Modification of the Properties of Polyurethane by Blending, Reinforcing, or Plasticizing*

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Synopsis

In order to study modifications of the properties of a polyurethane adhesive, we have prepared polyblends with a siliconic polymer and mixtures with some fiber reinforcing agents or with plasticizers. Stress–strain measurements were done on the samples using an Instron Model 1125 Universal testing machine. For comparison, some specimens were kept at normal room conditions, while others were cycled in an artifical weathering chamber. Results are discussed and conclusions drawn.

INTRODUCTION

Some of the main properties of polymeric systems such as the bond rotational energy and the chain flexibility can be altered by changing the environments of the macromolecules by incorporation of different types of additives.

Most polymers are incompatible with each other, so that blending two polymers usually leads to a class of materials whose properties are due to the presence of two phases. While high compatibility is desirable for ease of blending, some degree of incompatibility often leads to useful properties. Sometimes synergistic effects occur, and, in these situations, one or more properties are superior to those of any of the components of the polyblend.

More often than not, polymers do not adhere to each other well, and poor mechanical properties of mixtures result.

A few polyblends have been commercialized, but this does not approach the very large potential for new materials through polyblending.[1,2]

There are often reasons to blend two polymers, even though the two do not adhere adequately, so that methods for improving the adherance are of great interest.[3]

By the careful formulation of two or more polymers, it is often possible to obtain more desirable properties than any of the components alone, in the end product. This is a great advantage in formulations for specific environments, where perhaps one of the polymers alone would not serve the purpose.

Specific properties such as mechanical, electrical, or thermal properties may be modified to great advantage. The weatherability of one of the polymers may be improved by the use of a polyblend. Such characteristics as low temperature flexibility may be altered, as well as high temperature thermal resistance.[4]

Because plasticizers act at the molecular level, the primary requirement is that polymer and plasticizer should be mutually soluble. Using plasticizers, we have to take into account the fact that these additives or other compounding ingredients may reduce the stability of compounds compared to the neat polymer.[5]

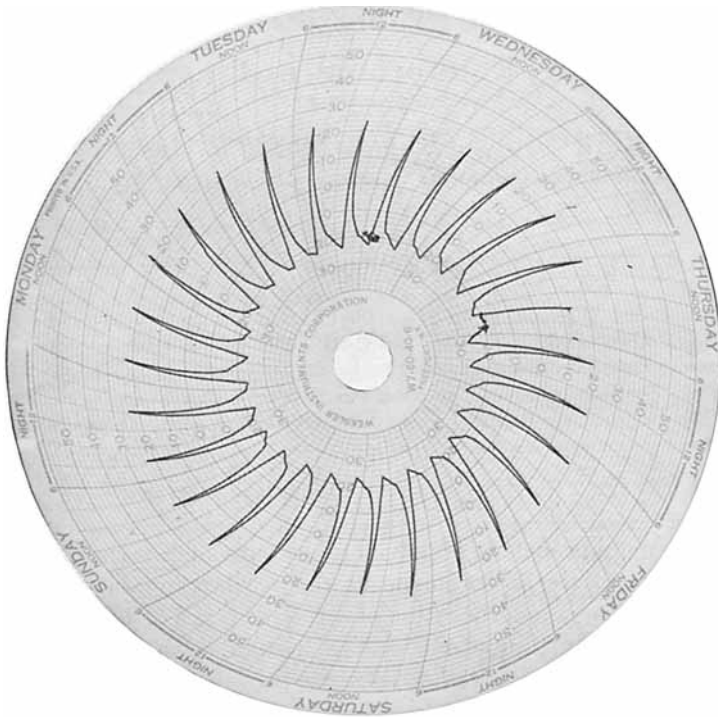* Paper presented at the 21st Canadian High Polymer Forum, Kingston, Ontario, 12–14 August 1981.

Fig. 1. Graph of the temperature variation during 1 week of accelerated weathering.

