

# Modification of the properties of some polyblends and reinforced polymers

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In the present paper we shall deal with: (a) Polyblends made of a polyurethane (PU) based on a polyether and diphenyl-methane-diisocyanate and an acrylic terpolymer (AT) system and, (b) glass fibre reinforced poly-(organosiloxane), (SR). We now report some differential scanning calorimetry (d.s.c.) measurements and the effect of thermal cycling exposure on these polymers. Stress-strain tests were done on an Instron universal testing machine. The modification of the properties on the polymers after blending and reinforcing respectively are discussed. At certain ratio PU to AT the behaviour of the polyblend to thermal cycling exposure is better than that of PU. The presence of the reinforcing agent in the silicone polymer significantly improves its mechanical and thermal properties.

**Keywords** Weatherability; differential scanning calorimetry; mechanical tests; miscibility; polyurethane; poly-(organo siloxane)

## INTRODUCTION

The weatherability of polymers may be modified tremendously by the use of polyblend techniques. In previous papers<sup>1-4</sup> we have reported the behaviour of some polyurethane (PU) polyblends with various vinyl polymers or with a silicone polymer. We also discussed the influence of some reinforcements and plasticizers there.

In this paper we deal with the study of the modification of the properties of polyblends made of PU and acrylic terpolymer (AT) and glass fibre reinforced SR during thermal cycling in view of their application as adhesives for building materials in the conditions of the Canadian climate characterized by very significant variations of the temperature along the year and during the day time.

The PU (Reichhold Chem. Ltd.), was made with a diolpolyether and diphenylmethanediisocyanate (MDI) in the ratio 1:1 by weight, and is usually used as an adhesive. The second partner of the polyblend was a one part AT sealant (Mulco) with a relatively good service temperature range ( $-30^{\circ}\text{C}$  to  $+30^{\circ}\text{C}$ ). The polyblends of these two polymers were made in the ratios of 2:1 and 1:1 (weight by weight) PU to the AT. For the reinforcing experiments we have used a silicone sealant (Dow Corning).

## EXPERIMENTAL

Infra-red spectra ( $200-4000\text{ cm}^{-1}$ ) were obtained with a Perkin Elmer Infrared spectrometer. Differential scanning calorimeter data were obtained on a DuPont 1090 thermal analyser with the d.s.c. module. The heating rate was  $20^{\circ}\text{C min}^{-1}$  and sample size was 15–20 mg.

### PU-AT blends

The polyblends were prepared with a view to study the influence of AT on the adhesive properties and weatherability of PU. AT was first mixed with the

polyether and in a second step this mixture was carefully blended with MDI. Homogeneous mixing is very important in order to obtain reproducible results. Specimens were prepared according to American Standards<sup>5,6</sup>. They were beads of PU or AT or of their blends cast between two prismatic substrates made either of Portland cement mortar, California redwood or aluminum. Before the application of the polymers the substrates were prepared as reported previously<sup>1-3</sup>. After curing for 24 h at room temperature, the specimens were subjected to two different conditions.

(a) The first series was maintained before testing 145 days at room temperature ( $22^{\circ}\text{C}$ ) and 20–50% r.h.

(b) At the same time, the second series was cycled between  $-26^{\circ}$  and  $+40^{\circ}\text{C}$  in a dark cooling chamber at a rate of about two cycles per 24 h. Each sample of this series was subjected to 283.5 cycles.

In all our experiments the differences between normal conditions and thermal cycling exposure were studied by changes in the tensile stress-strain relationship. The tests were done on an Instron model 1125 universal testing machine at  $22^{\circ}\text{C}$ .

### Fibre reinforced SR

Short glass fibres (10–15 mm length) were mixed with SR to establish their influence on the adhesive properties and thermal stability of the silicone polymer. The amounts of fibres were 2.5, 5.0 or 7.5% by weight. Specimens were prepared and tests were done as in the case of polyblends.

## RESULTS AND DISCUSSIONS

In the i.r. spectrum (KBr pellet), PU shows (Figure 1) a carbonyl absorption at  $1725\text{ cm}^{-1}$ , a N-H absorption at  $3300\text{ cm}^{-1}$ , methylene group absorptions at  $2970\text{ cm}^{-1}$  and in the  $1420-1430\text{ cm}^{-1}$  region, and a phenylic group absorption at  $1600\text{ cm}^{-1}$ .

