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Acrylic Terpolymer-Based Blends with Improved Properties

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ABSTRACT

Blending of acrylic terpolymer (AT) with vinyl acetate-vinyl chloride (VAc-VC) copolymer, polyvinyl alcohol (PVA) polymer, and polyvinyl acetate (PVAc) polymer, respectively, resulted in sealant compositions with improved properties and enhanced outdoor weathering resistance. The morphology of these blends was studied by SEM, energy-dispersive x-ray analysis (EDXA), and DSC. The blends are heterogeneous and 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 and AT-(VAc-VC) copolymer blends contains mixed AT, whereas that of AT-PVA and AT-PVAc does not. The AT-based blends have

generally improved mechanical properties (e.g., ultimate tensile strength, adhesive strength). The improvement in mechanical properties is particularly strong in mixtures of AT with (VAc-VC) copolymer, probably because the added component has greater specific interaction capabilities with AT than the polymers incorporated in the other blends. Whereas the unblended AT has very low outdoor durability, the AT-based blends display enhanced resistance to weathering, as evidenced by substantially higher ultimate tensile strength of weathered specimens than those of the controls (unweathered).

INTRODUCTION

Blending has become a very useful method for developing new polymer compositions. 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 from acrylic terpolymer and some vinyl-type polymers. Partial results of this work have been reported recently on blends of acrylic terpolymer with PVC [1], polyorganosiloxane, and glass fiber reinforcement [2].

Previous papers [3-9] 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 acrylic terpolymer and acrylic terpolymer modified by blending with (VAc-VC) copolymer, poly(vinyl acetate), and poly(vinyl alcohol). The paper also discusses the effect of outdoor weathering on the morphology and mechanical properties. Results on the morphology on the blends were obtained by scanning electron microscopy, energy dispersive x-ray analysis, and differential scanning calorimetry.

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 to +30°C) and which is used for window glazing, metal curtain walls, and concrete and masonry joints. Other materials used were also commercial polymers and are as follows: (vinyl acetate-vinyl chloride) copolymer [(VAc-VC) copolymer, Hoechst, A.G.] ;

poly(vinyl alcohol) (PVA, Mowiol 4-98, Hoechst, A.G.); poly(vinyl acetate) (PVAc, Mowilith D-50, Hoechst, A.G.).

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 first coated with carbon and then with gold to prevent electrical charging. DSC curves were recorded with a Du Pont 1090 thermal analyzer over a temperature range of -100 to 160°C under nitrogen.

To assess the state of mixing in At-(VAc-VC) copolymer 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).

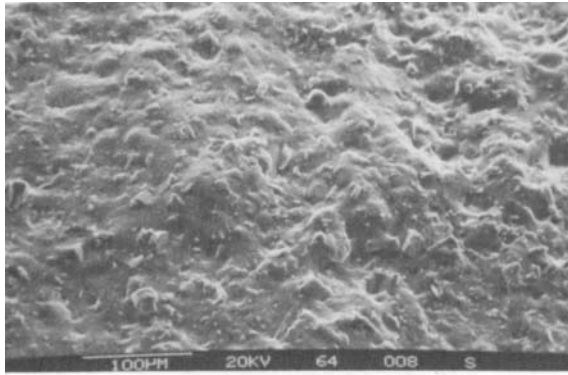
Tensile stress-strain measurements were carried out at 22°C using an Instron Model 1125 Universal Testing Machine at a cross-head speed of 5 mm/min and a chart speed of 100 mm/min. The test specimens (12.5 × 12.5 × 50.0 mm) consisted of a bead of material (AT or modified AT) cast between two prismatic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

To assess the effect of outdoor weather on the properties of modified and unmodified AT, samples were exposed in a highly polluted area in Montreal (Quebec, 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.

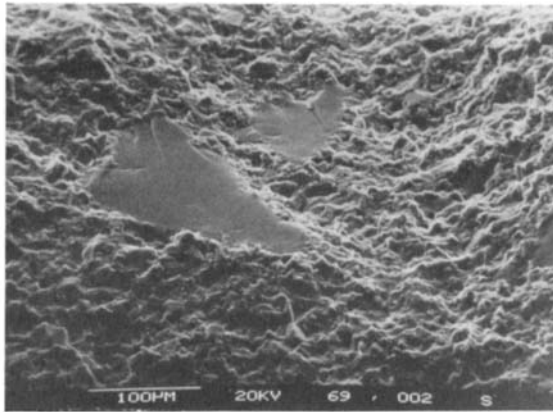
RESULTS AND DISCUSSION

Morphology

The morphology of the AT-based blends is illustrated in the SEM photomicrographs presented in Figs. 1 and 2.



(a)



(b)

FIG. 1. SEM photomicrograph of fracture surfaces: (a) unblended acrylic terpolymer (AT); (b) AT-(VAc-VC) copolymer blend (7.5% copolymer).

Mixing of acrylic terpolymer with (VAc-VC), PVA, or PVAc copolymer results in heterogeneous blends. SEM observations of fracture surface indicate that in these blends, the AT polymer constitutes the continuous phase, whereas the added polymer occurs as discrete particles of varying sizes having either irregular or spherical shape (Table 1).

In Fig. 1 the morphology of the fracture surfaces material of AT-(VAc-VC) copolymer blend is compared with that of AT (unmodified).

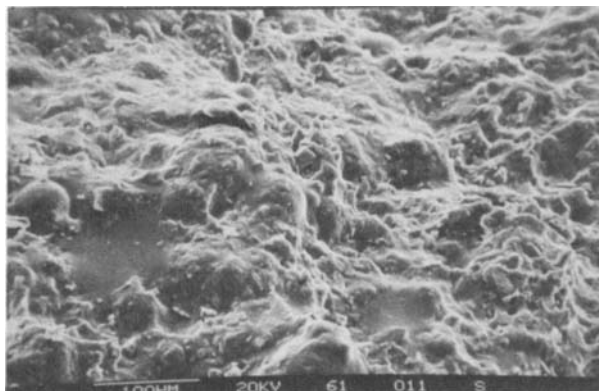


FIG. 2. AT-PVAc (33% PVAc).

The smooth areas of Fig. 1(b) represent fracture surfaces of (VAc-VC) copolymer particles which are embedded in the AT continuous phase. The surface texture of the continuous phase has the same features as that of unmodified AT shown in Fig. 1(a). EDXA results revealed that the AT phase of these blends is pure at concentrations of PVC of 7.5% or lower, but that it becomes increasingly more miscible (increasing C1 count) with increasing content of the added component in the mixture. It is possible that the (VAc-VC) particles may also contain some mixed AT. This could, however, not be ascertained by DSC, as the corresponding curves were complicated by overlapping and the occurrence of several thermal transitions that were not present in those of the components.

The morphological structure of the fracture surface material of the AT-PVA blends was similar to that of the AT-(VAc-VC) blends; that is, it consisted of irregularly shaped particles of PVA distributed in a continuous phase with a texture similar to that of unblended AT. The DSC results provided additional information regarding the miscibility of the components. In AT-PVA blends of low PVA concentration (7.5 or 15%), the T_g 's occur at the same temperatures (and have the same width) as the corresponding glass transitions of the unblended components (T_g of AT = -23°C and T_g of PVA = 27°C). Thus, AT and PVA are not miscible at these concentrations. This interpretation is in agreement with the SEM results, which showed that the material in the fracture surface of these blends has a heterogeneous nature. However, in blends containing 33% of PVA, the T_g of AT is shifted from -23 to -17°C , but the T_g corresponding to PVA is unchanged. These results suggest that at higher concentrations some PVA has diffused

TABLE 1. Results of SEM and EDXA Observations of Fracture Surfaces of Acrylic Terpolymer (AT)-Based Blends^a

Sample ^b	Amount of added polymer, %	Observations
AT		Fracture surface material has rough texture; material consists of one phase
AT-(VAc-VC) copolymer	7.5	Heterogeneous blends: AT-(VAc-VC) copolymer particles evenly distributed in the continuous phase of AT. At concentrations $\leq 7.5\%$, EDXA results indicate the presence of (VAc-VC) copolymer in the AT phase
AT-(VAc-VC) copolymer	15.0	
AT-(VAc-VC) copolymer	25.0	
AT-PVA	7.5	Heterogeneous blends, consisting of a continuous phase (AT) ^c and a particulate phase (PVA)
AT-PVA	15.0	
AT-PVA	33.0	
AT-PVAc	7.5	Heterogeneous blends: PVAc (spherical) particles well distributed in the AT continuous phase
AT-PVAc	15.0	
AT-PVAc	25.0	

^aThe adhesion between the component phases of all blends was very good.

^bSEM and EDXA observations indicated that the morphology of the samples weathered outdoors is not significantly different from that of samples kept under laboratory conditions (22°C and 50% RH).

^cEvidence from DSC indicates that in the AT-PVA blend containing 33% PVA, the AT phase was mixed with some PVA, but the PVA phase was pure.

into, and is miscible with, the AT phase, and that the AT polymer is not present in the PVA particles.

The topography of the fracture surface of AT-PVAc is shown in the SEM photomicrograph of Fig. 2. The AT-PVAc blend is heterogeneous, consisting of approximately spherical particles dispersed in a matrix having the morphological features of unblended AT. The PVAc particles are covered with a layer of AT material. The (two) smooth areas of the photomicrograph correspond to fracture surfaces of PVAc particles. SEM observations of these blends indicate that fracture usually occurs within the AT phase, and that the PVAc par-

ticles undergo fracture only infrequently. As with AT-(VAc-VC) blends, the DSC results could not be used to determine the occurrence of partial miscibility of the two components.

The texture of the fracture surfaces of all the AT-based blends weathered outdoors was similar to that of the control samples. Also, the DSC curves of weathered samples were not significantly different from those of the unweathered blends. Thus, these results indicate that outdoor weathering did not induce any significant changes in the morphology of the blends. The adhesion between the components of the AT-based blends (unweathered and weathered) was good.

Ultimate Tensile Strength

The stress-strain curves of the various AT-based blends (unweathered and weathered) tested on specimens mounted on aluminum, Portland cement, and California redwood, respectively, are presented in Figs. 3 to 19.

