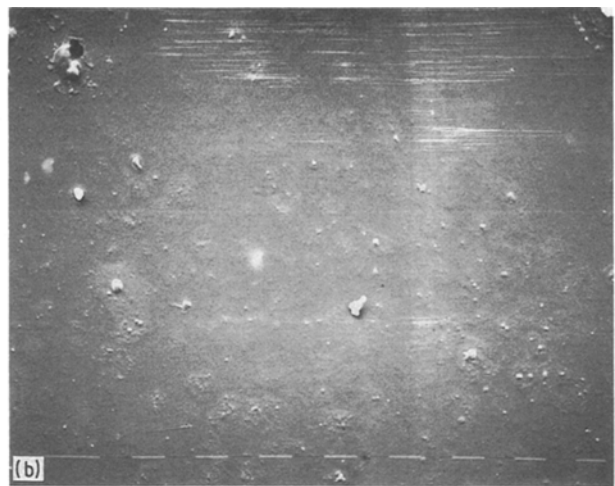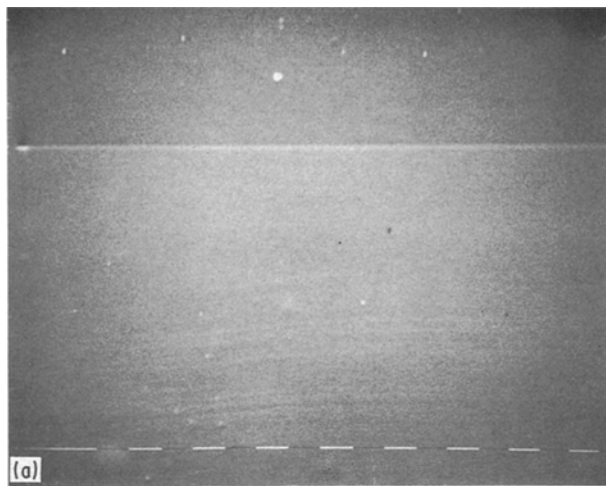
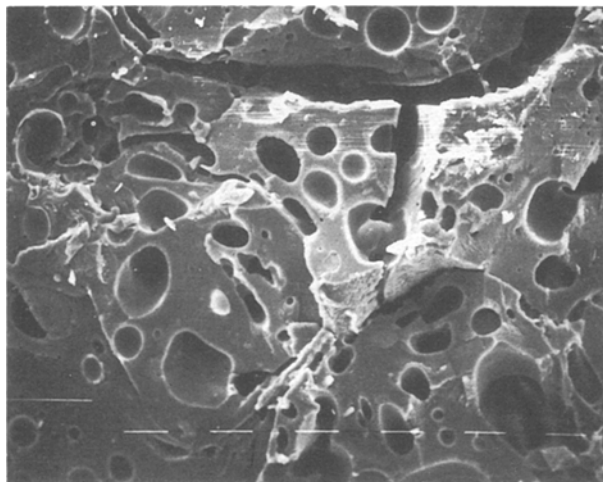*Figure 1* (a) Maleic resin (A); (b) modified maleic resin (D) ( × 640).



*Figure 2* A + PS ( × 80).



