Acrylic Terpolymer–PVC Blends with Improved Properties

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Synopsis

Adhesive sealant compositions with improved properties and enhanced outdoor resistance were prepared by blending acrylic terpolymer (AT) with PVC. The morphology of these blends was studied by SEM, energy-dispersive X-ray analysis (EDXA), and DSC. The blends are heterogeneous. They consist of a continuous phase, which is either pure or mixed AT, and a particulate phase having the morphology of the added component. The particulate phase of AT–PVC contains mixed AT. The AT–PVC blends have improved mechanical properties (e.g., ultimate tensile strength, adhesive strength, etc.). The improvement in mechanical properties is strong, probably because the added PVC has strong specific interaction capabilities with AT. Whereas the unblended AT has very low outdoor durability, the AT–PVC blends display enhanced resistance to weathering, as evidenced by substantially higher ultimate tensile strength of weathered specimens than those of the controls (unweathered).

INTRODUCTION

Recent industrial research and development activity in the polymer field is focussed more on the modification of existing polymer compositions rather than on synthesizing new polymers. An important method used to develop polymer compositions with improved properties including mechanical, electrical, and thermal characteristics consists of blending two or more polymers. The main goal of polymer blending is to achieve commercially useful products with unique properties for specific applications at lower cost than by other known methods.

In this study, blending was used to prepare adhesive sealant compositions, with markedly improved properties and outdoor weather resistance, from acrylic terpolymer and PVC.

Previous papers[1-7] regarding research work on blends reported results on the morphology and other properties of mixtures of polyurethane and epoxy polymer, respectively, with vinyl type polymers, polysiloxane (SR), and glass fiber reinforcement. This paper reports the results of a study of morphology and mechanical testing of weathered and unweathered acrylic terpolymer and blends of acrylic terpolymer with poly(vinyl chloride). Results on the morphology on the blends were obtained by scanning electron microscopy, energy dispersive X-ray analysis, and differential scanning calorimetry.

CCC 0021-8995/84/113421-10$04.00

EXPERIMENTAL

Materials

The basic material used in this study was a commercial acrylic terpolymer (Unicrylic 60, Molco), a sealant having a relatively wide temperature range ($-30-+30°C$) and which is used for window glazing, metal curtain wall, concrete, and masonry joints. The other material used was also a commercial polymer and is as follows: poly(vinyl chloride) (PVC, Geon 103E-PF Resin, B. F. Goodrich). The polymer blends were prepared by mixing (10–15 min) appropriate weighed amounts of the solid materials (paste or powder) in a mortar, using a pestel, without heating.

Apparatus and Procedures

A Cambridge Stereoscan S250 scanning electron microscope (SEM) (operated at 20 kV and tilt angle of 45°) was used to observe the fracture surfaces of polymer blend specimens. The fracture surfaces were obtained by using a chisel and hammer to split samples cooled at liquid nitrogen temperature. The specimens were coated first with carbon and then with gold to prevent electrical charging. DSC curves were recorded with a DuPont 1090 Thermal Analyzer over a temperature range of $-100-160°C$ 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 (AT or modified AT) cast between two prismoidal pieces of substrate (aluminum, Portland cement mortar, California redwood). The values used for plotting the stress–strain curves are averages of 5–10 successful determinations.
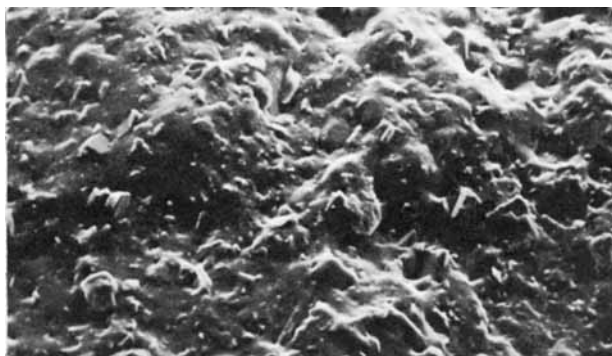