Blends of AT-(VAc-VC) Copolymer

Blending of AT with (VAc-VC) copolymer caused a considerable improvement in the ultimate tensile strength (UTS) of the resulting mixture. For example, the UTS of blend specimens mounted on aluminum substrate and containing 7.5 and 15% of (VAc-VC) copolymer is greater than that of unblended AT by a factor of 2 and 4, respectively (Fig. 3). The improvement in UTS of blends tested in conjunction with Portland cement or California redwood followed similar trends, the increase in UTS being only slightly lower (Figs. 5 and 7).

Blends of AT with PVA and PVAc

Addition of either PVA or PVAc to AT has approximately the same effect on the UTS of the resulting blends. As in blends of AT-(VAc-VC), the UTS of these mixtures (tested on the three substrates) is increasing with the concentration of the added component (Figs. 8 to 19). However, the increase in UTS is generally less than in the AT-(VAc-VC) blends with corresponding concentrations. For example, the UTS of blend specimens mounted on aluminum substrate and containing 15% of either PVA or PVAc is higher than that of the unblended AT by a factor of approximately 2 (Figs. 8 and 14), which is half the amount of increase observed in a AT-(AT-VC) blend with the same concentration (Fig. 3) of components.

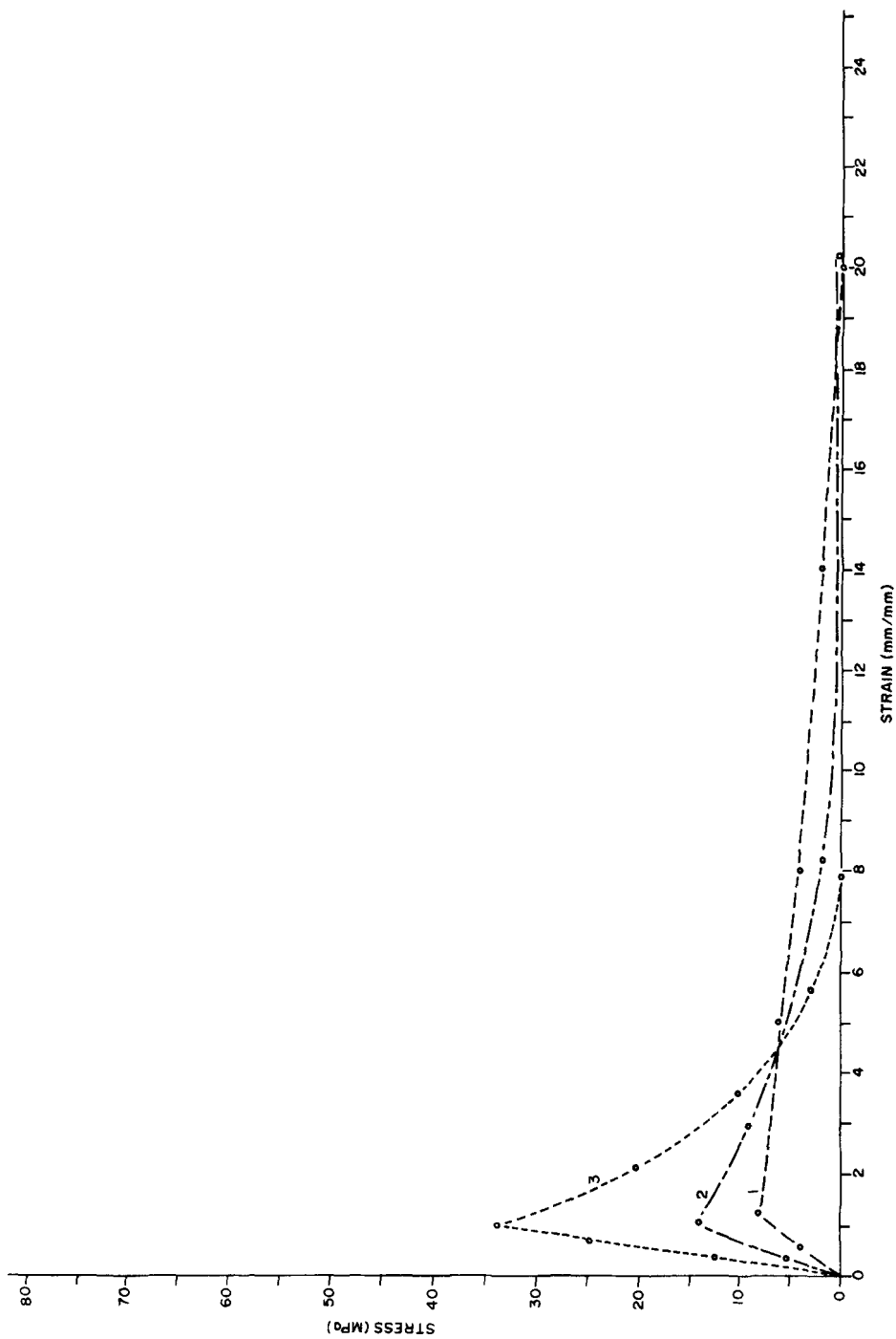


FIG. 3. Effect of (VAc-VC) copolymer on the ultimate tensile strength (control specimens). Aluminum substrate. (1) AT; (2) AT-(VAc-VC) copolymer (7.5%); (3) AT-(VAc-VC) copolymer (15%).

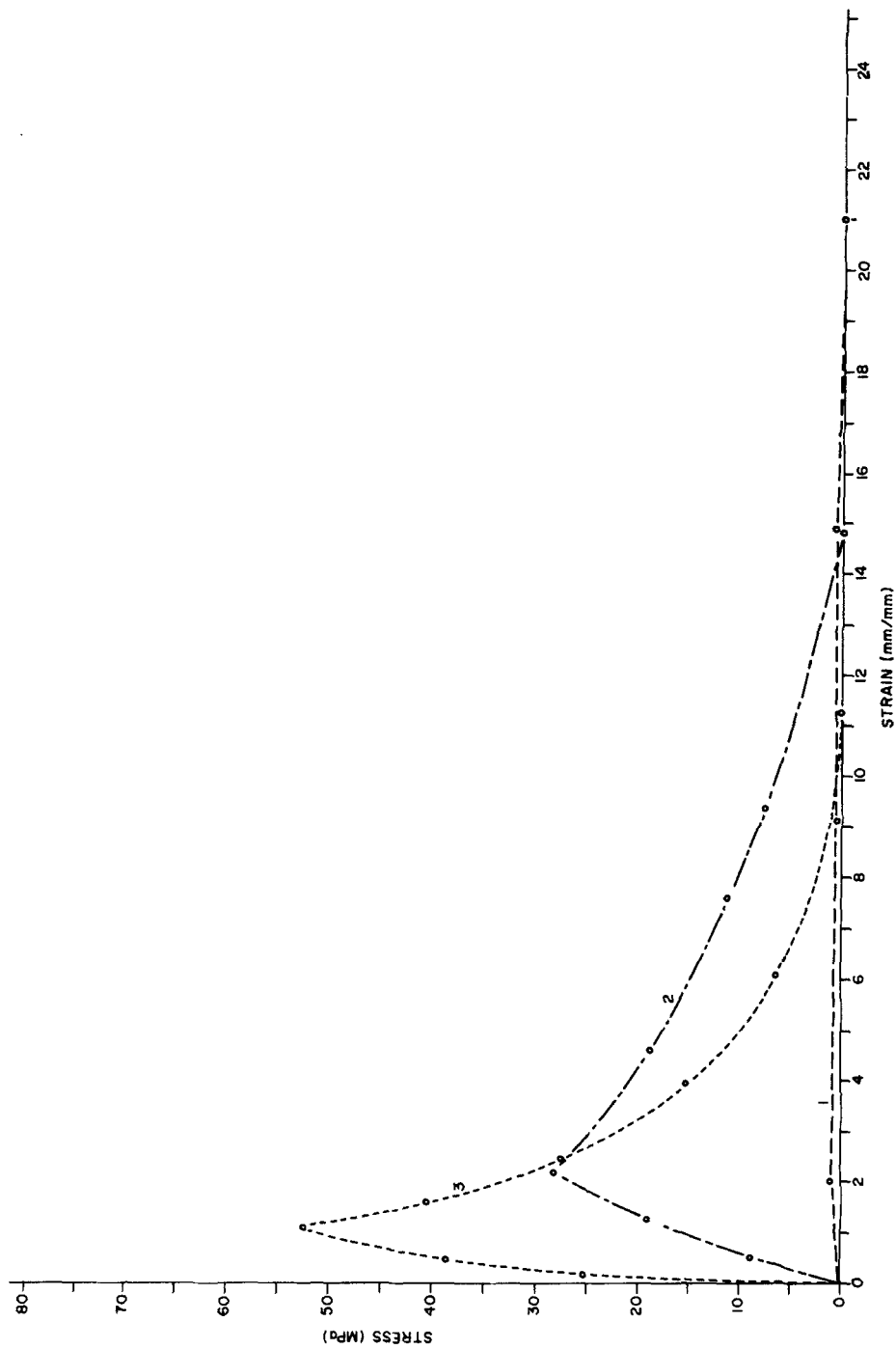


FIG. 4. Effect of (VAc-VC) copolymer on the ultimate tensile strength (weathered specimens). Aluminum substrate. (1) AT; (2) AT-(VAc-VC) copolymer (7.5%); (3) AT-(VAc-VC) copolymer (15%).