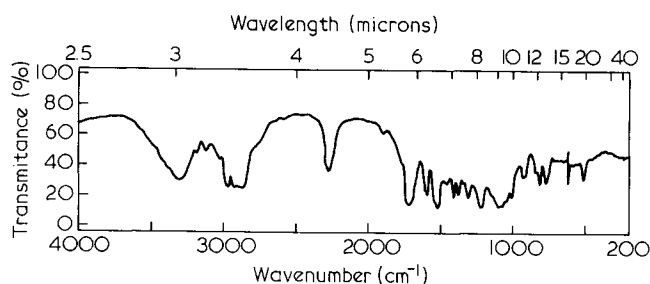


Figure 1 Infrared spectrum of PU

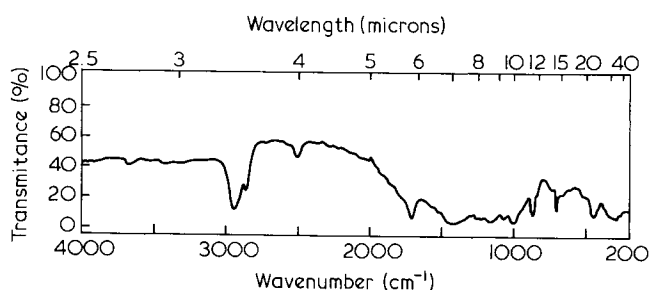


Figure 2 Infrared spectrum of AT

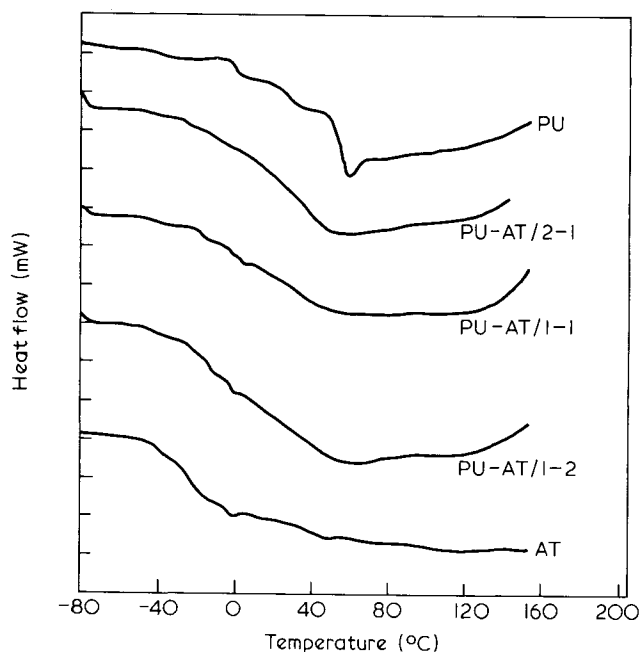


Figure 3 D.s.c. scan ( $-80^{\circ}$  to  $150^{\circ}\text{C}$ ) on PU, AT and some of their blends

The most characteristic absorptions in the AT spectrum (Figure 2) are: the carbonyl one for acrylates and methacrylates at  $1725\text{ cm}^{-1}$  and for  $-\text{C}-\text{O}-$  group at  $1155$  and  $1235\text{ cm}^{-1}$ .

In Figure 3 we compare d.s.c. curves of PU, AT and their blends. It is well known that the shape of d.s.c. curves is strongly influenced by factors such as: the ratio between the components (in the case of PU, the polyether-MDI ratio) molecular mass, additives, thermal history, etc.<sup>7-12</sup>

The d.s.c. curve of PU discussed in detail in a previous paper<sup>4</sup> shows three  $T_g$ 's at  $-40^{\circ}$ ,  $12^{\circ}$  and  $60^{\circ}\text{C}$ . The endothermic transition at about  $60^{\circ}\text{C}$  well marked in Figure 3 at  $58.1^{\circ}\text{C}$  is attributed to the disruption of

domains with limited short range order. AT with a more complicated microstructure is characterized by two endothermic transitions at  $-1^{\circ}\text{C}$  and  $50^{\circ}\text{C}$  and a less marked one at  $87^{\circ}\text{C}$ .

