Acrylic terpolymer modified by blending with polyorganosiloxane polymer or reinforcing

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Blending of acrylic terpolymer (AT) and polyorganosiloxane (PSP) resulted in homogeneous blends with improved mechanical properties and better outdoor weathering resistance. Similarly, incorporation of glass fibres in concentrations of 1–3% produced substantially better mechanical properties and enhanced outdoor durability in the resulting blends.

(Keywords: acrylic terpolymer; polyorganosiloxane; morphology; SEM; energy dispersive X-ray analysis (EDXA); reinforcing; glass fibre blends; mechanical properties; tensile strength; weathering resistance)

INTRODUCTION

The research work reported here is part of a study of properties of an acrylic terpolymer modified by blending or reinforcing with glass fibres. Previously, results were reported on acrylic terpolymer-based blends with improved properties and enhanced outdoor weathering resistance[1]. Other recent papers[2–7] reported results on the morphology and properties of mixtures of polyurethane and epoxy, respectively, with vinyl type polymers, polyorgonosiloxane or glass fibre reinforcement.

This paper reports results on the morphology, mechanical testing and outdoor weathering resistance of acrylic terpolymer modified by blending with a polyorganosiloxane polymer or by reinforcing with glass fibres. The morphology of these blends was studied by SEM in conjunction with energy dispersive X-ray analysis (EDXA) probe and d.s.c. Mechanical testing was used to assess the outdoor weathering resistance.

EXPERIMENTAL

Materials

The materials used in this study are as follows: acrylic terpolymer (Unicrylic 60, Molco), a commercial sealant having a relatively wide temperature range (−30°C–+30°C), and which is used for window glazing, metal curtain wall, concrete and masonry joints; a silicone sealant (Dow Corning); glass fibres with a length distribution in the range of 20–25 mm. The blends were prepared by mixing (10–15 min) appropriate weighed amounts of the solid materials, using a mortar and pestel (without heating).

Apparatus and procedures

A Cambridge Stereoscan S250 scanning electron microscope (SEM) (operated at 20 kV and tilt angle of 45 degrees) was used to observe the fracture surfaces of the various blends. The fracture surfaces were obtained by using a chisel and hammer to split samples cooled at liquid nitrogen temperature. This technique was found to provide the most satisfactory fracture surface for observation and for drawing conclusions about the morphology of the bulk.

The specimens were coated first with carbon and then with gold to prevent electrical charging. D.s.c. curves were recorded with a Du Pont 1090 thermal analyser over a temperature range of −100 to 160°C under nitrogen.

To assess the state of mixing in AT–PVC blends, an energy dispersive X-ray analysis attachment (on the SEM), equipped with a lithium drifted detector, Si (Li), was used. The Si (Li) detector is able to detect sodium (Na) and elements with atomic numbers greater than Na, but does not see elements with lower atomic numbers (e.g., C, N, O, etc.).

Tensile stress–strain measurements were carried out at 22°C, using an Instron Model 1125 Universal Testing Machine at a crosshead speed of 5 mm/min and chart speed of 100 mm/min. The test specimens (12.5 × 12.5 × 50.0 mm) consisted of a bead of material cast between two prismoidal pieces of substrate (aluminium, Portland cement mortar, California redwood). The values used for plotting the stress–strain curves are averages of 5–10 successful determinations.

To assess the effect of the outdoor weather on the properties of modified and unmodified AT, samples were exposed in a highly polluted area in Montreal (P.Q., Canada) for 260 days between June 1982 and March 1983. The lowest temperature recorded during this period was −25°C (January 19th and February 4th). Control specimens were kept in the laboratory at 22°C and 20 to 50% relative humidity for the same period.

RESULTS AND DISCUSSION

Morphology

The morphology of acrylic terpolymer (AT) and modified AT is illustrated in the selected SEM photomicrographs presented in *Figures 1–4*.

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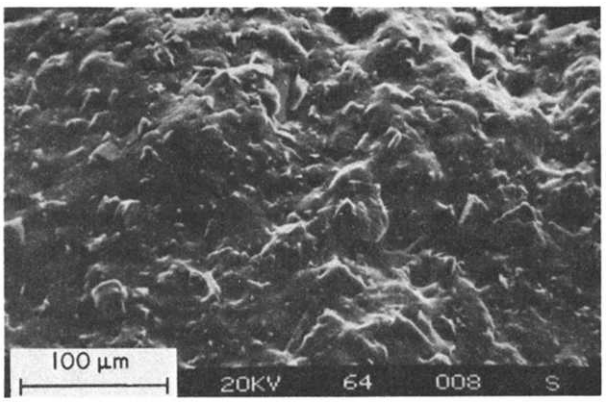