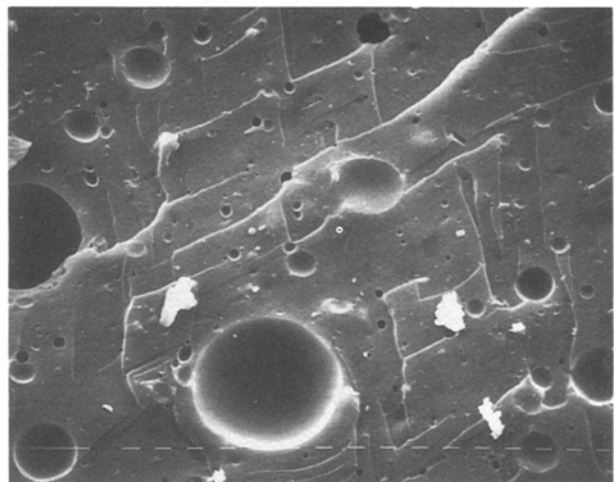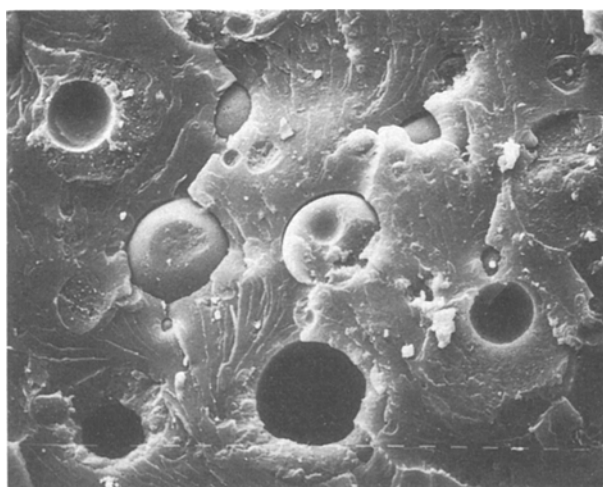*Figure 4* C + PS ( × 80).



*Figure 3* B + PS ( × 320).



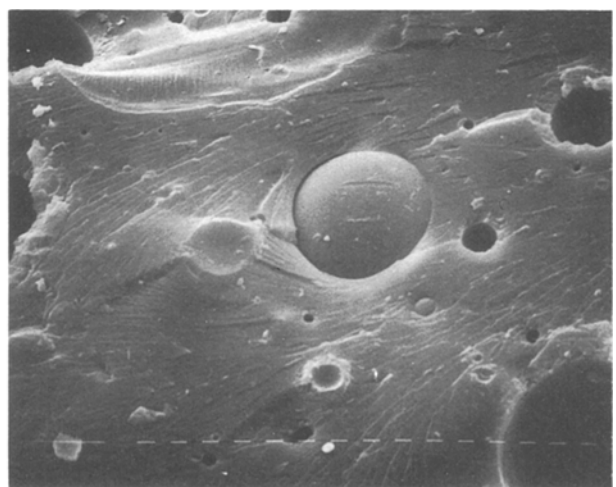*Figure 5* D + PS ( × 320).

solubility parameters of the components (styrene and low-profile). However it is known that solubility parameters have to be used with great care [5]. In view of this, some questions may be raised about our system.

(i) Our starting system is a ternary one (polyester + styrene + low-profile), and usually the interactions among the three components were not considered.

(ii) Normally the solubility parameters are calculated at room temperature, while the curing reaction occurs at higher temperatures (140–160 °C).