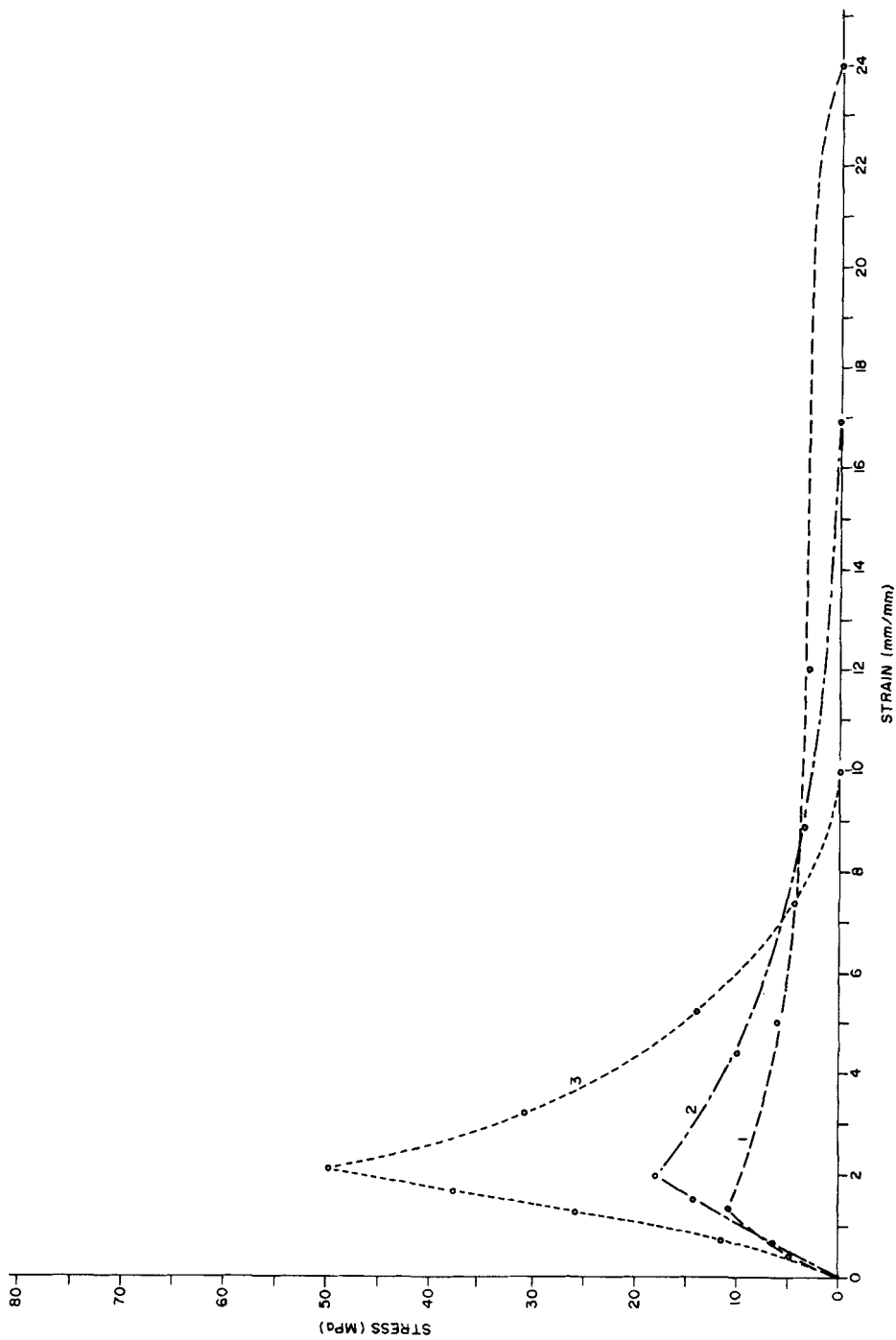


FIG. 5. Effect of (VAc-VC) copolymer on the ultimate tensile strength (control specimens), Portland cement mortar substrate. (1) AT; (2) AT-(VAc-VC) copolymer (7.5%); (3) AT-(VAc-VC) copolymer (15%).

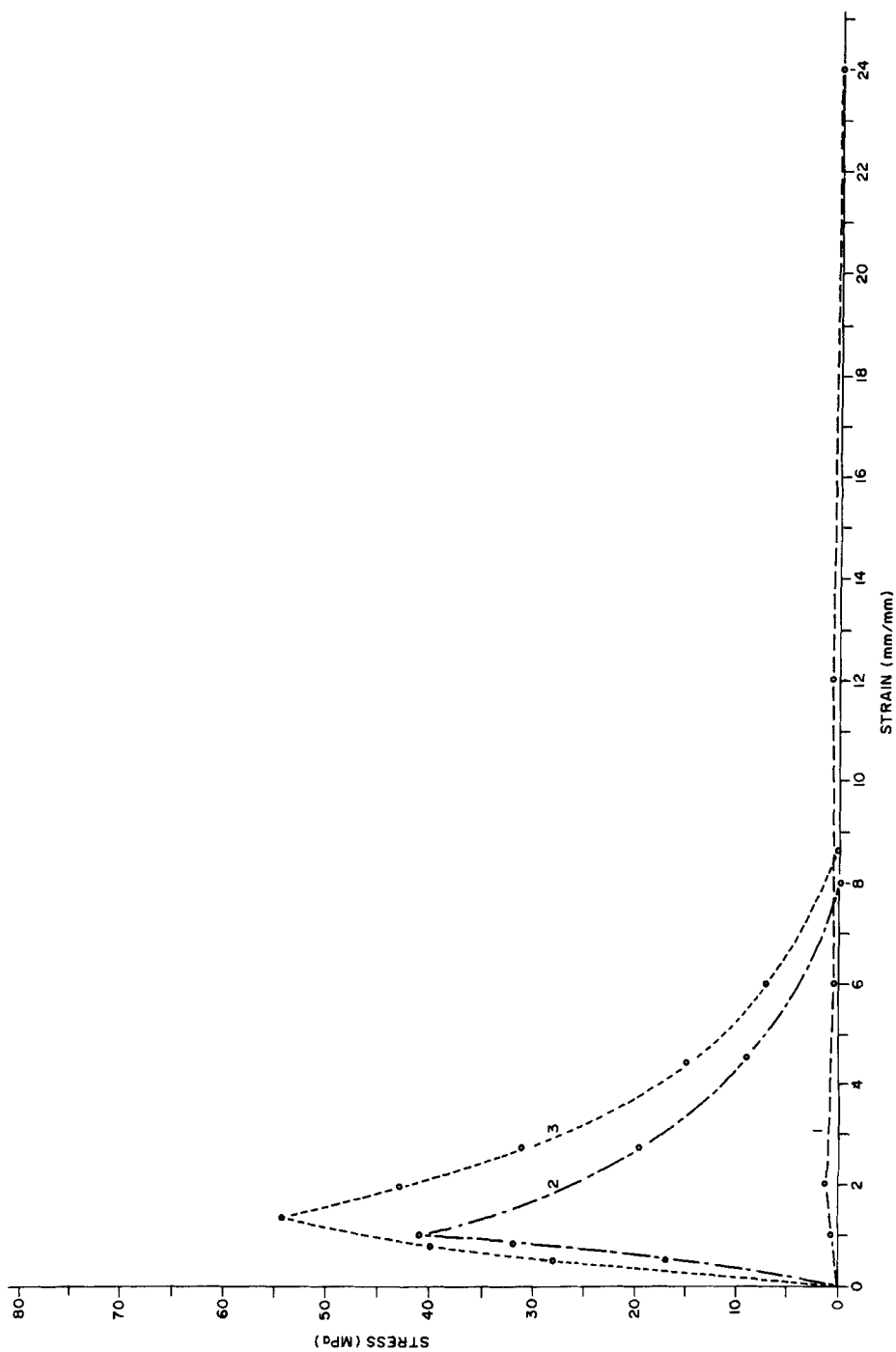


FIG. 6. Effect of (VAc-VC) copolymer on the ultimate tensile strength (weathered specimens). Portland cement mortar substrate. (1) AT; (2) AT-(VAc-VC) copolymer (7.5%); (3) AT-(VAc-VC) copolymer (15%).

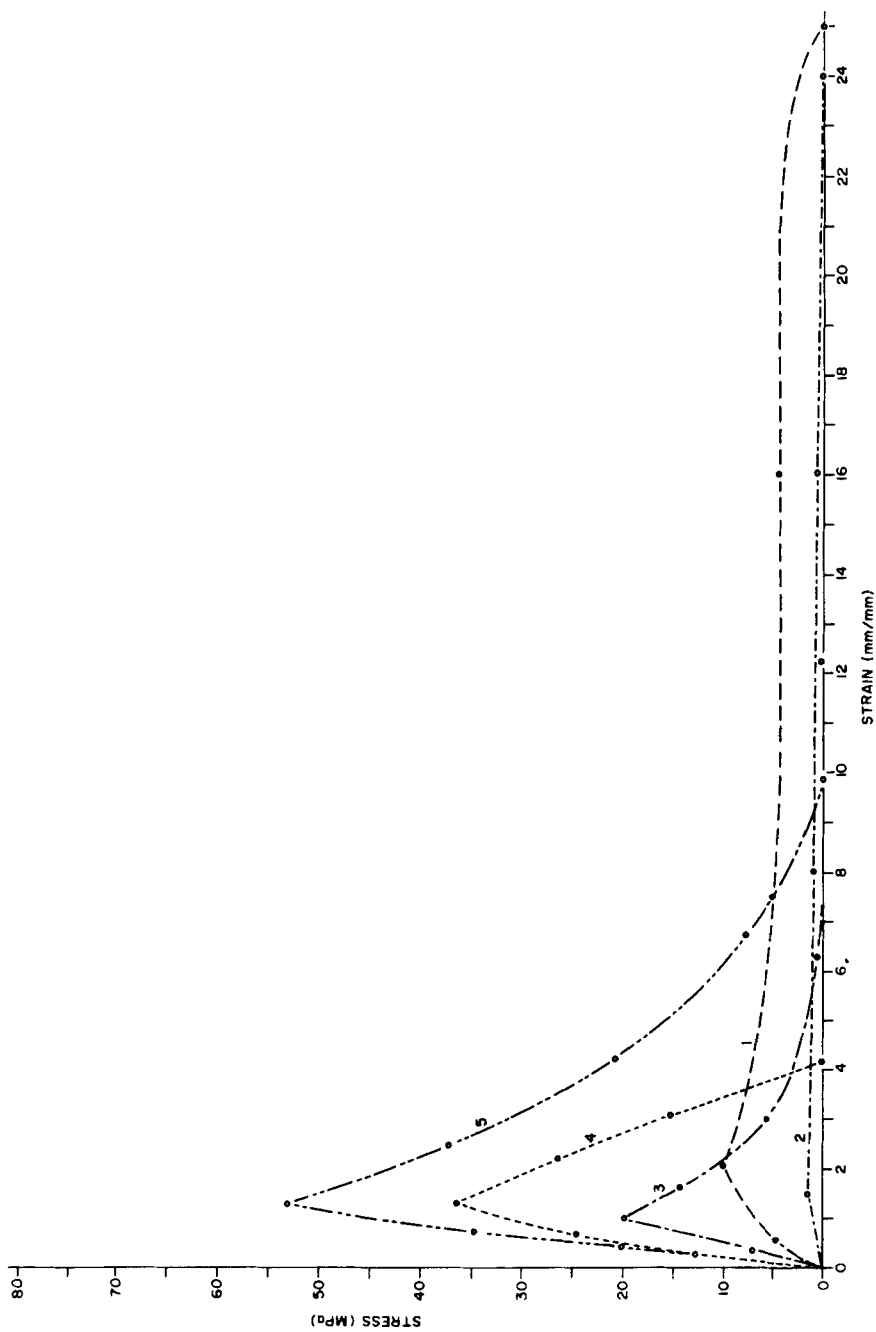


FIG. 7. Effect of (VAc-VC) copolymer on the ultimate tensile strength. California redwood substrate. (1) AT (control specimen); (2) AT (weathered specimen); (3) AT-(VAc-VC) copolymer (7.5%) (control specimen); (4) AT-(VAc-VC) copolymer (15%) (control specimen); (5) AT-(VAc-VC) copolymer (15%) (weathered specimen).