Figure 1 SEM photomicrograph of fracture surface of unblended acrylic terpolymer (AT)

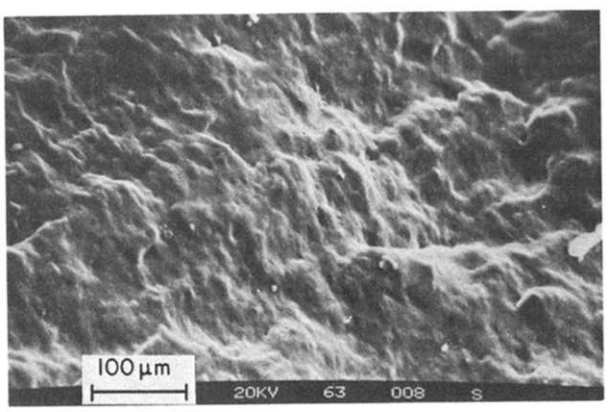

Figure 2 AT–polyorganosiloxane polymer (PSP) (50% PSP)

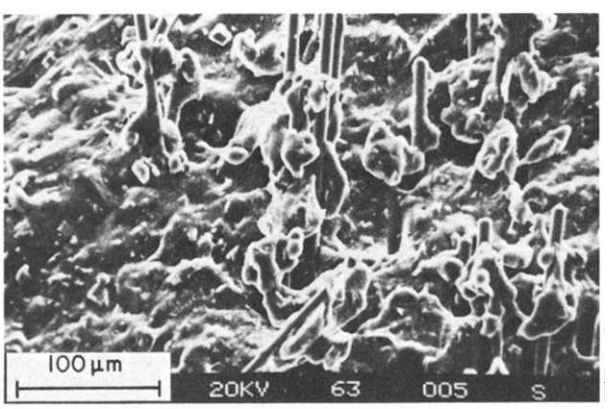

Figure 3 AT–glass fibre (GF) (3% GF)

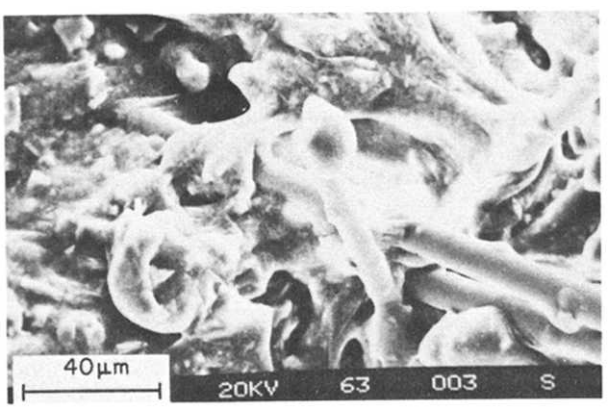

Figure 4 AT–GF (3% GF)

AT–polyorganosiloxane polymer (PSP) blends

SEM observations under relatively high magnification (up to 100 000) indicate that mixing of AT with PSP in concentrations of 25–50%, inclusive of the second component, yields homogeneous blends. In *Figures 1* and *2*, the morphology of the fracture surface of AT is compared with that of an AT–PSP blend (containing 50% of PSP). The topography of the surface material of the blend is very similar to that of the unblended AT. The PSP component is well distributed in the different AT–PSP blends, as evidenced by a relatively constant Si count (by EDXA) at various randomly tested microsites of the material in the fracture surface.

The d.s.c. results could not be used to confirm SEM and EDXA observations regarding miscibility of the two components in these blends, because the T_g of AT (−23°C) was not sufficiently separated from that of the PSP (−43°C), and thus complete overlapping of the corresponding endotherms occurred (d.s.c. curves of AT–PSP not shown).

Glass-fibre reinforced AT

The topography of AT reinforced with glass fibre (GF) is illustrated in the SEM photomicrographs of *Figures 3* and *4*. In these blends the texture of the surface is evidently similar to that of the unreinforced AT, and the glass fibres are well distributed. The bond between the matrix (AT component) and the reinforcing fibres is strong, as indicated by the nature of the fracture in the AT–glass interface region. Indeed, the fracture generally occurs within the matrix; the surface of the reinforcing fibres is covered by a sheath of AT (*Figures 4* and *5*).

Incorporation of glass fibres into AT did not have any effect on the T_g of the resulting blends, which occurred at the same temperature as that of the matrix (−23°C). (D.s.c. curves of AT–GF not shown.)