(iii) During the first step of the polymerization, the double bonds disappear and the molecular weight of the polymer increases to create the tridimensional network; thus the chemical nature of material cannot be considered to be constant.
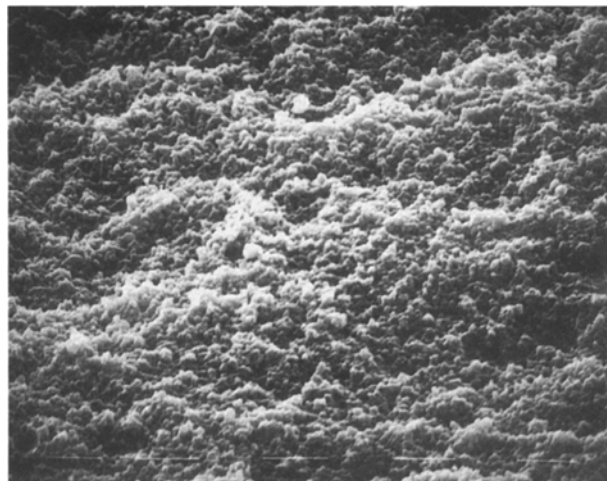
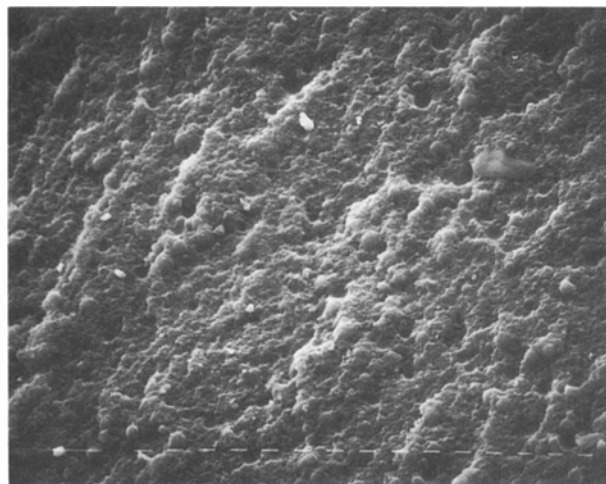*Figure 6* A + PVAc (×1250).
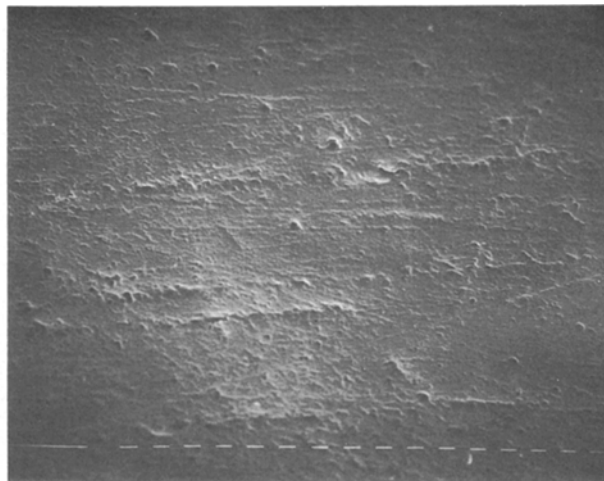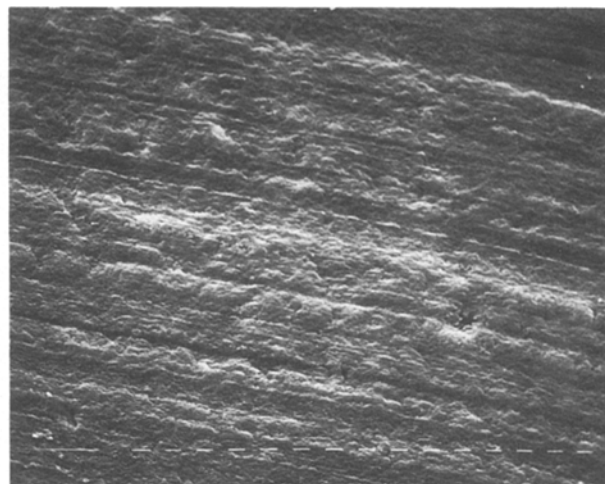


*Figure 9* D + PVAc (×320).
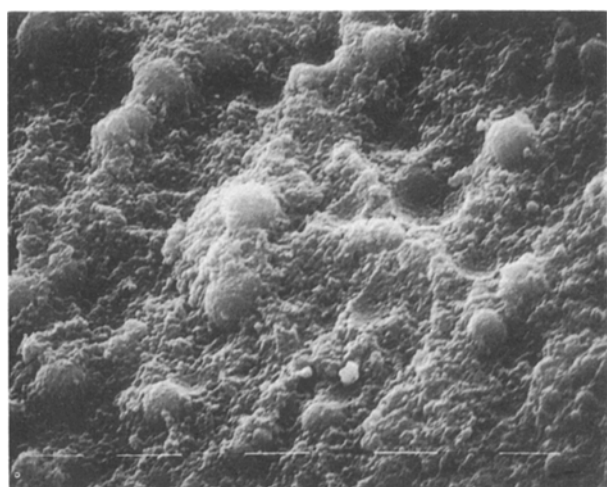


*Figure 7* B + PVAc (×320).