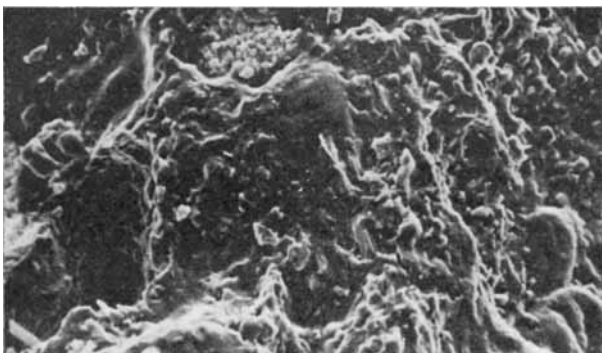Fig. 1.　SEM photomicrograph of fracture surface of unblended acrylic terpolymer (AT).

Fig. 2. AT–PVC blend (33% PVC).

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 for 260 days between June 1982 and March 1983. The lowest temperature recorded during this period was −25°C (January 19 and February 4). Control specimens were kept in the laboratory at 22°C and 20–50% relative humidity for the same period.

RESULTS AND DISCUSSION

Morphology

In Figures 1–5 selected SEM photomicrographs are presented to illustrate the morphology of unweathered and weathered blends of acrylic terpolymer sealant with PVC. DSC curves of AT–PVC blends are shown in Figure 6.

Observations by SEM and EDXA indicate that the AT–PVC blends are composed of a continuous phase, which is pure AT at the low PVC concentration (7.5%) and mixed (AT–PVC) at higher PVC concentrations (15–33%), and a particulate phase having the morphology of PVC.

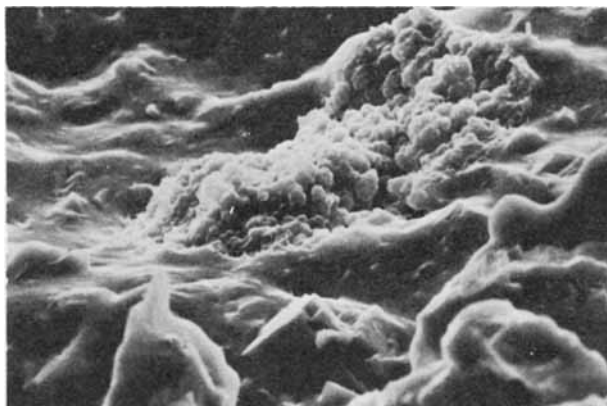In the mixed AT–PVC continuous phase, the proportion of PVC increases
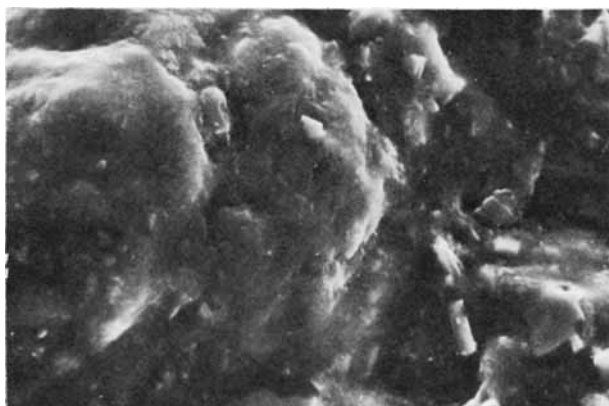

Fig. 3. AT–PVC (33% PVC).

Fig. 4. AT–PVC (33% PVC).

with its concentration in the blends, as evidenced by the chlorine count (by EDXA). Generally, the PVC particles are not evenly distributed in the continuous phase. As reported previously,[6] the PVC particles consist of aggregates of spherical microgranules (Figs. 2 and 3). The adhesion between the AT and PVC phase is good. The morphology of the continuous phase containing mixed PVC (Fig. 4) is microscopically the same as that of the pure AT phase (Fig. 1). Furthermore, SEM and EDXA observations also indicate that outdoor weathering of these blends does not induce any significant changes in the morphology of AT–PVC blends. Indeed, the morphology of a blend containing 33% PVC and weathered outdoors of 260 days (Fig. 5) is similar to that of the unweathered (control) blend (Fig. 3).