Ultimate tensile strength

The stress–strain curves of AT, AT–PSP blends and AT reinforced with glass fibres are presented in *Figures 5–16*.

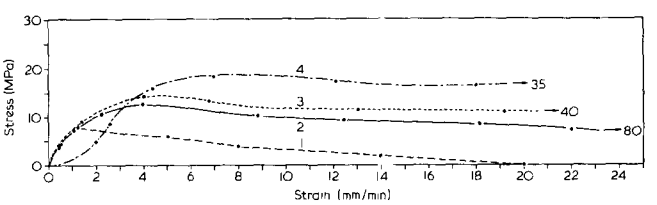

Figure 5 Stress–strain curves of AT–PSP blends (control specimens). Aluminium substrate. (1) AT; (2) AT–PSP (25% PSP); (3) AT–PSP (33% PSP); (4) AT–PSP (50% PSP)

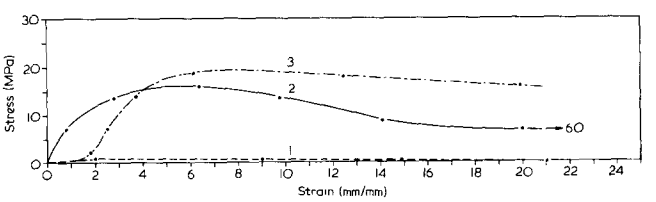

Figure 6 Stress–strain curves of AT–PSP blends (weathered specimens). Aluminium substrate. (1) AT; (2) AT–PSP (25% PSP); (3) AT–PSP (33% PSP)

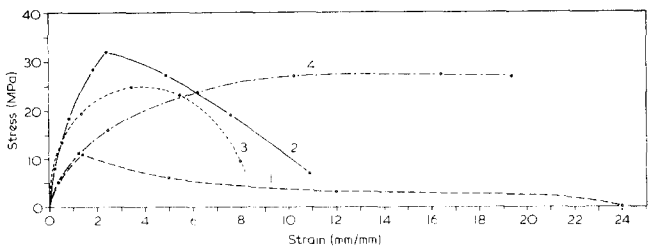

Figure 7 Stress–strain curves of AT–PSP blends (control specimens). Portland cement mortar substrate. (1) AT; (2) AT–PSP (25% PSP); (3) AT–PSP (33% PSP); (4) AT–PSP (50% PSP)

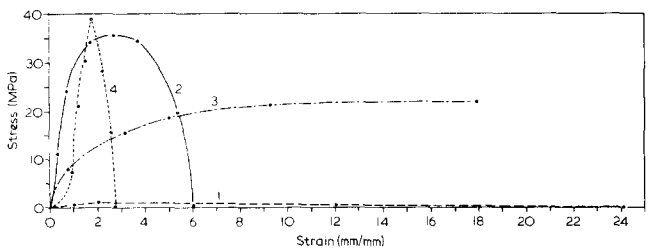

Figure 8 Stress–strain curves of AT–PSP blends (weathered specimens). Portland cement mortar substrate. (1) AT; (2) AT–PSP (25% PSP); (3) AT–PSP (33% PSP)

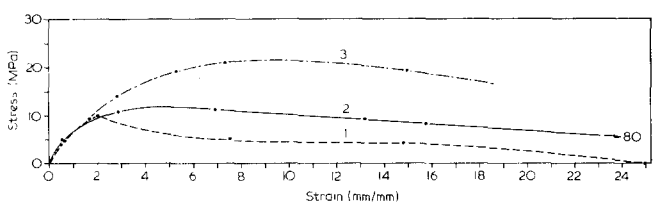

Figure 9 Stress–strain curves of AT–PSP blends (control specimens). California redwood substrate. (1) AT; (2) AT–PSP (25% PSP); (3) AT–PSP (33% PSP); (4) AT–PSP (50% PSP)

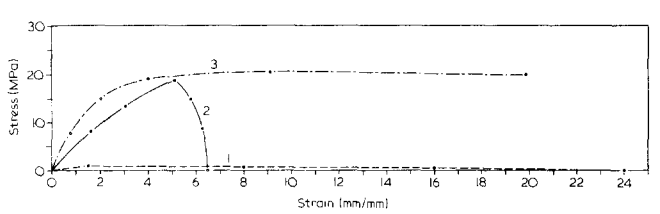

Figure 10 Stress–strain curves of AT–PSP blends (weathered specimens). California redwood substrate. (1) AT; (2) AT–PSP (25% PSP); (3) AT–PSP (33% PSP)

AT–PSB blends

The ultimate tensile strength (UTS) of these blends increases with the concentration of the added component (PSP). For example, the UTS of blends containing 25 and 50% of PSP tested in conjunction with aluminium substrate was higher than that of unmodified AT by a factor of 1.5 and 1.4, respectively (*Figure 5*). The UTS of the blend with a PSP concentration of 33 per cent had an intermediate value, as it increased by a factor of 1.9, in comparison to that of AT (*Figure 5*). Similar trends in the variation of UTS with the PSP content of blends tested on Portland cement and California redwood substrates were obtained (*Figures 7* and *9*). However, the rates of change in UTS were higher in samples tested on Portland cement and lower in specimens tested on California redwood substrates.