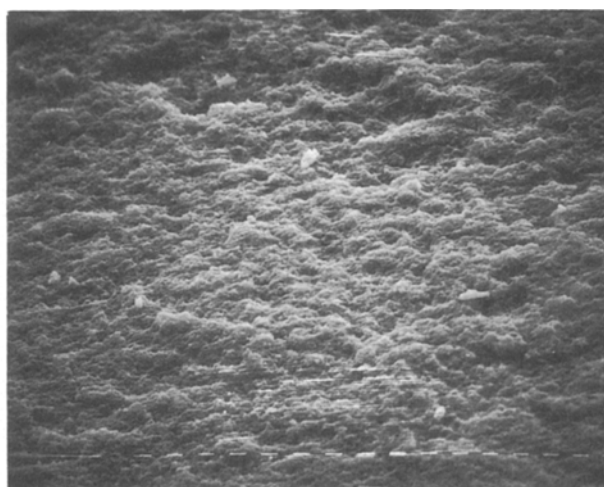

*Figure 10* A + LPU (×320).



*Figure 8* C + PVAc (×1250).



*Figure 11* B + LPU (×1250)

Table III shows the solubility parameter values calculated at room temperature using the Small method [6] for our low-profile agents, compared to the value of styrene that is the curing agent used. The results show that the styrene solubility parameter has a value very near to that of the hybrid polyester–polyurethane (LPU), then to that of PVAc, and finally to the polystyrene value. This finding confirms a better

interaction of LPU with styrene which also permits a fine dispersion of low-profile particles during the curing reaction, giving rise to the morphologies described above.

DSC of the compounds shows the presence of two glass-transition temperatures, $T_g$. This indicates incompatibility between the thermoplastic phase and the polyester. In particular, the low-profile $T_g$ values
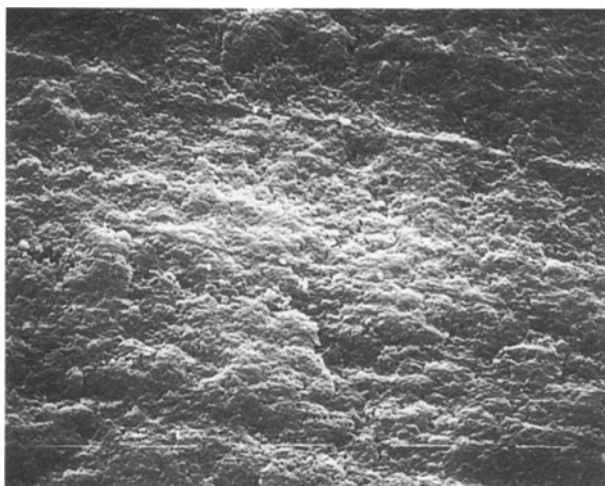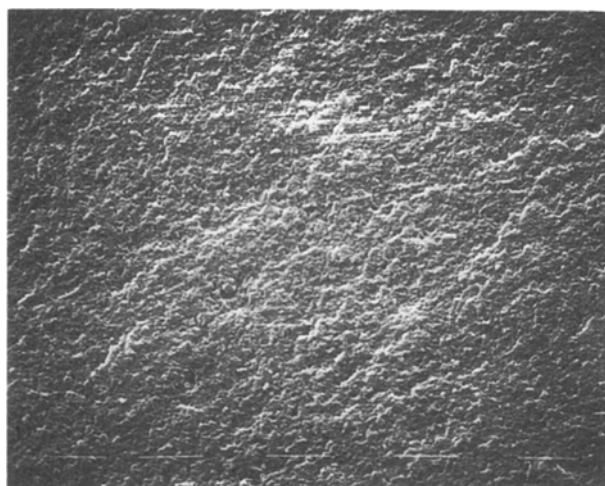
*Figure 12* C + LPU (× 1250).



*Figure 13* D + LPU (× 1250).