All of the PU-AT polyblends have one endotherm which shifts from  $53^{\circ}\text{C}$  for the polyblend PU-AT 2/1, to  $5.3^{\circ}\text{C}$  for the polyblend PU-AT 1/1 and to  $0.6^{\circ}\text{C}$  for the polyblend PU-AT 1/2. This may indicate a good miscibility of these two polar polymers. It is known<sup>13</sup> that a miscible polymer blend will exhibit a single glass transition between the  $T_g$ 's of the components, about as sharp as those of the components. Figure 4 shows the variation of  $T_g$  with different per cent of AT in the PU-AT polyblends.

The d.s.c. curves for unreinforced and reinforced SR are presented in Figure 5. We may observe that the presence of fibre glass shifts the endothermic peak of SR from  $-34.3^{\circ}$  to  $-32.1^{\circ}\text{C}$ , the latent heat for this transition decreases to  $16.9\text{ J g}^{-1}$  for the reinforced specimen from  $21.1\text{ J g}^{-1}$  for the pure specimen.

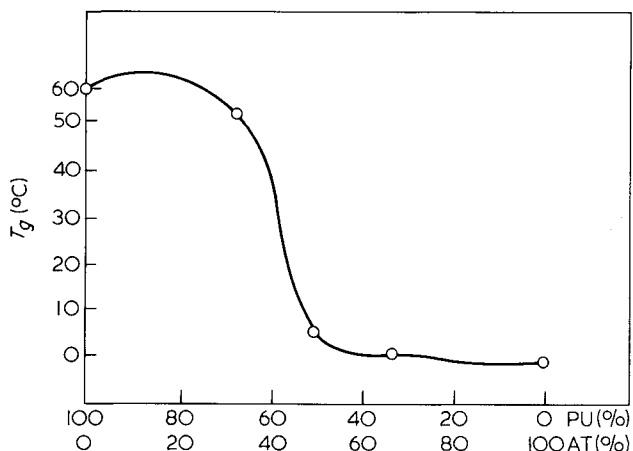


Figure 4 Variation of  $T_g$  for PU/AT blends

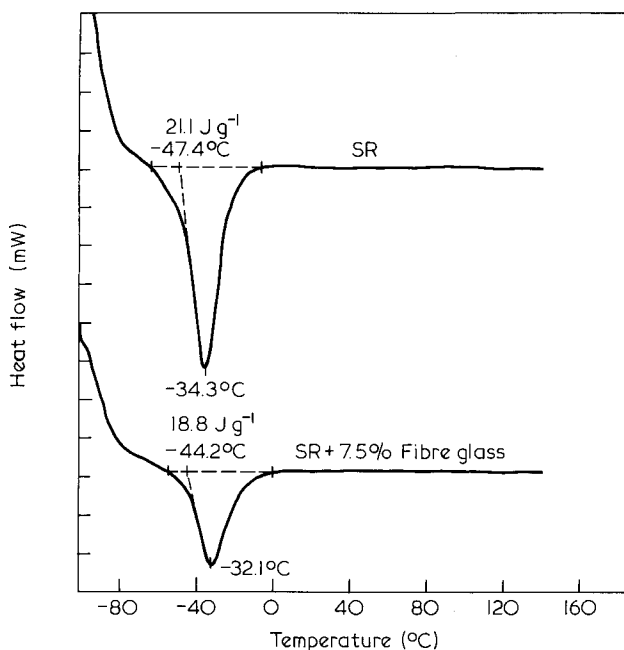


Figure 5 D.s.c. scan ( $-80^{\circ}$  to  $150^{\circ}\text{C}$ ) on SR and glass fibre reinforced SR