Because of the rubbery nature of PSP materials, the various AT–PSP blends have significantly higher strain in comparison to that of the unmodified AT.

Whereas the unmodified AT undergoes considerable deterioration during exposure to outdoor weathering, the AT–PSP blends generally exhibit moderate improvement or maintain their original properties (*Figure 6*, *8* and *10*). For example, the UTS of unmodified AT tested in conjunction with the three substrates is lowered by a factor of 10 to 11 during outdoor weathering for 260 days (*Figure 6* and *8*). The UTS of AT–PSP blends is either approximately the same or becomes higher by a factor of 1.2–1.7. The blends containing 25% of PSP have the best outdoor resistance, regardless of the substrate used in the testing of specimens.

The adhesive strength (AS) of specimens mounted on the three substrates varies as follows: AS of specimens on

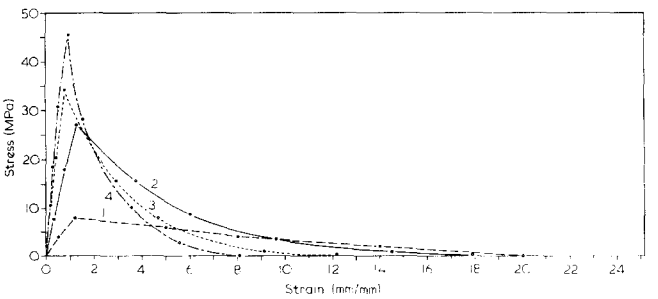

Figure 11 Stress–strain curves of AT–glass fibre (GF) blends (control specimens). Aluminium substrate. (1) AT; (2) AT–GF (1% GF); (3) AT–GF (2% GF); (4) AT–GF (3% GF)

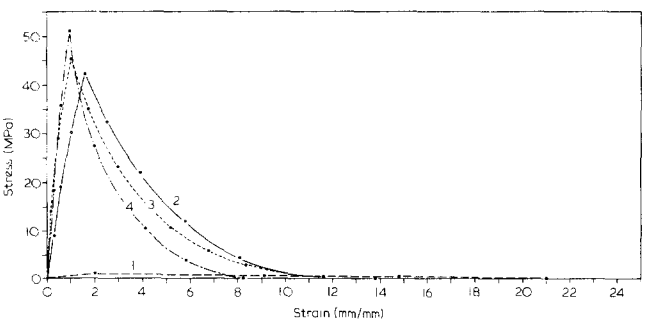

Figure 12 Stress–strain curves of AT–GF blends (weathered specimens). Aluminium substrate. (1) AT; (2) AT–GF (1% GF); (3) AT–GF (2% GF); (4) AT–GF (3% GF)

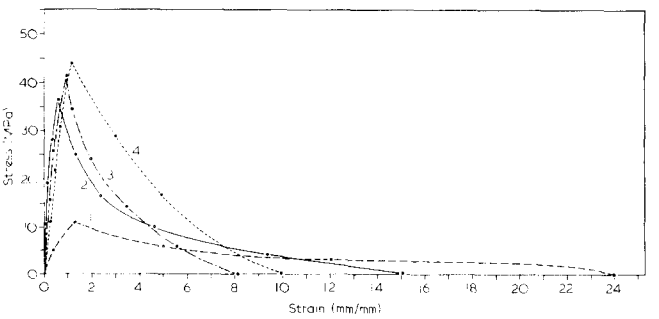

Figure 13 Stress–strain curves of AT–GF blends (control specimens). Portland cement mortar substrate. (1) AT; (2) AT–GF (1% GF); (3) AT–GF (2% GF); (4) AT–GF (3% GF)