TABLE III Solubility parameters, δ, calculated by Small method [6]

| δ (at 25 °C) | $(cal\ cm^{-3})^{0.5}$ |
| --- | --- |
| Styrene | 10.5 |
| LPU | 9.6 |
| PVAc | 9.4 |
| PS | 9.2 |

TABLE IV Glass-transition temperatures, $T_g$, of the four polyesters and of the low-profile phase in polyester compounds

| Polyester | $T_g$ (°C) | Low-profile $T_g$ (°C) | | |
| --- | --- | --- | --- | --- |
| | | PS | PVAc | LPU |
| A | 170 | 56 | 38 | 65 |
| B | 135 | 55 | 35 | 64 |
| C | 130 | 56 | 38 | 64 |
| D | 150 | 58 | 39 | 65 |

do not vary by changing the polyester formulations which are strongly variable (see Table IV).

From this finding, chemical compatibility between low-profile agents and polyesters must be excluded; however a weak interaction between the polar groups present in the polyester chain, with those existing in LPU and PVAc low-profile additives, probably can exist. This hypothesis is supported by the fact that the thermoplastic particle dispersion increases in the matrices rich in polar groups as with those having a high maleic content.

## 3.2. SEM analysis of fractured surfaces of glass fibres/polyester/low-profile agent systems

As previously described, this first part of work was a study of the separation morphology of low-profile additives of different chemical structure during the formation of cured polyester, and is the basis for the second stage of the work: the influence of the presence of low-profile agents on the fibre/matrix adhesion of polyester-based composite materials reinforced by glass fibres.

The performance of polyester reinforced with glass fibres strongly depends on the fibre/matrix adhesion [7]. Generally, to obtain better interface properties appropriate coupling agents (e.g. silane) which are able to realize chemical linkages between the matrix (polyester) and the reinforcement (glass fibre) [8] are used to cover the glass-fibre surface. These agents carry their function during curing: when the reaction starts, the coupling agent participates in chemical bridges between polyester and coated glass fibres, giving rise to composite materials with a good fibre/matrix adhesion.

In this study, we tried to determine if there is some influence due to the presence of low-profile agents on the fibre/matrix adhesion, and to individualize the type of low-profile agent that can act better on the final fibre/matrix adhesion.

The polyester-based resin used was the maleic/orthophtalic (C in Table I). The low-profile agent was blended in the liquid polyester/styrene solution in a ratio 40/60 by weight.

All the composites examined were filled with $CaCO_3$. In the final compound, the percentage by weight of $CaCO_3$ was about 50% SEM micrographs of fractured composites constituted by glass fibres/polyester resin type A filled with $CaCO_3$, but without any low-profile agents, are shown in Fig. 14. From observation of the figures, the fibre/matrix adhesion seems to be very poor. On the other hand, a good adhesion between fibres and matrix is obtained when low-profile agent PVAc is added to the composite (Table V; LP1 sample) (see Fig. 15). The interfacial adhesion (see Fig. 15c) is noticeable, and no phenomena of debonding and pull-out are present.

TABLE V List of examined composites constituted by polyester + filler + low-profile and reinforced with glass fibres

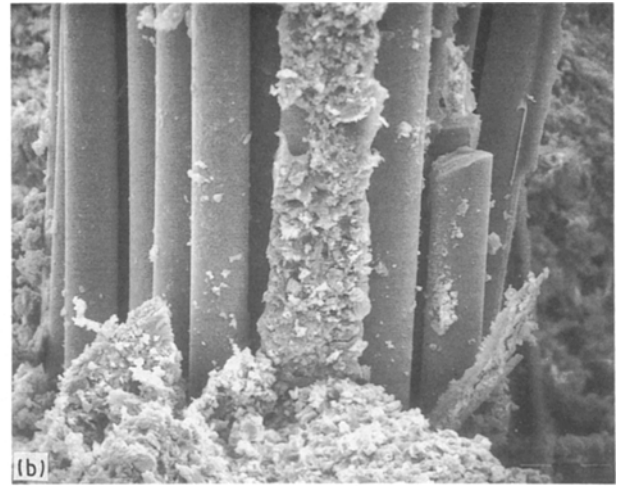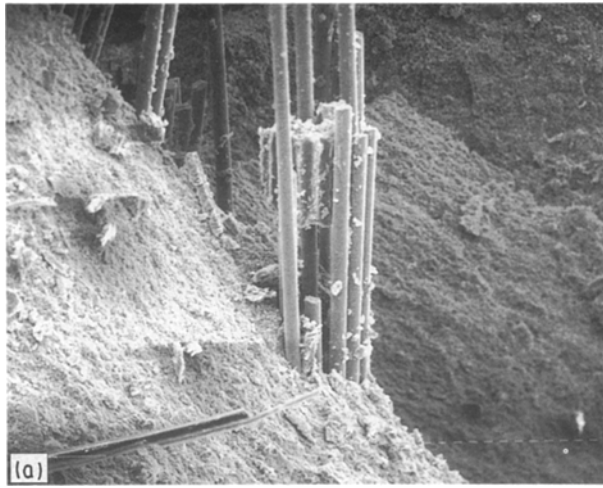| Sample | Code | Low-profile |
| --- | --- | --- |
| 1 | LP1 | Poly (vynilacetate) (PVAc) |
| 2 | LP2 | Hybrid polyester–polyurethane (LPU) |
| 3 | LP3 | Polystyrene (PS) |
| 4 | LP4 | PVAc-PS Copolymer (50/50) |
| 5 | LP5 | PVAc-LPU Copolymer (50/50) |