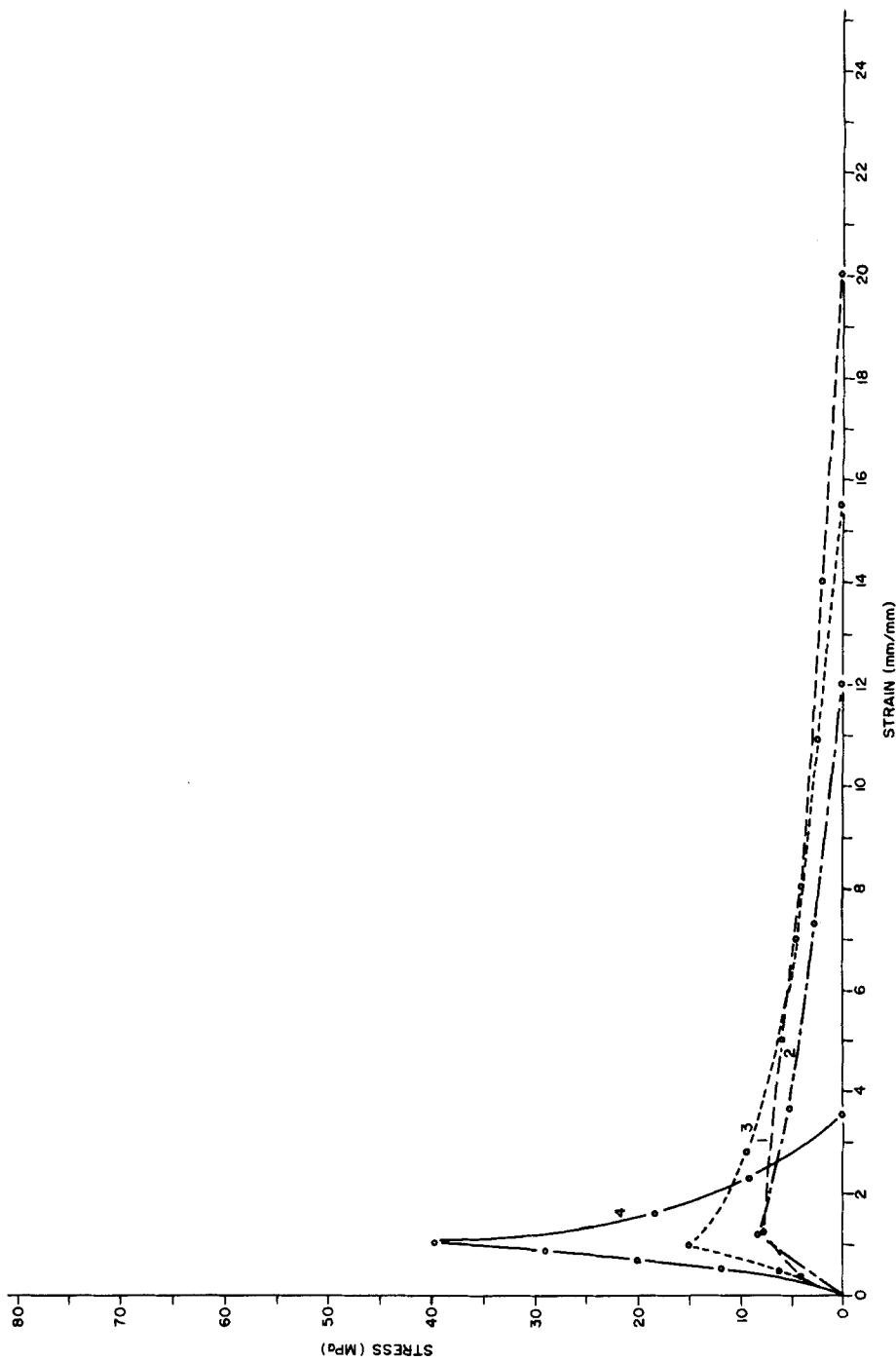


FIG. 8. Effect of PVA on the ultimate tensile strength (control specimens). Aluminum substrate. (1) AT; (2) AT-PVA (7.5% PVA); (3) AT-PVA (15% PVA); (4) AT-PVA (33% PVA).

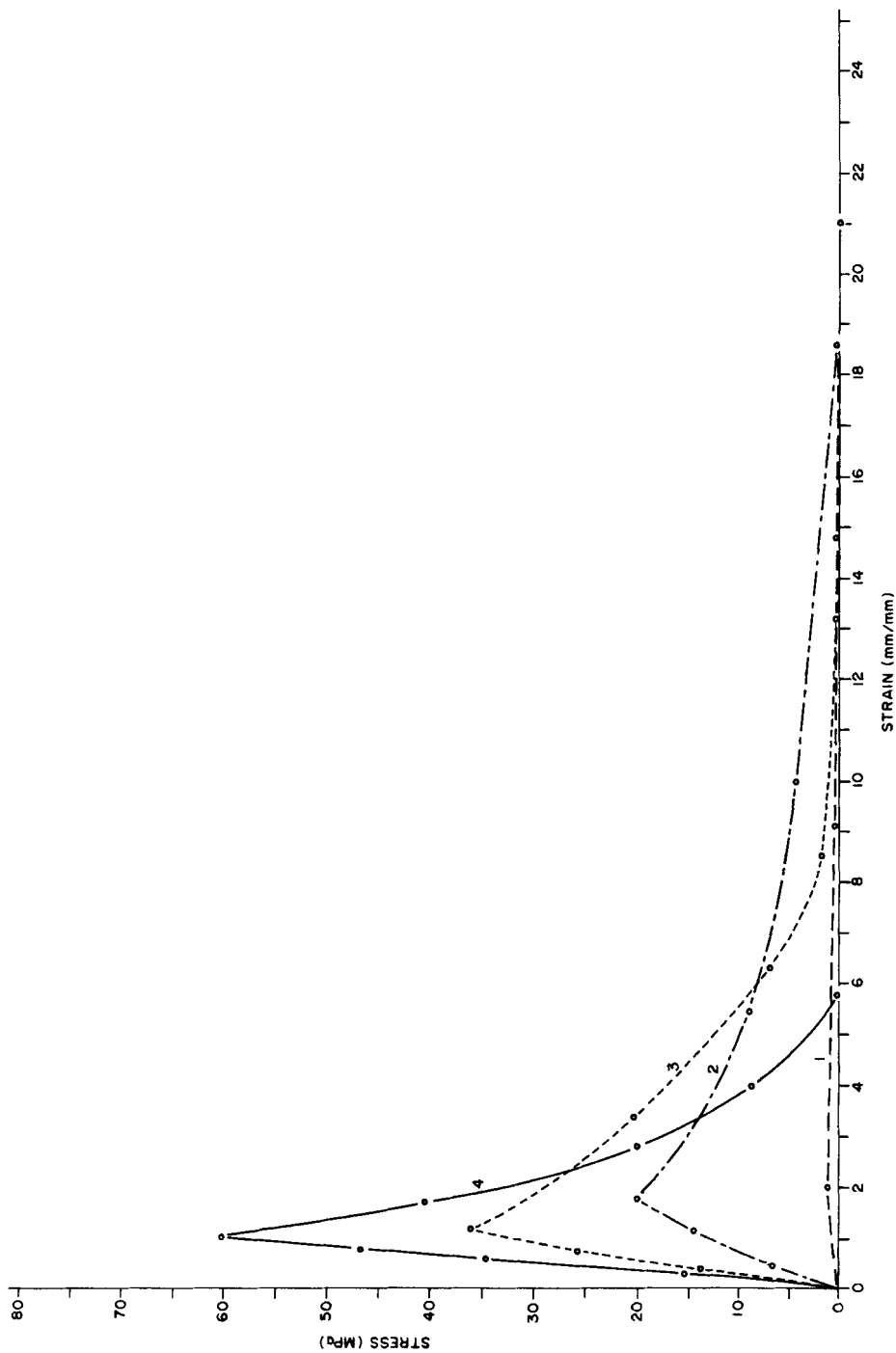


FIG. 9. Effect of PVA on the ultimate tensile strength (weathered specimens). Aluminum substrate. (1) AT; (2) AT-PVA (7.5% PVA); (3) AT-PVA (15% PVA); (4) AT-PVA (33% PVA).