The thermal behavior of the AT–PVC blends is illustrated in Figure 6. At lower PVC concentrations (7.5% or 15%), the T_g of AT ($-23°C$) is independent of the concentration of the second component, indicating that the AT phase is not mixed. In blends containing 33% PVC, the T_g of AT increases to $-17°C$. This indicates that the AT phase, the component of low T_g, is mixed with PVC, the polymer component of higher T_g ($+89°C$). Furthermore, the T_g corresponding to PVC is gradually lowered to 58°C, as the
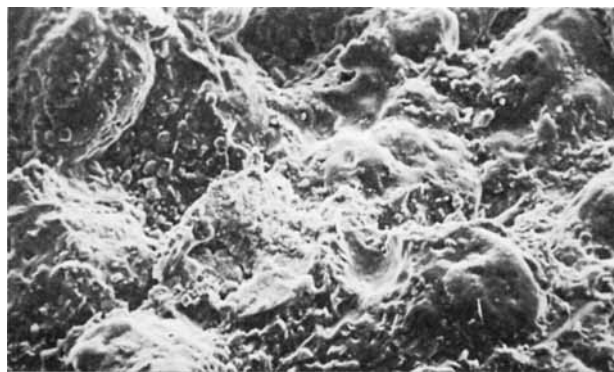

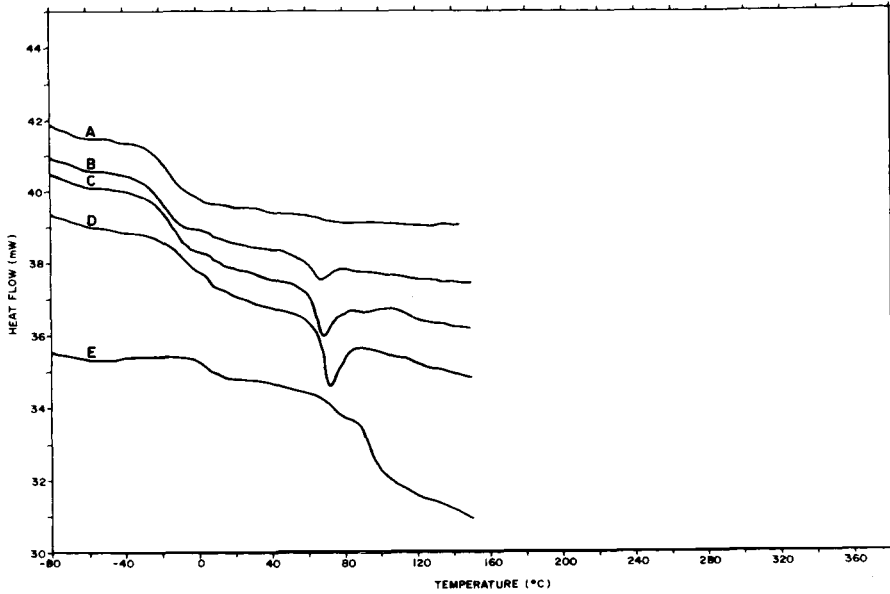Fig. 5. AT–PVC (33% PVC) weathered outdoors for 260 days.

Fig. 6. DSC curves of AT and AT–PVC blends (unweathered): (A) AT; (B) AT–PVC (7.5% PVC); (C) AT–PVC (15% PVC); (D) AT–PVC (33% PVC); (E) PVC.

concentration of AT in the blends varies from 67% to 82.5% (Fig. 6). This suggests that PVC polymer phase contains AT and becomes progressively more miscible with increasing concentration of AT in the blends.