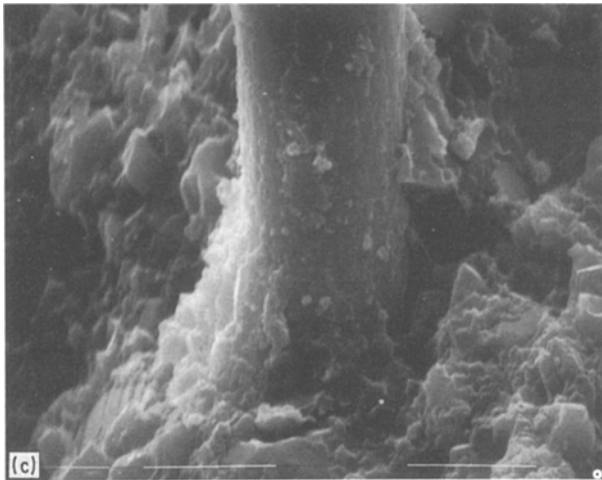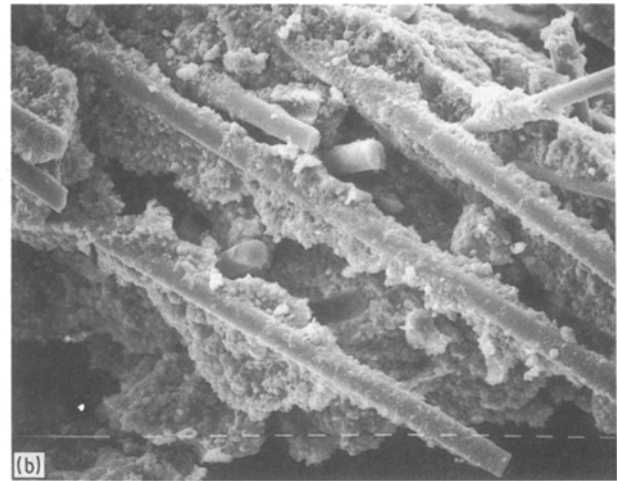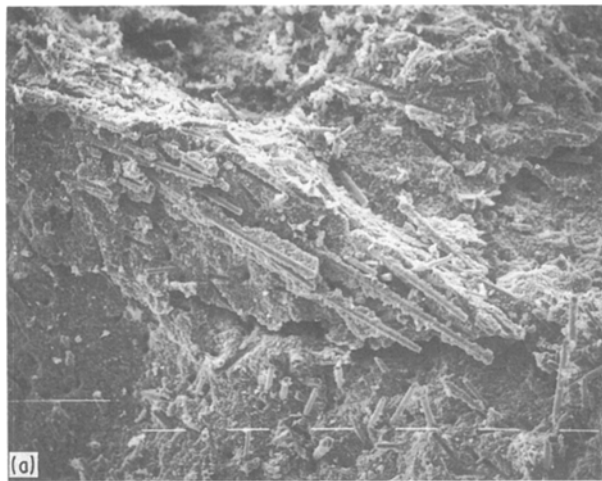*Figure 14* A + Glass + CaCO$_3$. (a) × 160; (b) × 640.