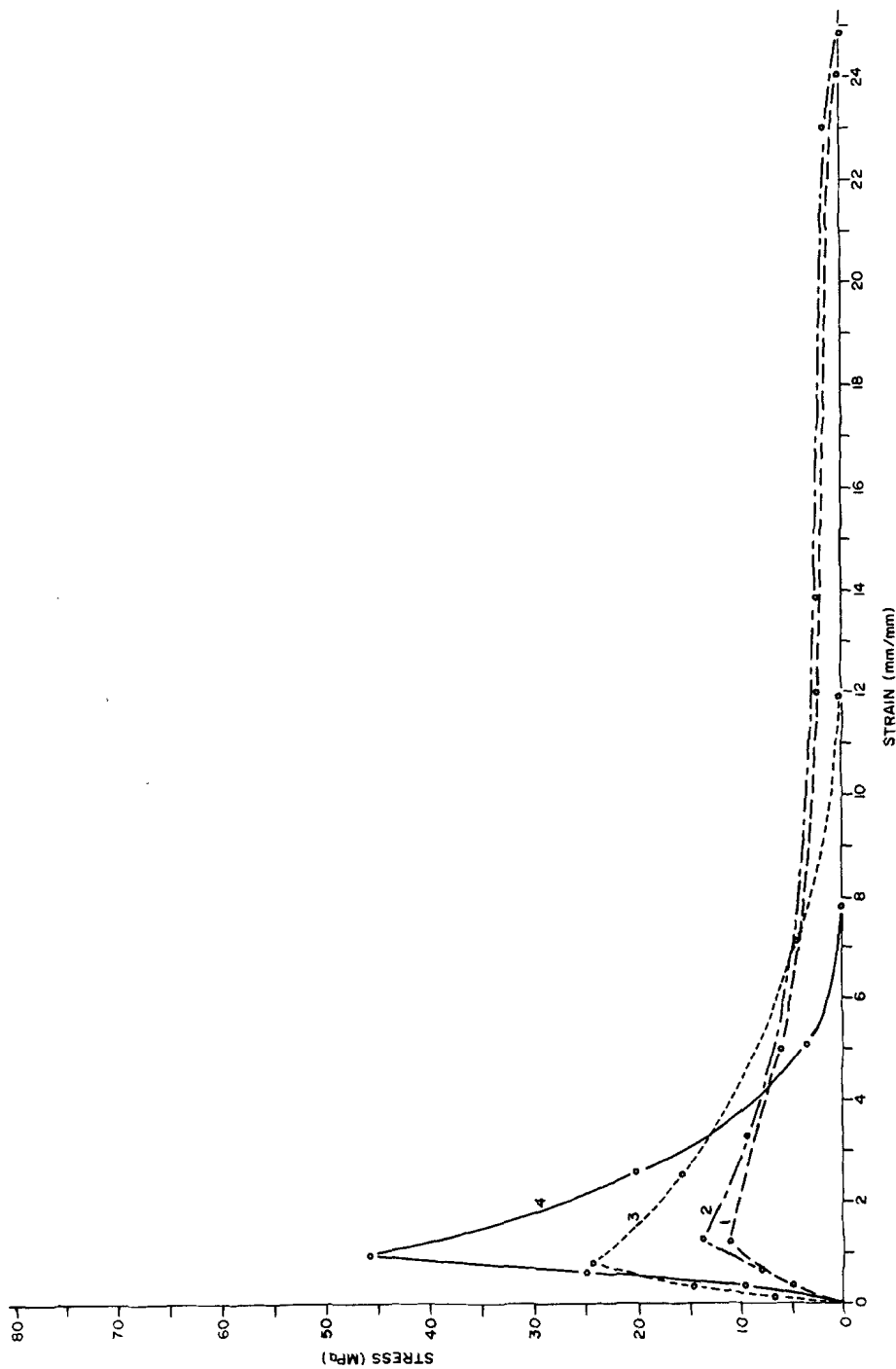


FIG. 10. Effect of PVA on the ultimate tensile strength (control specimens). Portland cement mortar substrate. (1) AT; (2) AT-PVA (7.5% PVA); (3) AT-PVA (15% PVA); (4) AT-PVA (33% PVA).

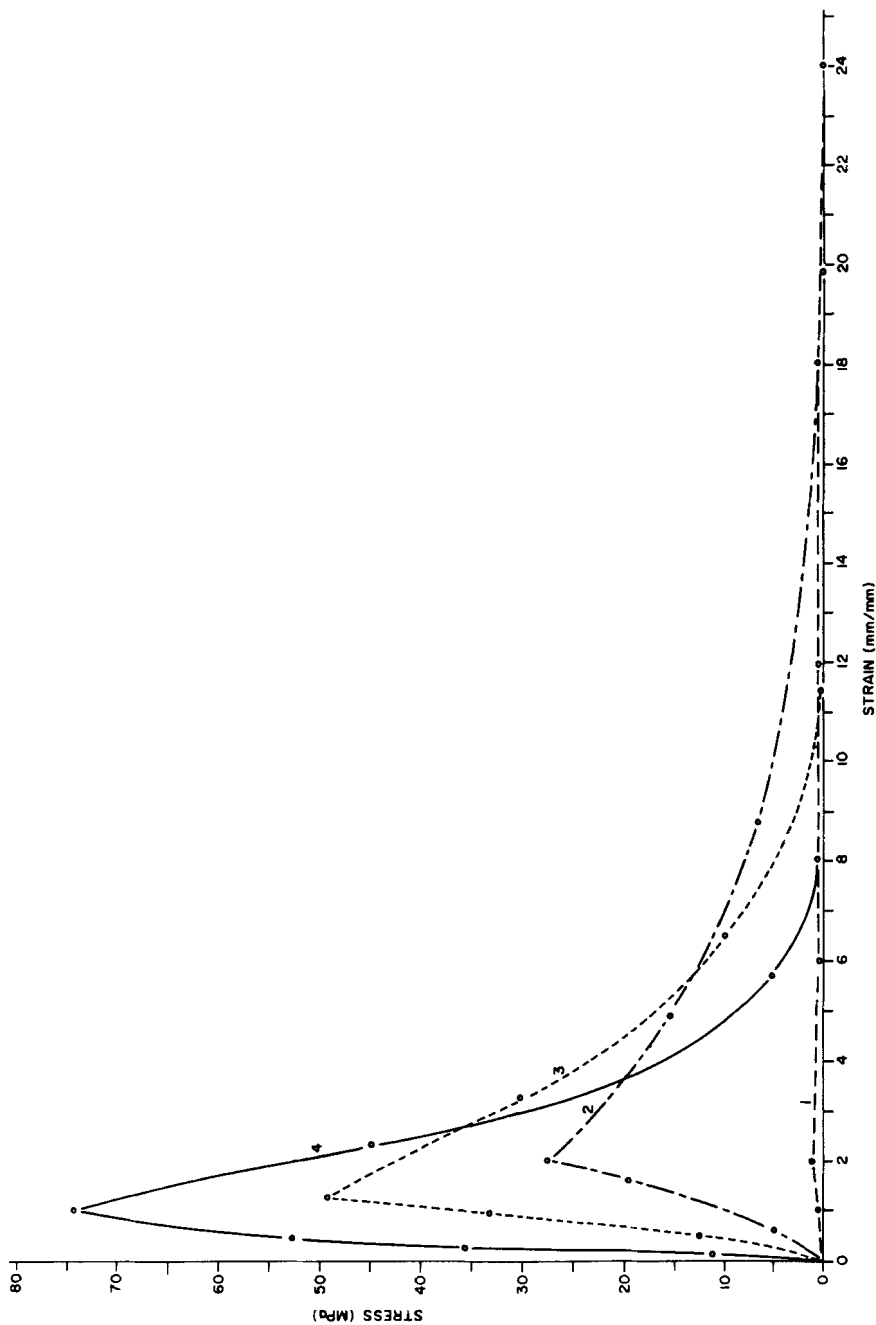


FIG. 11. Effect of PVA on the ultimate tensile strength (weathered specimens). Portland cement mortar substrate. (1) AT; (2) AT-PVA (7.5% PVA); (3) AT-PVA (15% PVA); (4) AT-PVA (33% PVA).

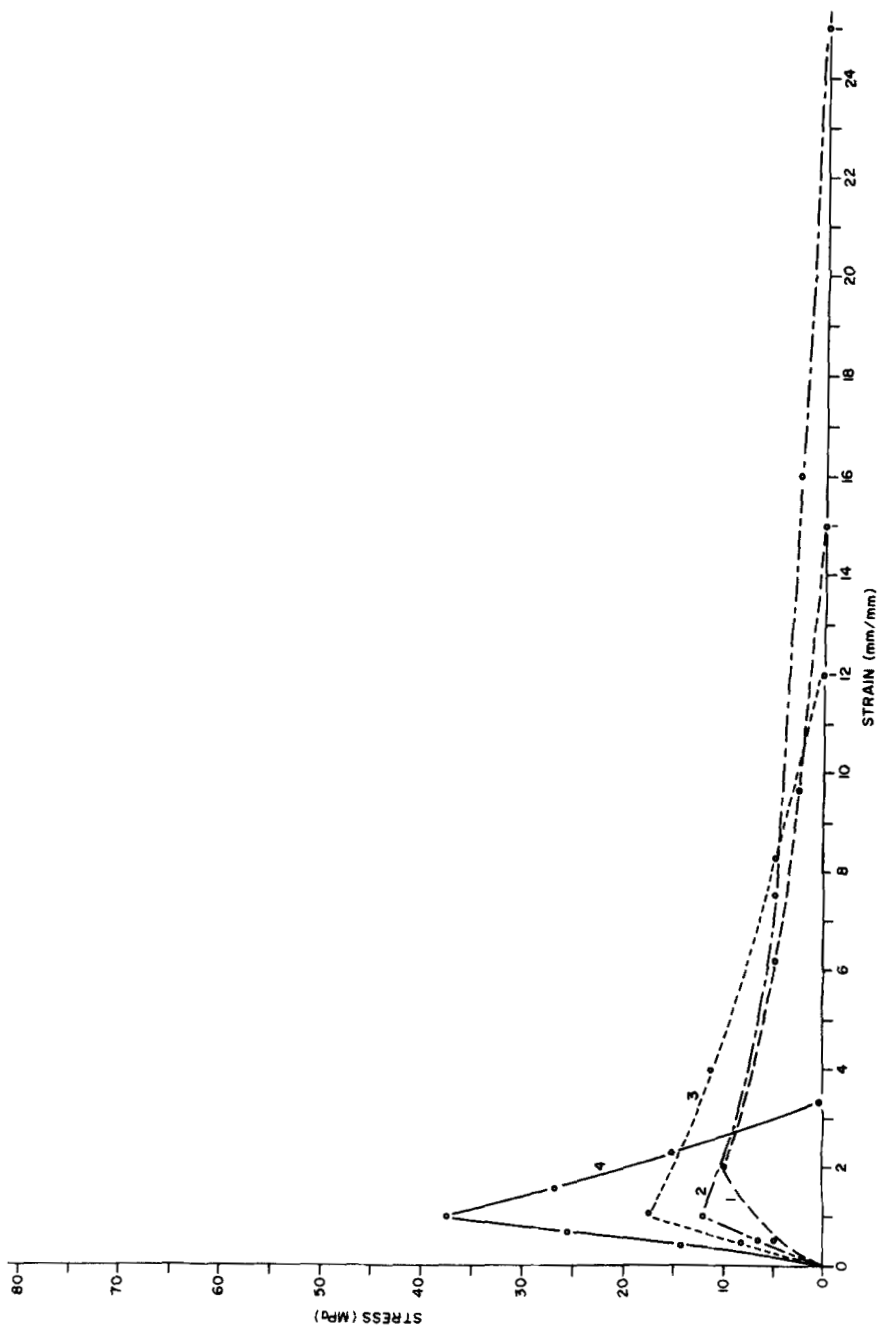


FIG. 12. Effect of PVA on the ultimate tensile strength (control specimens), California redwood substrate. (1) AT; (2) AT-PVA (7.5% PVA); (3) AT-PVA (15% PVA); (4) AT-PVA (33% PVA).