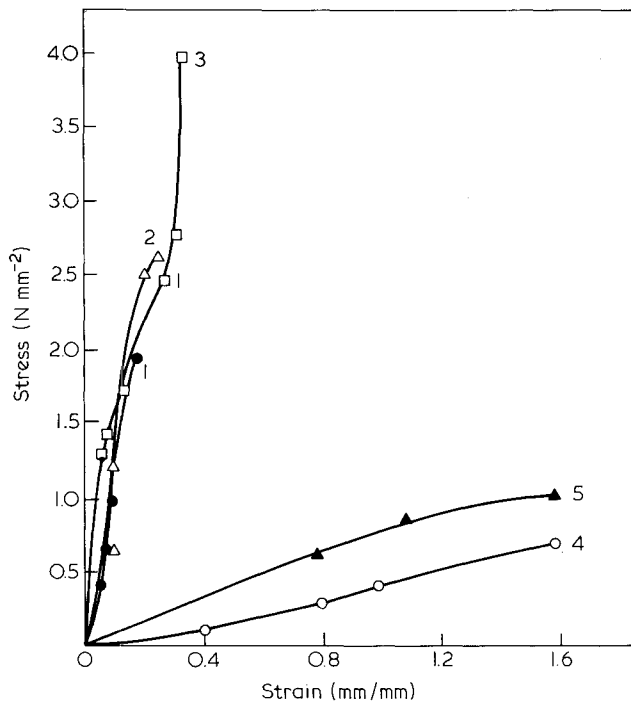


Figure 6 Stress-strain curves obtained with PU. Curve 1—Portland cement, series A; curve 2—California redwood, series A; curve 3—Aluminum, series A; curve 4—Portland cement, series B; curve 5—California redwood, series B

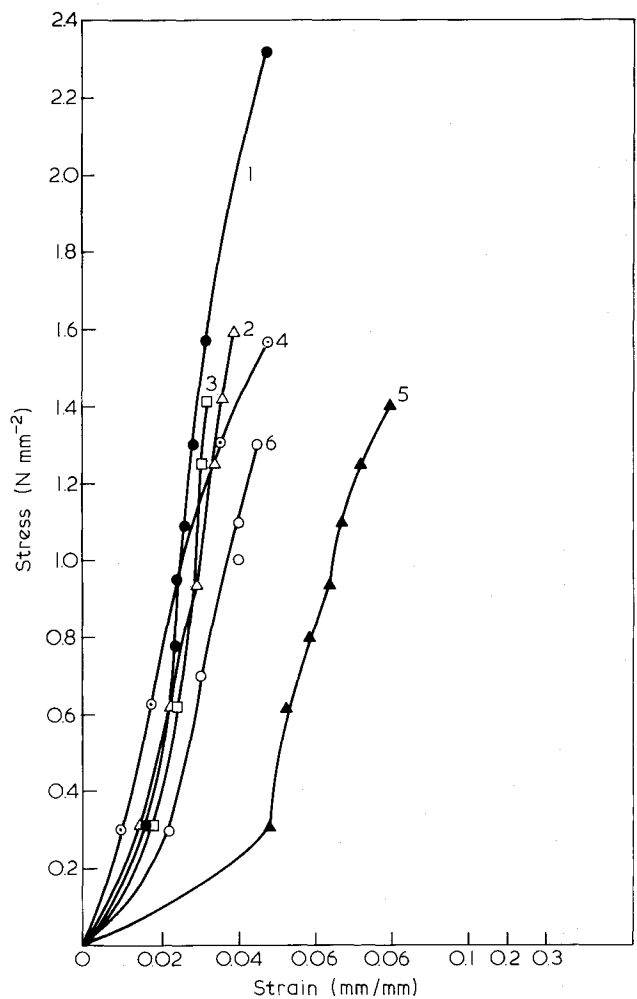


Figure 8 Stress-strain curves obtained with PU-AT, 2:1 (w/w) polyblend. Curve 1—Portland cement, series A; curve 2—California redwood, series A; curve 3—Aluminum, series A; curve 4—Portland cement, series B; curve 5—California redwood, series B; curve 6—Aluminum, series B