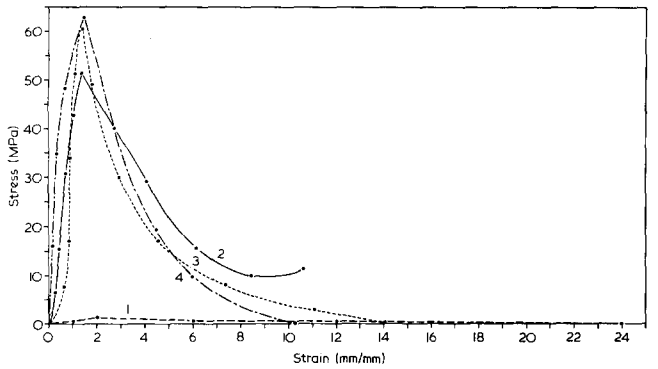

Figure 14 Stress–strain curves of AT–GF blends (weathered specimens). Portland cement mortar substrate. (1) AT; (2) AT–GF (1% GF); (3) AT–GF (2% GF); (4) AT–GF (3% GF)

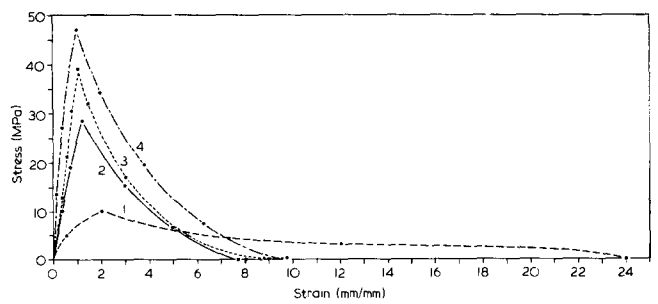

Figure 15 Stress–strain curves of AT–GF blends (control specimens). California redwood substrate. (1) AT; (2) AT–GF (1% GF); (3) AT–GF (2% GF); (4) AT–GF (3% GF)

aluminium < AS of specimens on California redwood⟨AS of specimens on Portland cement. The AT–PSP specimens exhibit good cohesion.

Glass fibre-reinforced AT

In *Figures 11* to *16* the stress–strain curves of AT reinforced with 1, 2 and 3 per cent of glass fibres are presented. As these curves indicate, reinforcing of AT with glass fibres results in a marked increase of the UTS. The UTS of blends tested on aluminium substrate is an increasing function of the glass fibre concentration. Mixing of AT with 1, 2 and 3% of glass fibres resulted in blends with UTS 3.4, 4.2 and 5.6 times higher than that of the unmodified material (*Figure 11*). Similar trends were observed in glass fibre-reinforced AT tested in conjunction with Portland cement and California redwood (*Figures 13* and *15*). However, they were lower in comparison to mixtures of the same GF concentration tested by using aluminium substrate.

Glass fibre reinforcing of AT resulted in enhanced outdoor weathering resistance. The reinforced AT weathered outdoors had approximately 1.5 times higher UTS than the unreinforced material, regardless of the type of substrate used in the testing.

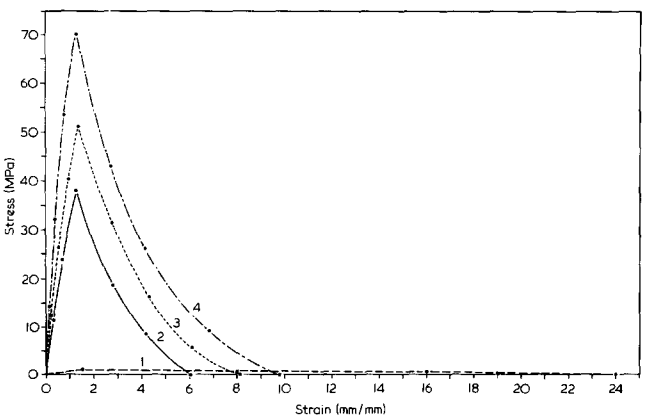

Figure 16 Stress–strain curves of AT–GF blends (weathered specimens). California redwood substrate. (1) AT; (2) AT–GF (1% GF); (3) AT–GF (2% GF); (4) AT–GF (3% GF)

CONCLUSIONS

SEM and EDXA observations indicated that addition of PSP to AT in concentrations of 25–50%, inclusive, results in homogeneous blends with improved mechanical properties. Whereas the mechanical properties of unblended AT deteriorate markedly in outdoor exposure, those of the AT–PSP blends remain unchanged or improve substantially during weathering.

The glass fibre in AT–GF mixtures are well distributed, as indicated by SEM observations. Failure during fracture of blend specimens is cohesive in nature, thus indicating good bonding between the matrix (AT) and the glass fibre reinforcement. Reinforcing of AT with glass fibre leads to blends with considerably improved tensile properties and enhanced durability.

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