Thus, there is an overall agreement between the observations made by SEM (in conjunction with EDXA) and results obtained by DSC regarding
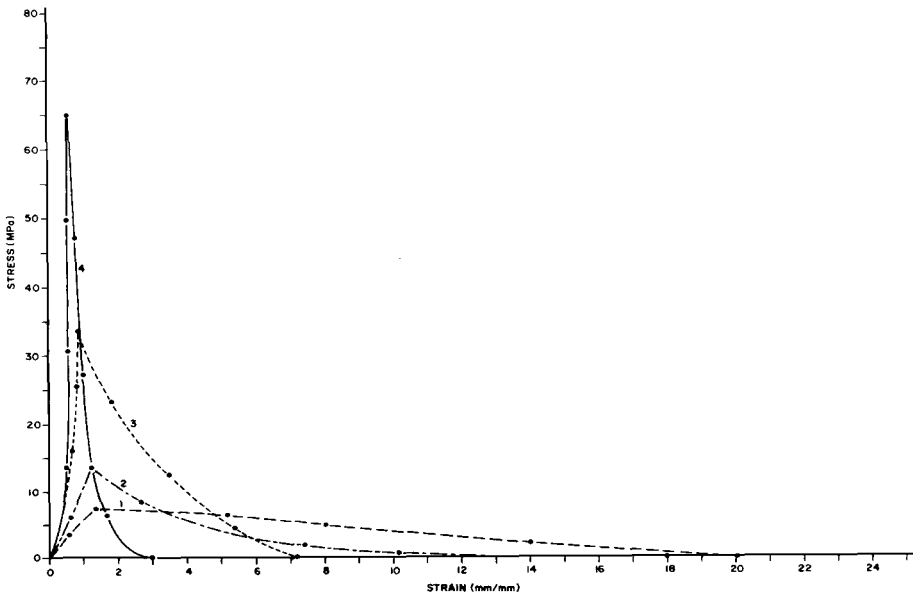

Fig. 7. Effect of PVC on the ultimate tensile strength (control specimens); aluminum substrate: (1) AT; (2) AT–PVC (7.5% PVC); (3) AT–PVC (15% PVC); (4) AT–PVC (33% PVC).
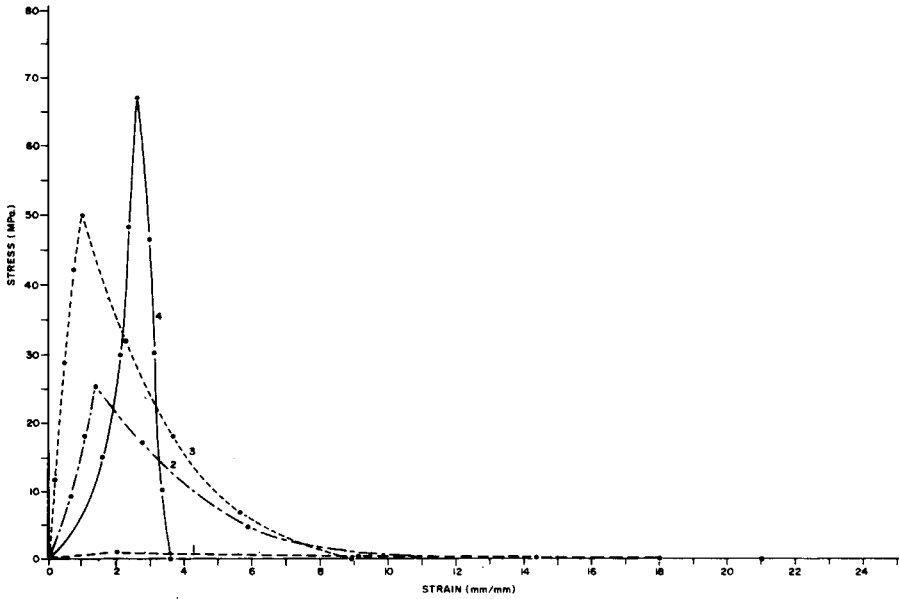
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Fig. 8. Effect of PVC on the ultimate tensile strength (weathered specimens); aluminum substrate: (1) AT; (2) AT–PVC (7.5% PVC); (3) AT–PVC (15% PVC); (4) AT–PVC (33% PVC).