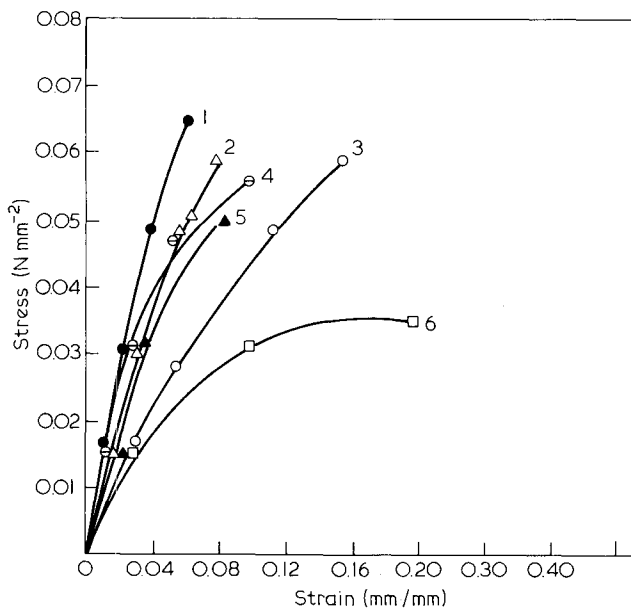


Figure 7 Stress-strain curves obtained with AT. Curve 1—Portland cement, series A; curve 2—California redwood, series A; curve 3—Aluminum, series A; curve 4—Portland cement, series B; curve 5—California redwood, series B; curve 6—Aluminum, series B

The tensile stress-strain curves averaged over 5-10 tests are presented in Figures 6-13.

*PU-AT blends*

The stress-strain curves obtained with pure PU are presented in Figure 6. Curves 1-3 belong to series A and we may see that the ultimate tensile strength ( $\sigma$ ) varies with the substrate used.

$$\sigma_{\text{aluminum}} > \sigma_{\text{wood}} > \sigma_{\text{cement mortar}}$$

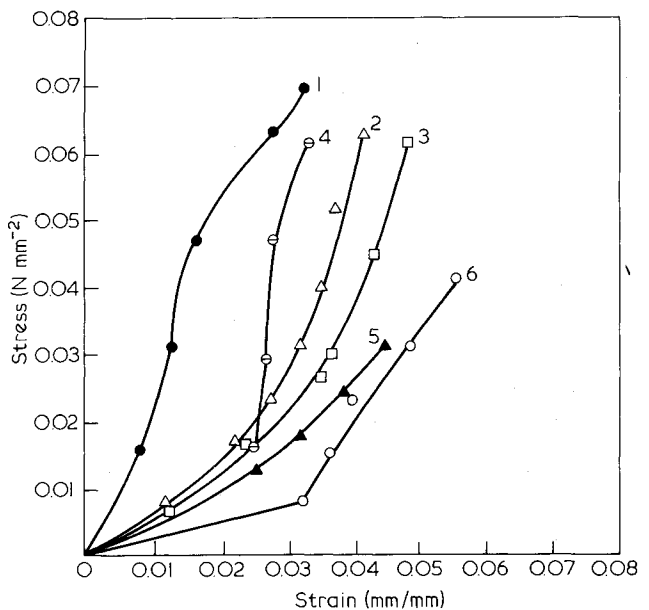


Figure 9 Stress-strain curves obtained with PU-AT 1:1 (w/w) polyblend. Curve 1—Portland cement, series A; curve 2—California redwood, series A; curve 3—Aluminum, series A; curve 4—Portland cement, series B; curve 5—California redwood, series B; curve 6—Aluminum, series B

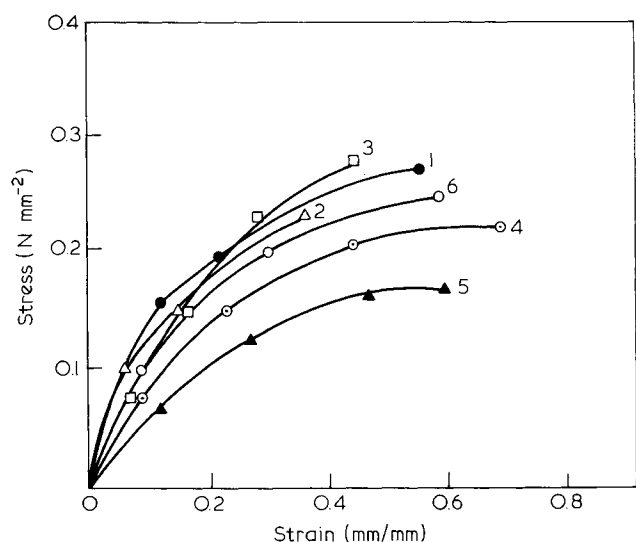


Figure 10 Stress-strain curves obtained with silicone polymer. Curve 1—Portland cement, series A; curve 2—California redwood, series A; curve 3—Aluminum, series A; curve 4—Portland cement, series B; curve 5—California redwood, series B; curve 6—Aluminum, series B