*Figure 15* LP1: (a) × 80; (b) × 320; (c) × 2500.

TABLE VI Influence of glass-fibre surface treatment on the interfacial shear strength, $\tau_s$, of polyester–glass fibre systems

| Surface treatment | $\tau_s$ (mn M$^{-2}$) |
|---|---|
| 0.3% A-174 silane | 52.3 |
| 5% PVAc | 37.1 |
| 0.3% silane (A174) + 5% PVAc | 60.5 |

In Fig. 16 micrographs of the composite obtained by using the LPU low-profile additive (LP2 sample) are shown. Also in this case the fibre/matrix adhesion is high, even higher than the LP1 sample (see Fig. 16b). In contrast, the samples with low-profile polystyrene (LP3 sample) (see Fig. 17) seems to have poor adhesion between fibres and matrix, and also numerous pulled-out fibres are observed. The samples LP4 and LP5 (Figs 18 and 19: PVAc-co-PS and LPU-co-PVAc low-profiles, respectively) do not present satisfactory
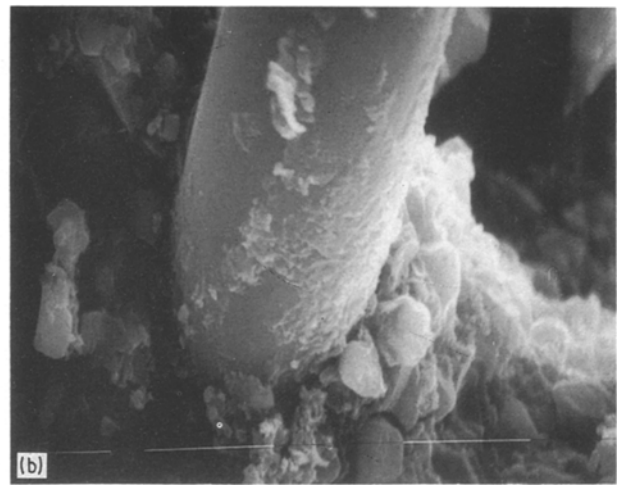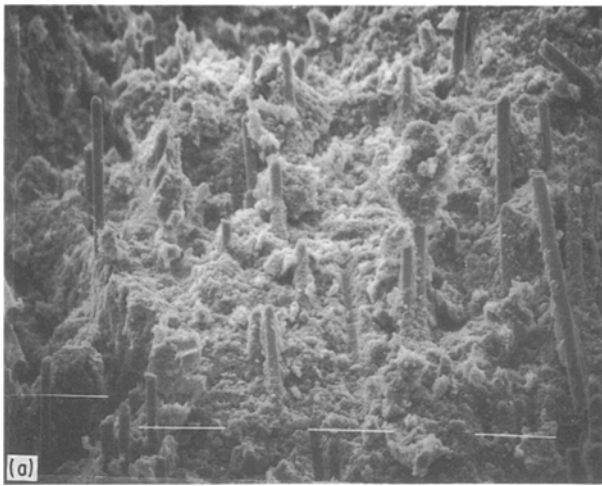
adhesion or pull-out. It is likely that the samples show different behaviour in fibres/matrix adhesion due to the presence of the different low-profile agents used. In particular, the samples with LPU and PVAc low-profile additives present a strong adhesion with respect to the other samples examined.

It is known that the fibre/matrix adhesion depends on the action of coupling agents present on the fibre surface. Probably the PVAc and LPU low-profile agents can promote the formation of chemical bonds between polyester and glass fibres, also participating with the double bond present.

This finding is in accordance with those of Shortall and Yip [9] shown in Table VI where the maximum adhesion ($\tau_s = 60.5$) is obtained by using a silane polyvynilacetate blend as sizing. The PS (LP3) and the

*Figure 16* LP2: (a) × 320; (b) × 2500.