the morphology of the AT–PVC blends. Accordingly, AT–PVC blends are heterogeneous mixtures consisting of a continuous phase, which is either pure AT (at lower PVC concentration) or mixed with PVC, and a PVC-rich particulate phase. The DSC curves of the blends weathered outdoors are not sufficiently different from those of the unweathered samples (control).
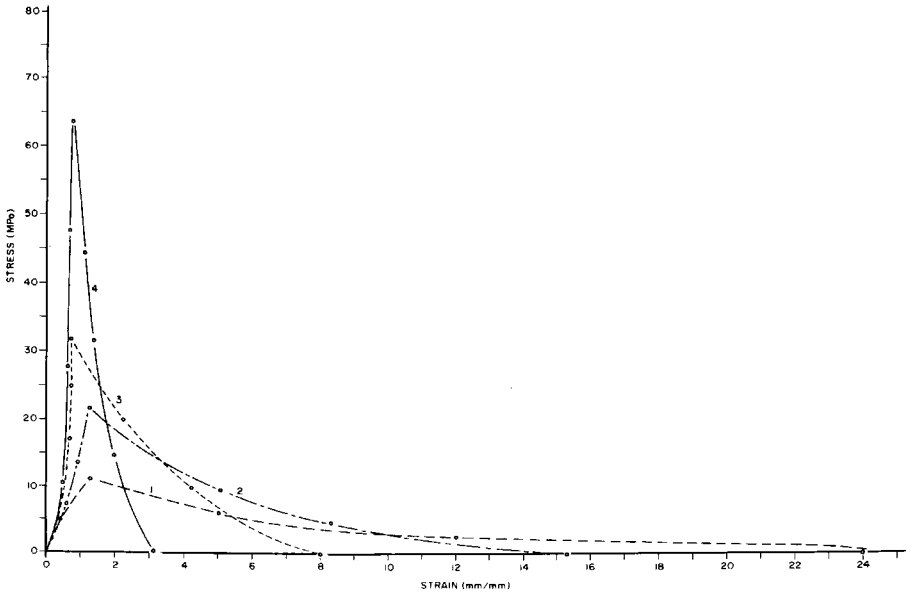