Curves 4 and 5 show a dramatic decrease of the ultimate tensile strength and an important increase of the maximum extension after thermal cycling exposure. As a consequence of the temperature variation (thermal shocks) during the weathering, a cryolysis process similar to that discussed before<sup>2,3</sup> occurs which changes the thermal and mechanical properties of PU. The AT shows an initial smaller ultimate tensile strength and higher strain than those of PU, as we may observe in Figure 7. After the thermal cycling exposure, there are some modifications in both these properties which may also be obtained by a degradation (cryolysis) process caused by the temperature variations.

The data obtained with the PU-AT polyblend at a ratio of the components 2/1 (w/w) are presented in Figure 8. The presence of AT in the PU adhesive improves the adhesion on Portland cement mortar and decreases the ultimate strength with aluminum and California redwood supports. In general, this polyblend shows a better strain, i.e. a better elasticity than PU. The elasticity is better after thermal cycling exposure. It seems that PU is more sensitive to thermal shock than AT. If we compare the microstructures of these polymers, the amide and urethane groups of PU are susceptible to hydrolytic or cryolytic attack. The acrylics, with a carbon backbone have better chemical resistance. When the amount of AT in the polyblend is increased up to a ratio of 1/1 (w/w) AT to PU, ultimate tensile strength decreases for both series (A and B) of specimens (Figure 9); the strains are close to those obtained with less AT.

#### Fibre reinforced silicone polymer

For the silicone polymer used with the same substrates, we observed (Figure 10) after thermal cycling exposure a decrease of about 20–22% in the ultimate tensile strength and some increase in the strain. However, when the silicone polymer is reinforced with 2.5% fibreglass, the strain is essentially unchanged, while the tensile stress increases dramatically: 260% for California redwood; 210% for aluminum; and 165% for Portland cement mortar (Figure 11). Thermal cycling exposure had no