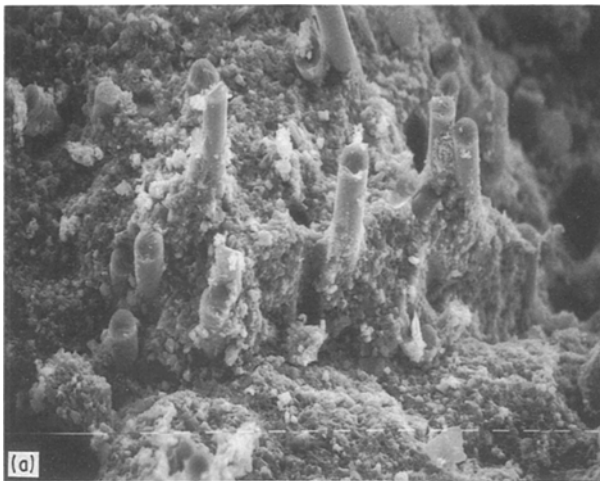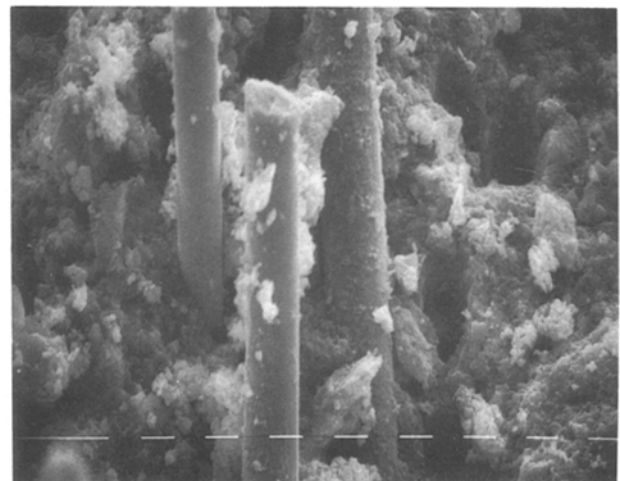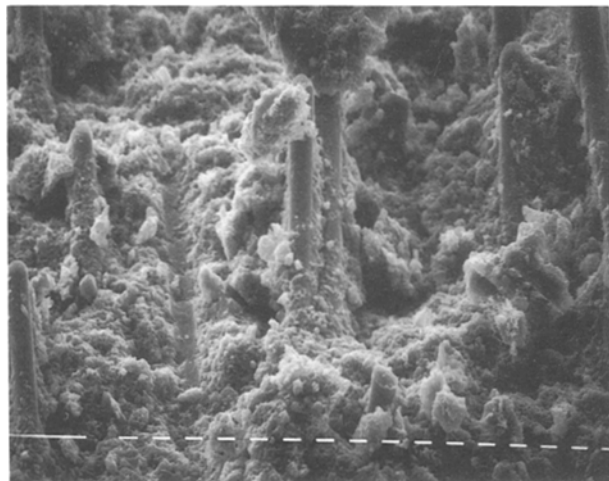*Figure 17* LP3: (a) × 160; (b) × 320.



*Figure 18* LP4 (× 320).



*Figure 19* LP5 (× 640).

two co-polymers (LP4 and LP5) seem to have an inhibiting action on polyester–silane linkages.

## 4. Conclusions

The polar-type low-profile additives in polyester-based compound can stick to the surface of glass fibres during the curing reaction, when the separation process occurs, while less polar additives present an opposite effect. Moreover, it was observed that the polar nature of low-profile additives allows a better compatibility at the fibre/matrix interface.

The interaction found between glass surface and low-profile agent can contribute to an understanding

of the complex mechanism of low-profile action. In fact, low-profile additives like polystyrene (poor adhesion with glass fibres) present an optimum low-shrink effect, but the system containing them shrinks; while the composites with PVAc or LPU which interact with glass fibres decrease in specific weight after polymerization.

## Acknowledgements

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