Fig. 9. Effect of PVC on the ultimate tensile strength (control specimens); Portland cement mortar substrate: (1) AT; (2) AT–PVC (7.5% PVC); (3) AT–PVC (15% PVC); (4) AT–PVC (33% PVC).
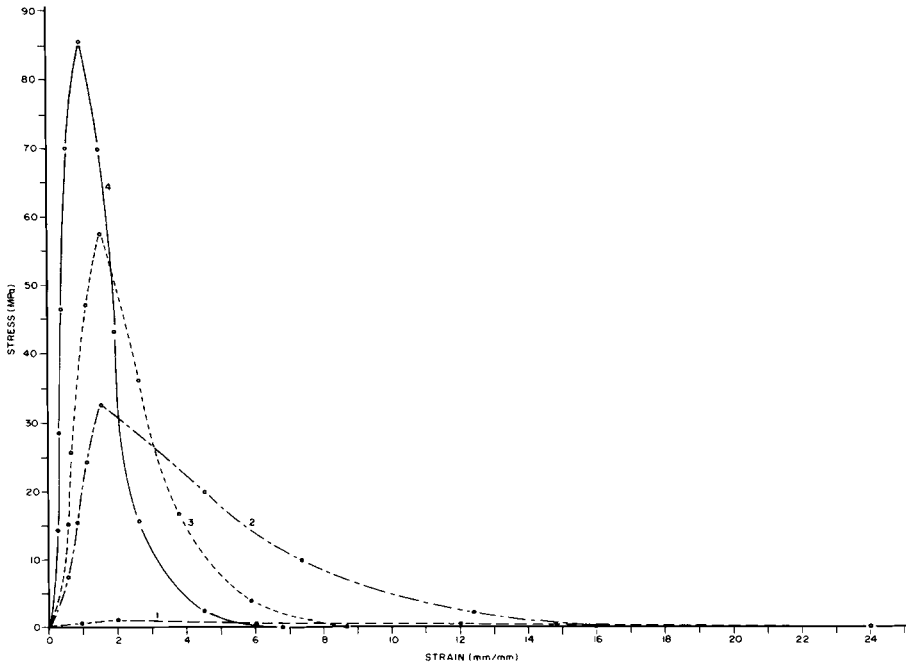
Fig. 10. Effect of PVC on the ultimate tensile strength (weathered specimens); Portland cement mortar substrate: (1) AT; (2) AT–PVC (7.5%); (3) AT–PVC (15% PVC); (4) AT–PVC (33% PVC).
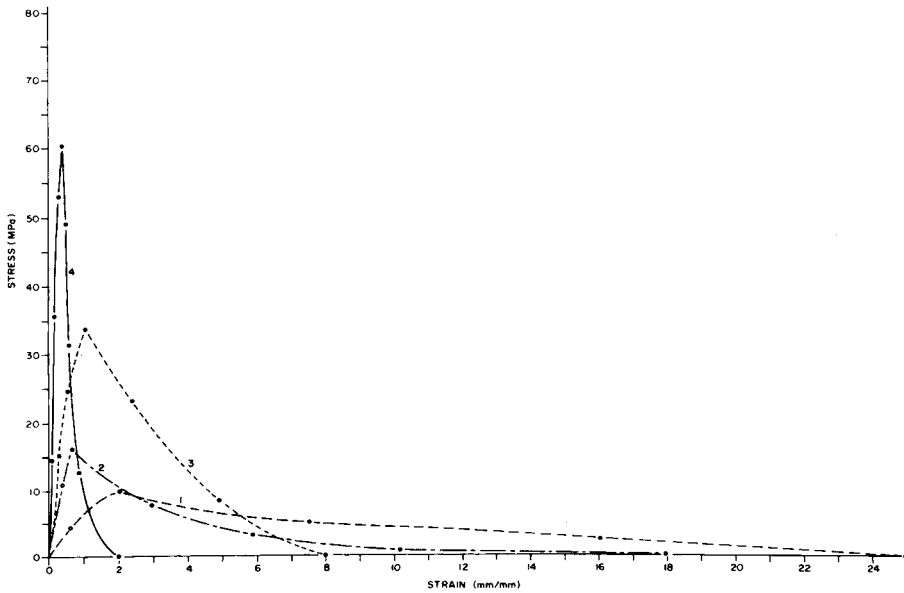