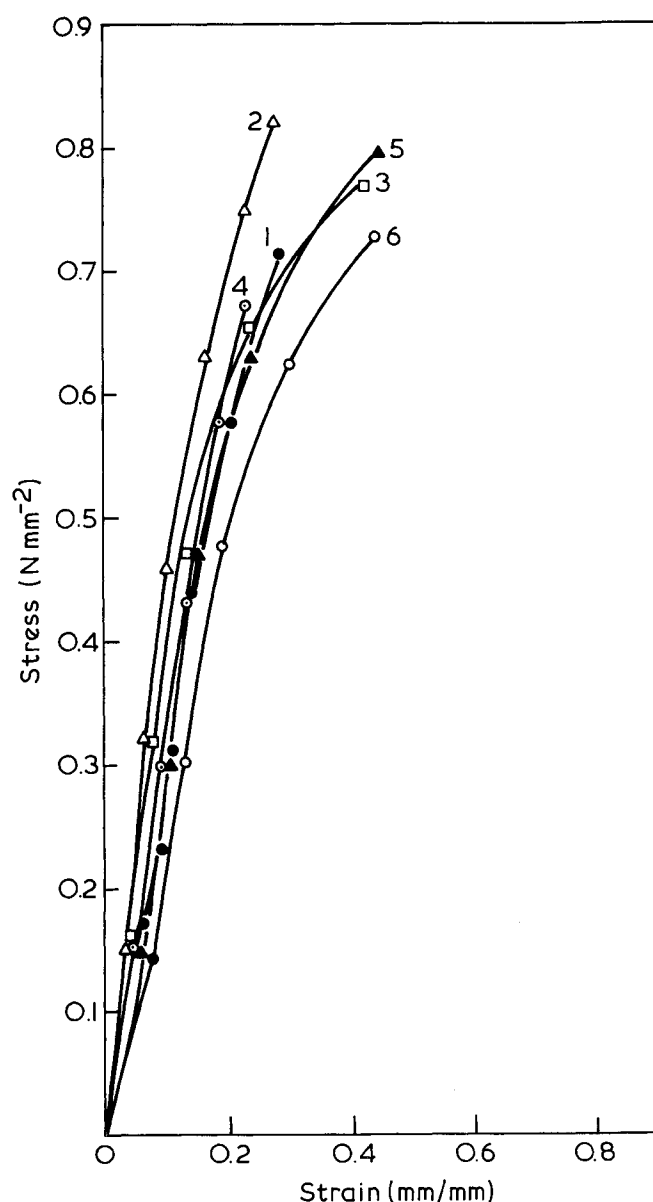


Figure 11 Stress-strain curves obtained with silicone polymer reinforced with 2.5% fibreglass. Curve 1—Portland cement, series A; curve 2—California redwood, series A; curve 3—Aluminum series A; curve 4—Portland cement, series B; curve 5—California redwood, series B; curve 6—Aluminum, series B

sensible effect on this improvement.

At 5% fibreglass the strain of the silicone polymer is affected and the specimens become more rigid. At this content the substrate effect is only significant for California redwood. The ultimate tensile strength of cycled wood specimens (series B) decreases 25% in comparison with those of uncycled specimens (series A) with the same amount of reinforcing agent and 33% in comparison with those with 2.5% fibreglass (Figure 12).

The rigidity of this reinforced polymer increases when the amount of fibreglass is increased to 7.5%; this is reflected by the modification of the strain (Figure 13). The best behaviour with regard to the ultimate tensile strength was found for aluminum. This decrease for the two other supports (in both series A and B) may be explained by a decrease of adhesion between the polymer and these materials because of the presence of the fibres and also because of some possible light deterioration of the supports surfaces.

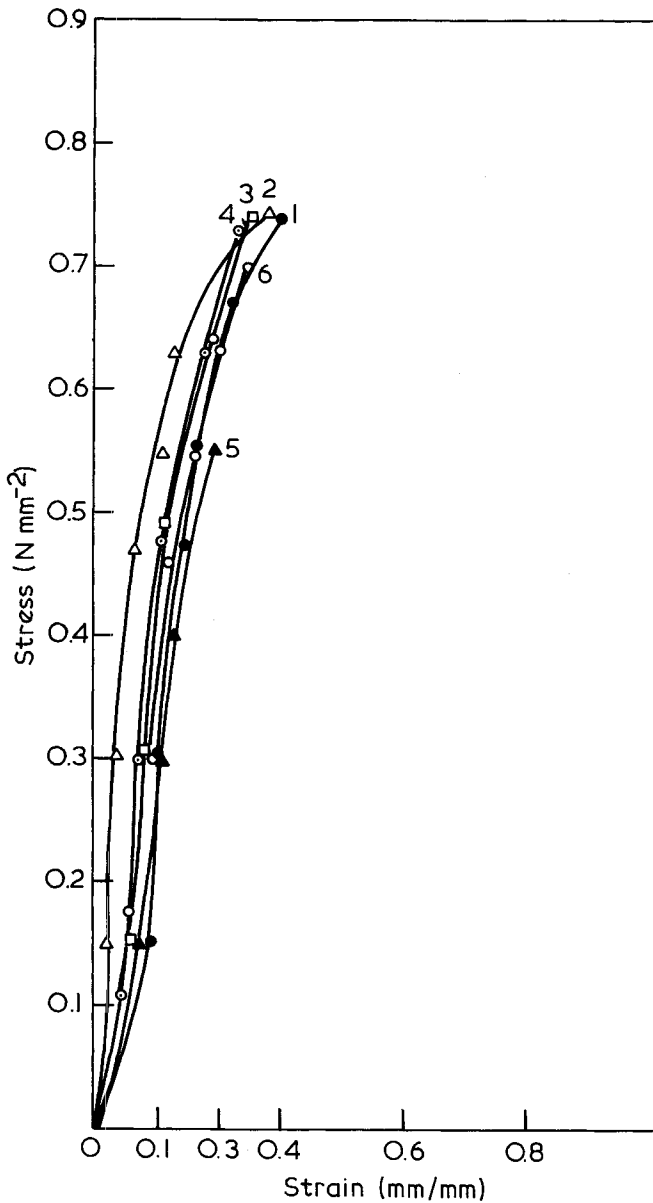


Figure 12 Stress-strain curves obtained with silicone polymer reinforced with 5% fibreglass. Curve 1—Portland cement, series A; curve 2—California redwood, series A; curve 3—Aluminum, series A; curve 4—Portland cement, series B; curve 5—California redwood, series B; curve 6—Aluminum series B

### CONCLUSIONS

D.s.c. data indicate a good miscibility of PU and AT and an insignificant influence of the fibreglass on the main endothermic transition of the silicone polymer.