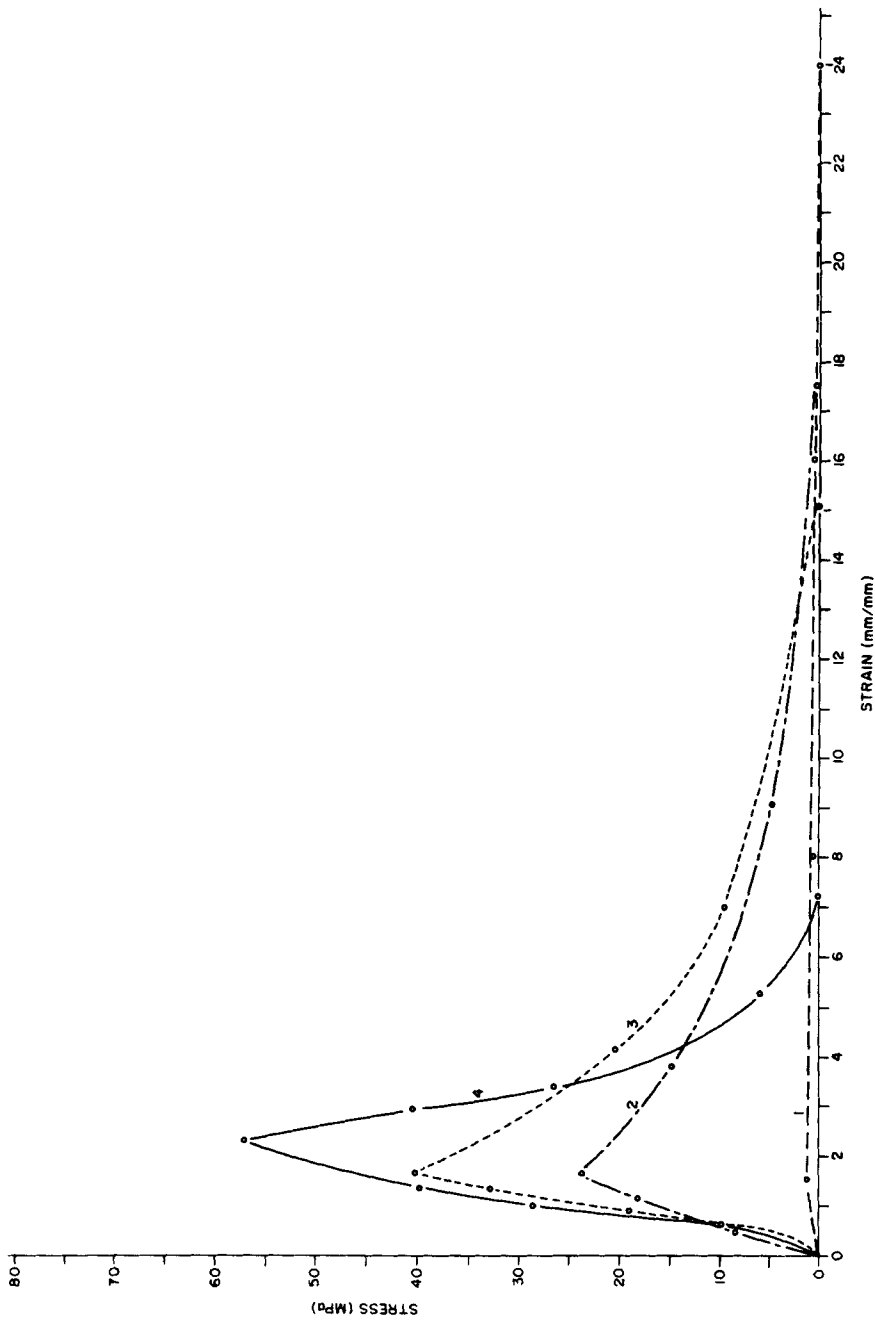


FIG. 13. Effect of PVA on the ultimate tensile strength (weathered specimens). California redwood substrate. (1) AT; (2) AT-PVA (7.5% PVA); (3) AT-PVA (15% PVA); (4) AT-PVA (33% PVA).

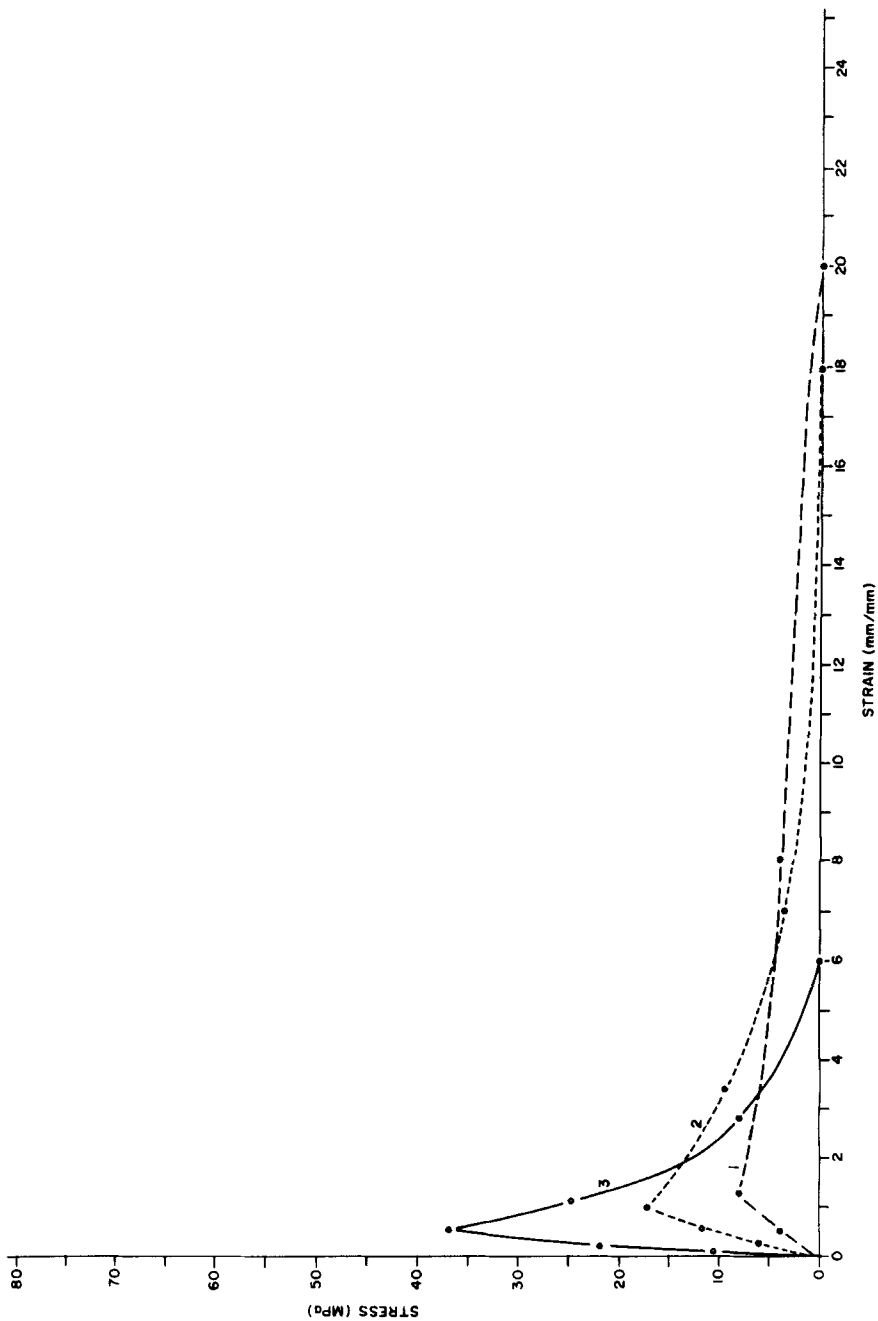


FIG. 14. Effect of PVAc on the ultimate tensile strength (control specimens). Aluminum substrate. (1) AT; (2) AT-PVAc (15% PVAc); (3) AT-PVAc (25% PVAc).