Fig. 11. Effect of PVC on the ultimate tensile strength (control specimens); California redwood substrate: (1) AT; (2) AT–PVC (7.5% PVC); (3) AT–PVC (15% PVC); (4) AT–PVC (33% PVC).

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Therefore, no inference can be made regarding improved miscibility of the two components or that any chemical changes have occurred during weathering.

Ultimate Tensile Strength

Generally, blending of AT with PVC produced a considerable improvement in the ultimate tensile strength (UTS) of the resulting mixtures in comparison to that of the unmodified polymer. It is also noteworthy to find that, contrary to what generally occurs in plastic-based materials, outdoor weathering resulted in a marked increase in the UTS of all blends. In Figures 7–12 are presented the stress–strain curves of the various AT–PVC blends tested on unweathered and weathered specimens mounted on aluminum, Portland cement, and California redwood, respectively.

The stress–strain curves of AT and AT–PVC blends tested by using specimens mounted on aluminum substrate are presented in Figures 7 and 8 for unweathered and weathered specimen samples. The UTS of these blends increases markedly with the concentration of PVC. For example, the UTS of blends containing 7.5% and 33% is greater than that of AT by a factor of 2 and 9, respectively (Fig. 7).

The unmodified AT material has a very low resistance to outdoor weathering, as evidenced by a decrease in its UTS during exposure. In fact, weathering for 260 days caused a lowering of the UTS of the unmodified AT by a factor of 7 (Fig. 8). It is interesting, however, to note that weathering causes a relatively large increase in the UTS of blends with lower PVC concentration. For example, blends containing 7.5% and 15% of PVC (Fig.
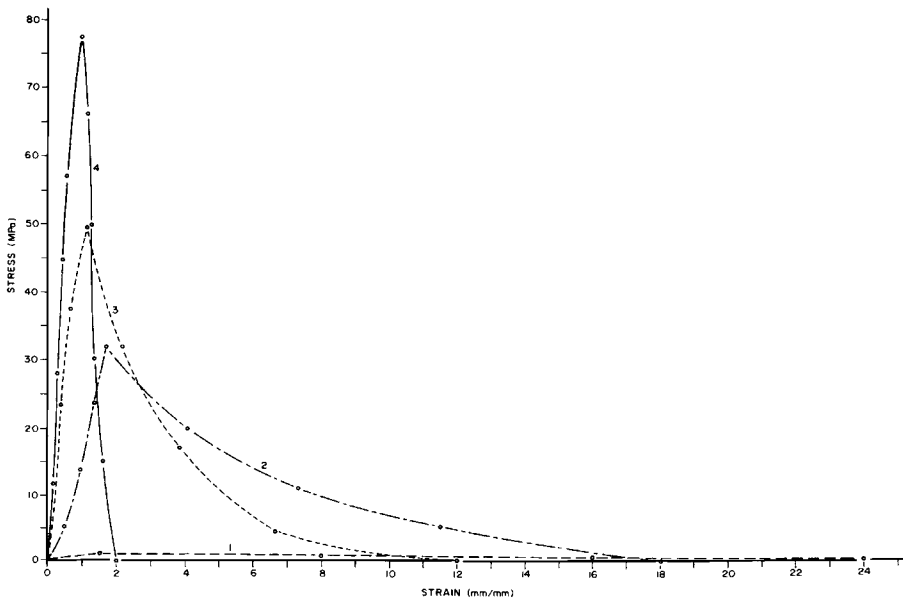

Fig. 12. Effect of PVC on the ultimate tensile strength (weathered specimens); California redwood substrate: (1) AT: (2) AT–PVC (7.5% PCV); (3) AT–PVC (15% PVC); (4) AT–PVC (33% PVC).

8) have, respectively, 2 and 1.5 times higher UTS than the unweathered blends with the same composition. The improvement in the UTS as a result of weathering diminishes with increasing concentration of PVC. Accordingly, weathering causes only a slight increase in this property of blends containing 33% of PVC (Fig. 8).

Generally, the strain decreases with increasing concentration of PVC, and is lower in weathered than in unweathered blends. Thus, the cohesion of the material increases with the PVC content.

Testing of unweathered and weathered blend specimens mounted on Portland cement and California redwood substrates, respectively, produced results similar to those obtained with aluminum substrate, as illustrated in Figures 9–12. However, at lower PVC concentration the UTS of specimens mounted on Portland cement and California redwood substrates is significantly higher than that of blends mounted on aluminum substrate.

The adhesive strength (AS) of the unweathered and weathered AT–PVC blends mounted on three different substrates increases in the following order: AS of specimens on aluminum < AS of specimens on California redwood < AS of specimens on Portland cement.

Improved mechanical properties of these blends is the result of specific interactions between the molecules of the constituent polymers. Specific interactions, such as hydrogen bonding, dipole–dipole interactions, charge transfer, etc., have been postulated to explain the miscibility (partial or complete) of different polymers,[8–11] leading to better mechanical properties of the resulting blends. In the vinyl chloride monomer unit the α-hydrogen atom (H-bond donor) can interact with the ester carbonyl (H-bond acceptor) of the acrylic terpolymer* to form a hydrogen bond, and is a key factor in achieving miscibility with many polymers containing acceptor groups. Furthermore, the possibility of charge–transfer and dipole–dipole interactions involving the chlorine atom of the vinyl chloride repeat unit and the ester oxygen of AT is also possible as has been suggested for blends of PVC and polymers containing an ester group.[10,11] Increased UTS of weathered AT-derived blends may be due to additional miscibility and/or crosslinking involving oxygen, promoted by heat and UV light during exposure.

CONCLUSIONS

Mixing of AT with PVC leads to a two-phase system: a continuous phase, which is either pure or mixed AT, and a particulate phase having the morphology of the added component and which may or may not contain mixed AT. The AT–PVC blends have markedly improved ultimate tensile strengths. Blending AT with PVC also leads to enhanced outdoor durability, as evidenced by considerably higher ultimate tensile strength of the weathered specimens in comparison to that of the controls (unweathered specimens). The improvement in the mechanical properties is particularly strong in these blends, probably because the added component has large specific interaction capabilities.

* A strong carbonyl infrared (IR) absorption band was detected in the AT (IR spectrum not shown).

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