The polyblends made of PU and AT show a higher strain than that of PU, and a lower tensile strength. At a 2/1 ratio PU to AT the resistance of this polyblend to thermal cycling exposure is better than that of PU. This may be explained by a lower sensitivity of AT to hydrolytic and cryolytic attack. This mixture also has a better adhesion to Portland cement mortar.

The presence of fibreglass in the silicone polymer improves the rigidity and the tensile strength of the polymer and its resistance to thermal cycling exposure significantly. The best results were obtained at an amount of glassfibres between 2.5 and 5%.

The results show that in regions with large variations of the temperature along the year, adhesives made of

mixtures of PU and AT may behave better than PU or AT alone; the same conclusion is valuable for using of reinforced SR instead of unreinforced SR.

The study will continue with the research of the influence of other environmental factors (light, moisture, etc.) and of other ways for the improvement of the properties of these polymers in view to be more suitable for applications in the Canadian climate.

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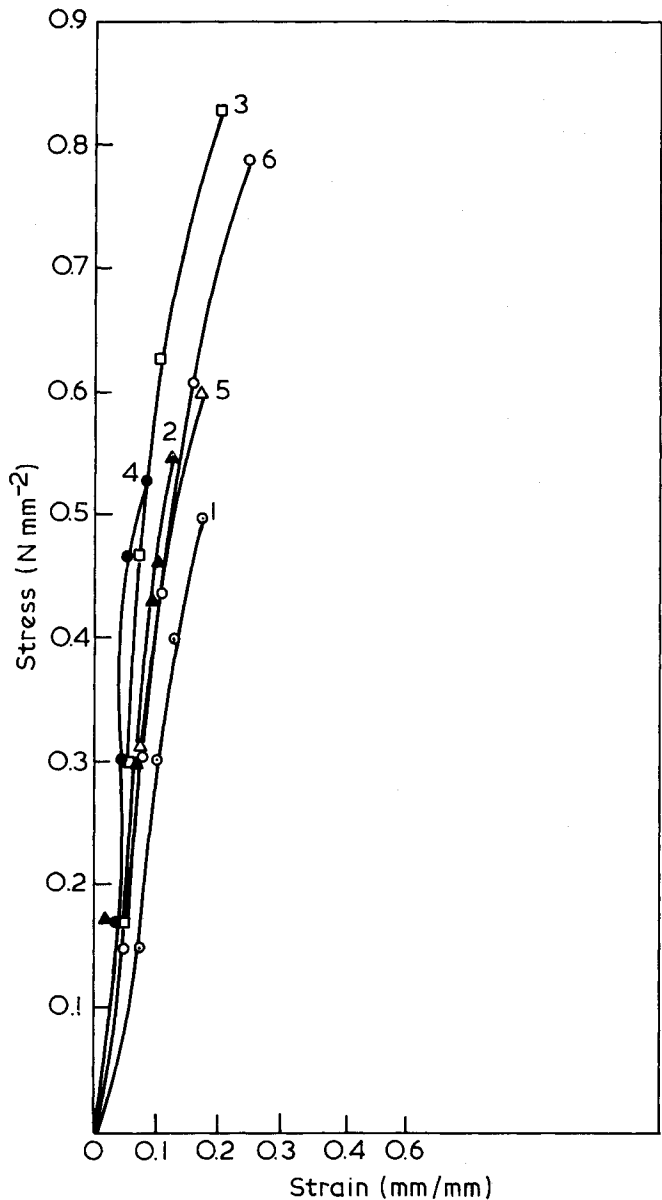


Figure 13 Stress-strain curves obtained with silicone polymer reinforced with 7.5% fibreglass. Curve 1—Portland cement, series A; curve 2—California redwood, series A; curve 3—Aluminum, series A; curve 4—Portland cement, series B; curve 5—California redwood, series B; curve 6—Aluminum, series B

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