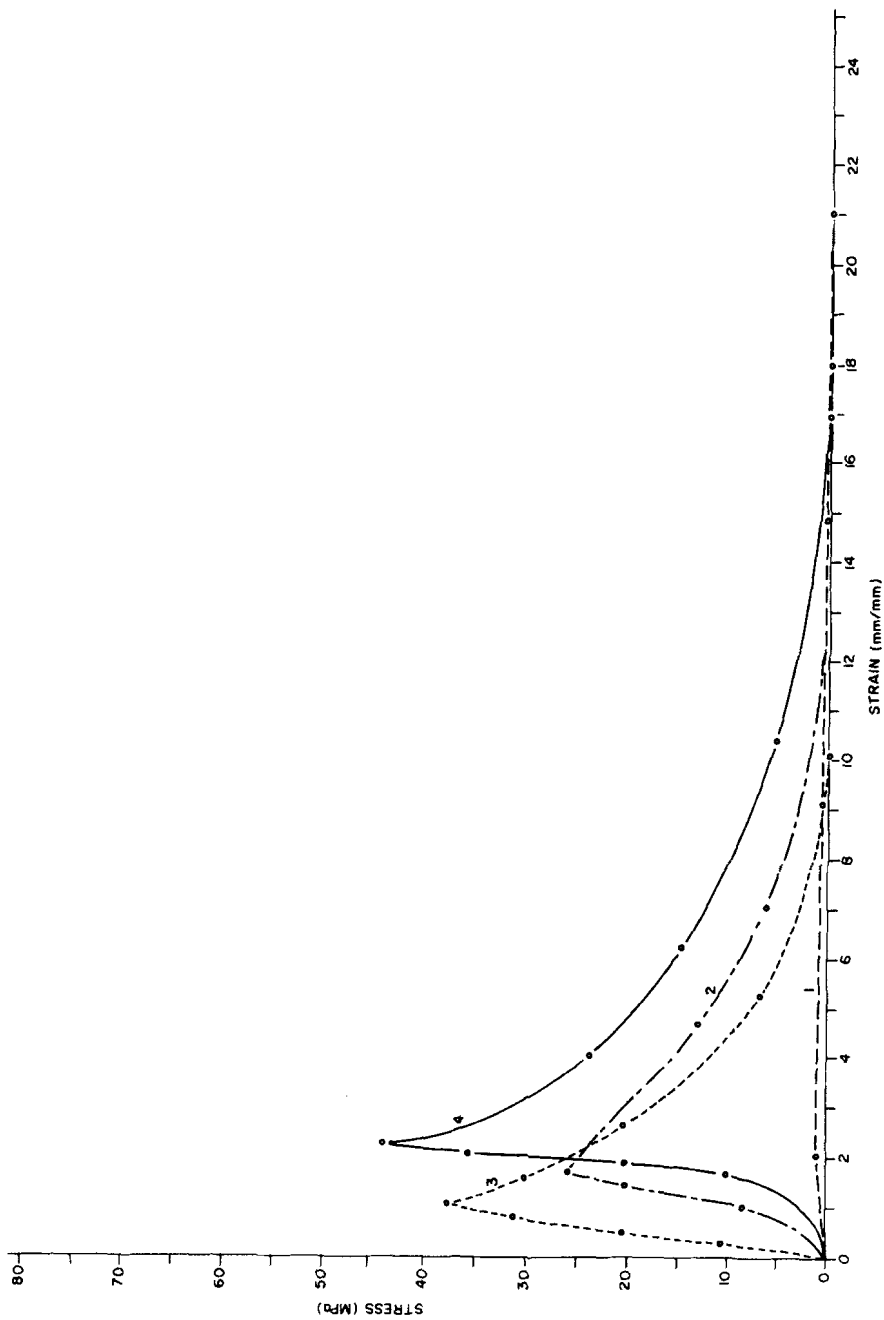


FIG. 15. Effect of PVAc on the ultimate tensile strength (weathered specimens). Aluminum substrate. (1) AT; (2) AT-PVAc (7.5% PVAc); (3) AT-PVAc (15% PVAc); (4) AT-PVAc (25% PVAc).

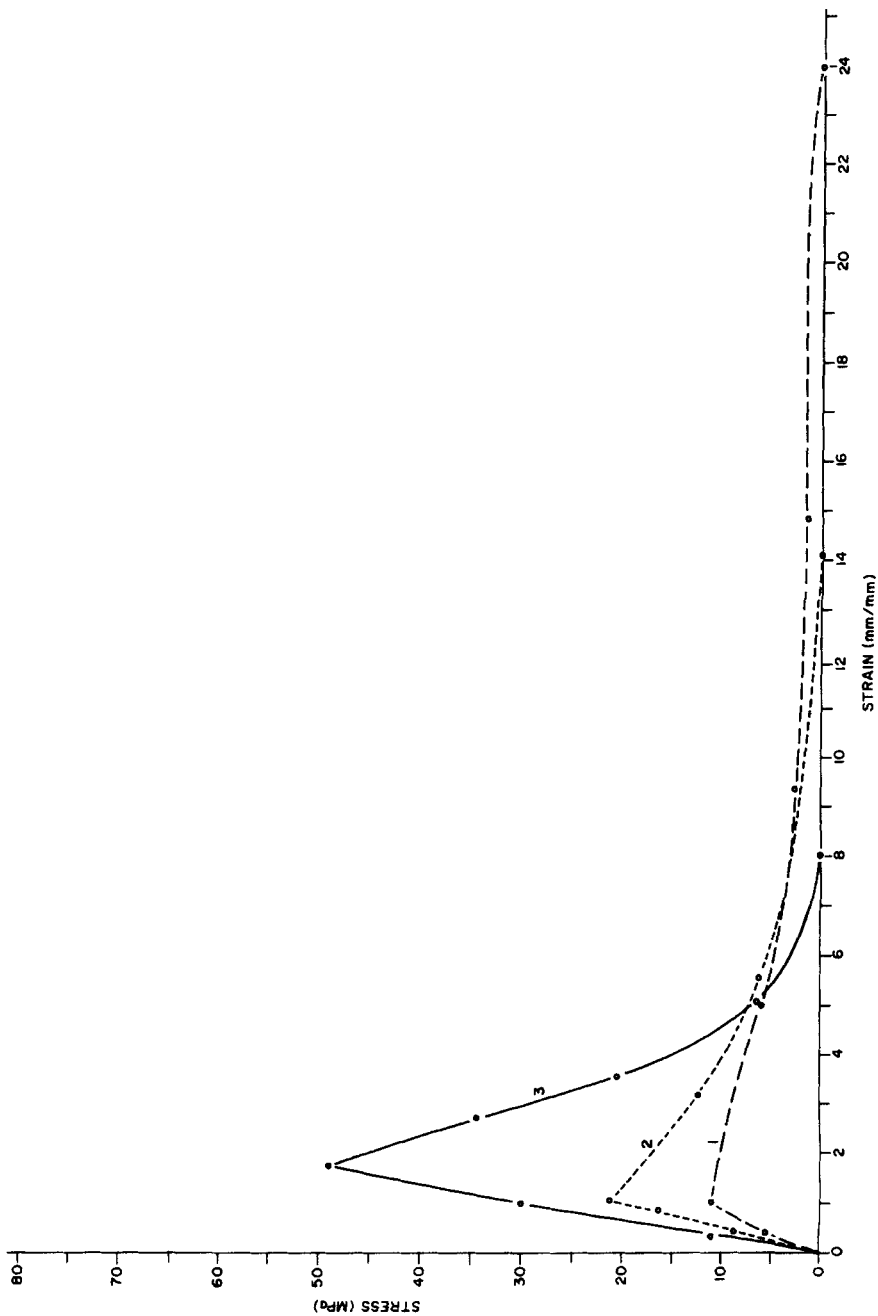


FIG. 16. Effect of PVAc on the ultimate tensile strength (control specimens). Portland cement mortar substrate. (1) AT; (2) AT-PVAc (15% PVAc); (3) AT-PVAc (25% PVAc).

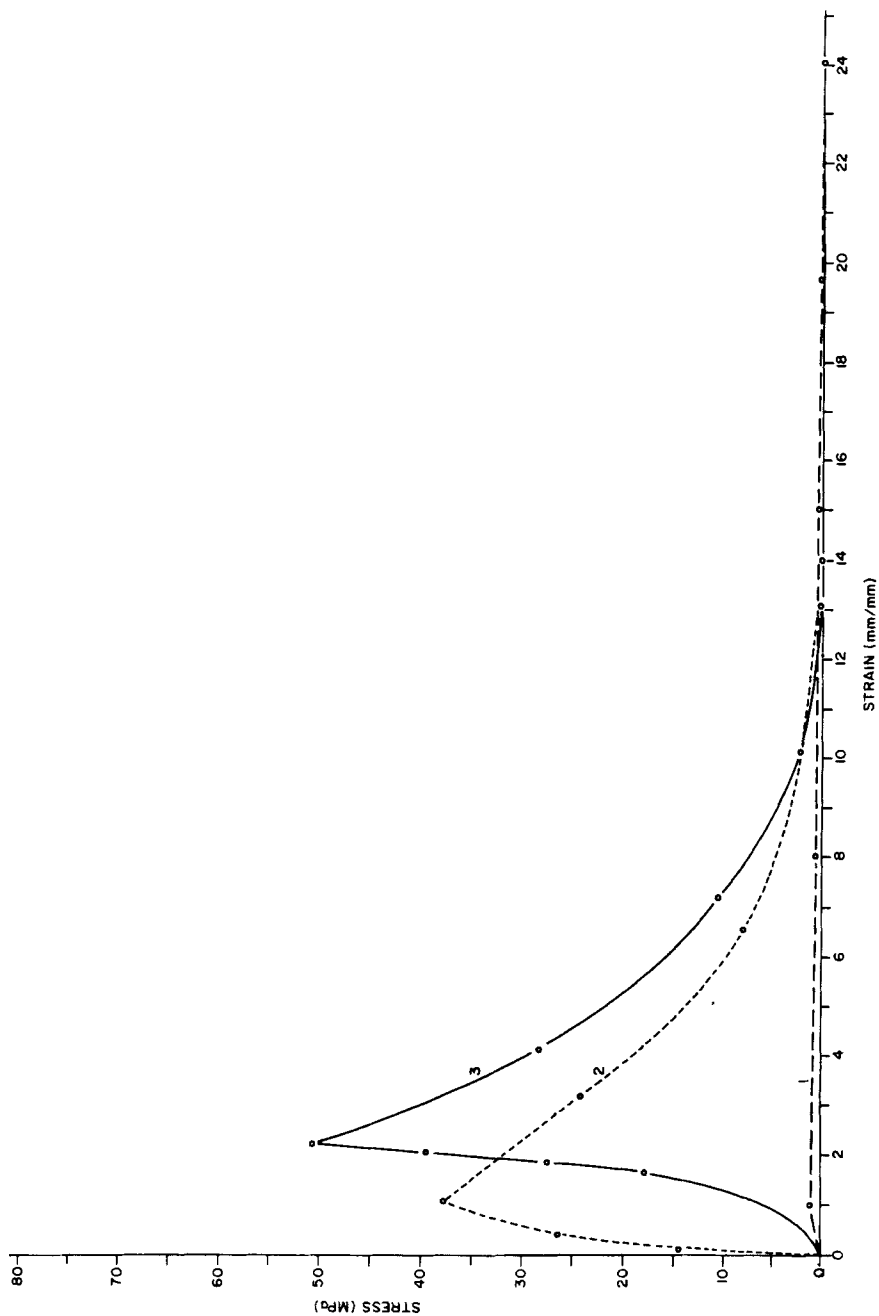


FIG. 17. Effect of PVAc on the ultimate tensile strength (weathered specimens). Portland cement mortar substrate. (1) AT; (2) AT-PVAc (15% PVAc); (3) AT-PVAc (25% PVAc).

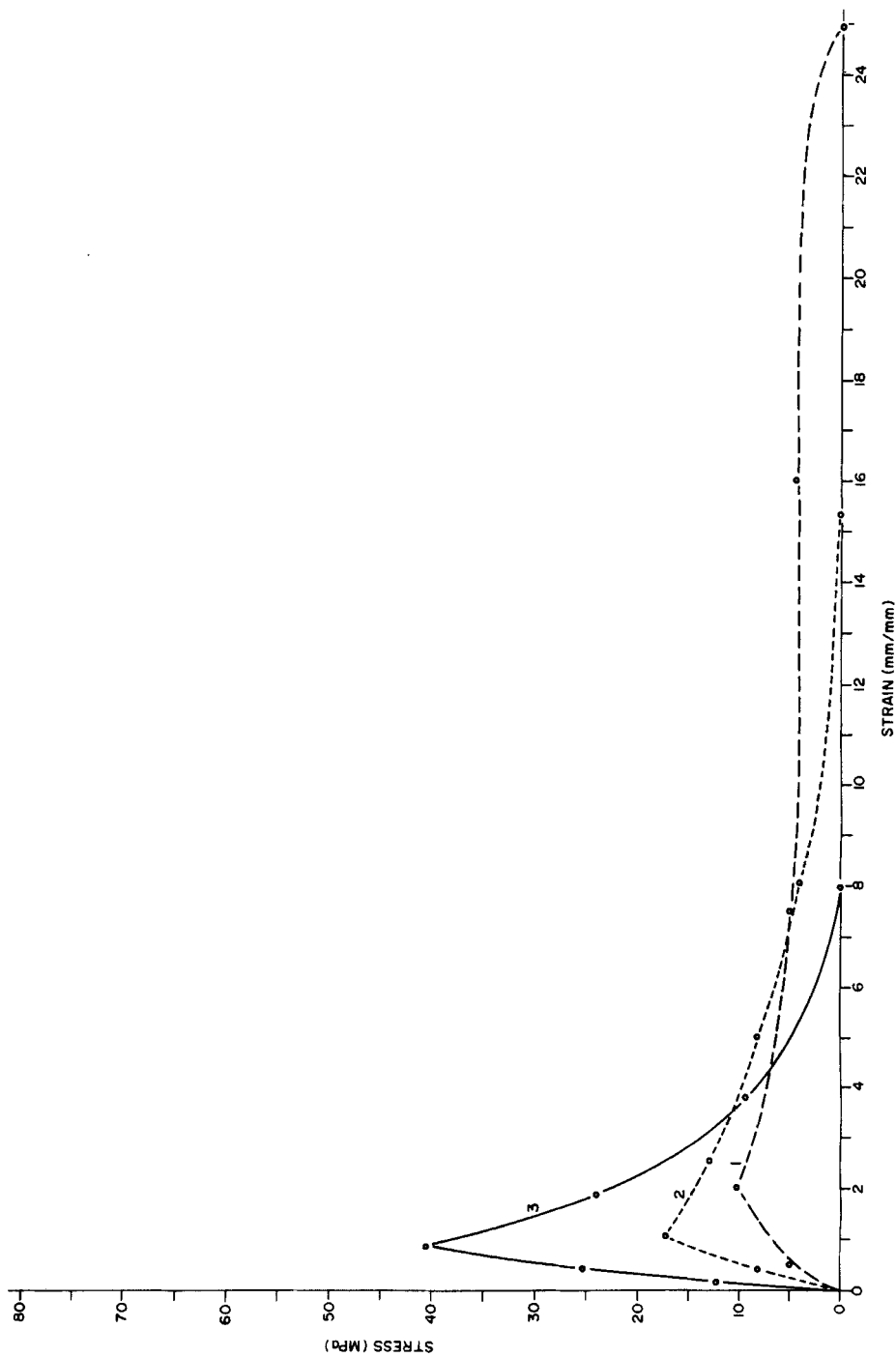


FIG. 18. Effect of PVAc on the ultimate tensile strength (control specimens). California redwood substrate. (1) AT; (2) AT-PVAc (15% PVAc); (3) AT-PVAc (25% PVAc).

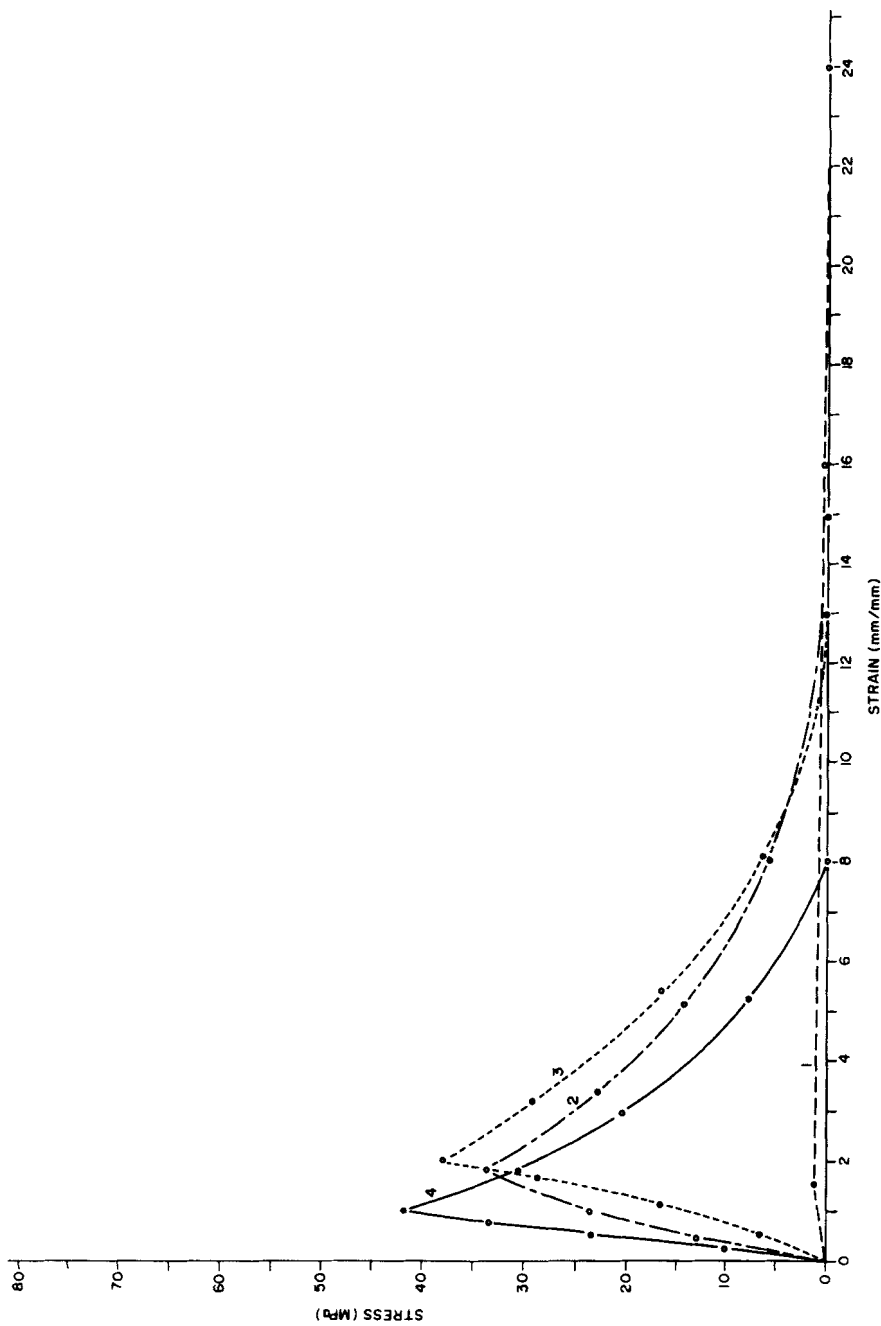


FIG. 19. Effect of PVAc on the ultimate tensile strength (weathered specimens). California redwood substrate. (1) AT; (2) AT-PVAc (7.5% PVAc); (3) AT-PVAc (15% PVAc); (4) AT-PVAc (25% PVAc).

Effect of Weathering on the Ultimate Tensile Strength

Weathering for 260 days caused a substantial increase in the UTS of most AT-based blends, the extent of increase depending on the nature of substrate used in the testing. Accordingly, the UTS of the weathered AT-based blends tested on the three substrates (aluminum, Portland cement, and California redwood) increased by a factor ranging from 1.05 to 2.5 in comparison to that of the unweathered samples (controls) (Figs. 4 to 19). In contrast, the UTS of the unblended AT tested on the same substrates decreased by a factor ranging from 5 to 20 as a result of weathering for the same duration.

The greatest increase in UTS occurred in weathered AT-based blends containing 7.5 and 15% of added component. The UTS of these blends increased by a factor of 2.2 to 2.5, and was not significantly influenced by the type of substrate.

The adhesive strength (AS) of the various AT-based blends (unweathered and weathered) mounted on the three different substrates varies as follows: AS of specimens on aluminum $\nless AS of specimens on California redwood < AS of specimens on Portland cement.$

The cohesion of the blend materials was better than that of the unblended AT, and increased with the concentration of the added component, both in unweathered and weathered samples. The best cohesion was observed in AT-PVA containing 33% of added component.

It is believed that improved mechanical properties of AT blends is the result of specific interactions between the molecules of the constituent polymers. Specific interactions, such as hydrogen bonding, dipole-dipole interactions, and charge transfer, have been postulated to explain the miscibility (partial or complete) of different polymers [10-13]. Thus, enhanced miscibility of partially miscible polymer and stronger interactions lead to better mechanical properties of the resulting blends than those of mixtures in which intermolecular forces are weaker. The improvement in the UTS is greatest in AT-(VAc-VC) copolymer blends, as the added components have greater specific interaction capabilities. For example, 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]. Smaller improvements in the mechanical properties of AT blends with PVA and PVAc

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

may be the result of weaker specific interactions between the molecules of the components.

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.

IR spectroscopy of the various AT-based blends did not reveal any difference in the chemical structure between the samples weathered outdoors and those kept in the laboratory (controls). This does not, however, preclude the occurrence of chemical reactions between the components of the blends during exposure, resulting in the formation of molecular structures not easily detected by IR spectroscopy [14].

CONCLUSIONS

Blending of AT with (VAc-VC) copolymer, PVA polymer, or PVAc polymer yields a heterogeneous mixture consisting of a continuous phase (the AT sealant) and a particulate phase (the added component). Generally, the blends have substantially better mechanical properties than the unblended AT sealant. Outdoor weathering induces a marked improvement in properties of the blends, but results in severe deterioration of those of the unblended AT.

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