EXPERIMENTAL

In previous papers,[6,7] we dealt with polyblends of polyurethane (PU) and different vinyl polymers and copolymers. The observed modifications of the properties after aging the polyblends at normal room conditions, outside and in an artificial weathering chamber, can be attributed to a decrease of the molecular mass of the polymers; at low temperatures the alterations are determined by a cryolysis process.
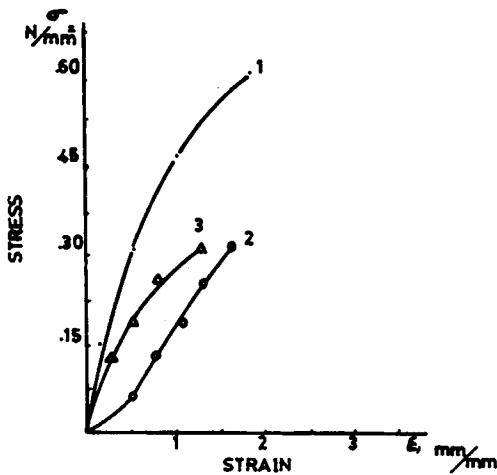

Fig. 2. Stress–strain curves of series A specimens made of silicone; curve 1—California redwood; curve 2—Portland cement mortar; curve 3—aluminum.
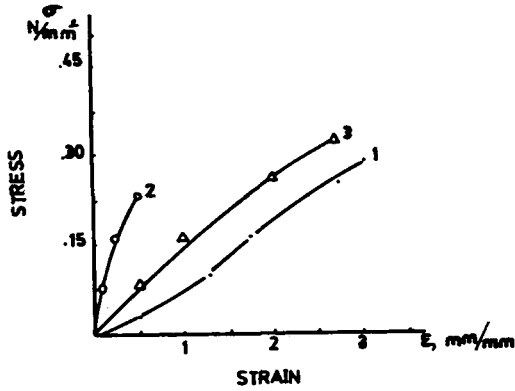
Fig. 3. Stress–strain curves of series B specimens made of silicone; curve 1—California redwood; curve 2—Portland cement mortar; curve 3—aluminum.

In this paper we deal with (1) polyblends made of polyurethane–silicone polymer system; (2) fiber-reinforced polyurethane; (3) plasticized polyurethane.
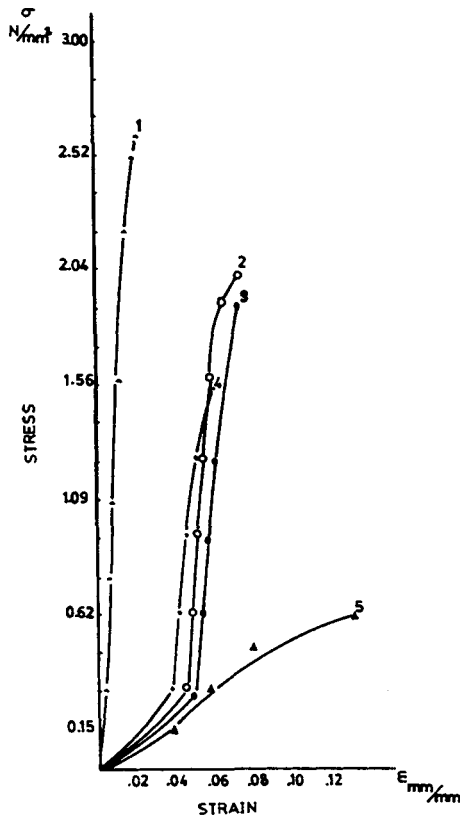

Fig. 4. Stress–strain curves of specimens made of PU—silicone polyblends at different ratios; substrate: California redwood. Curve 1—control specimen, PU, series A; curve 2—PU, series B; curve 3—PU—silicone, ratio 2:1, series B; curve 4—PU—silicone ratio 1:1, series B; curve 5—PU—silicone, ratio 1:2 series B.
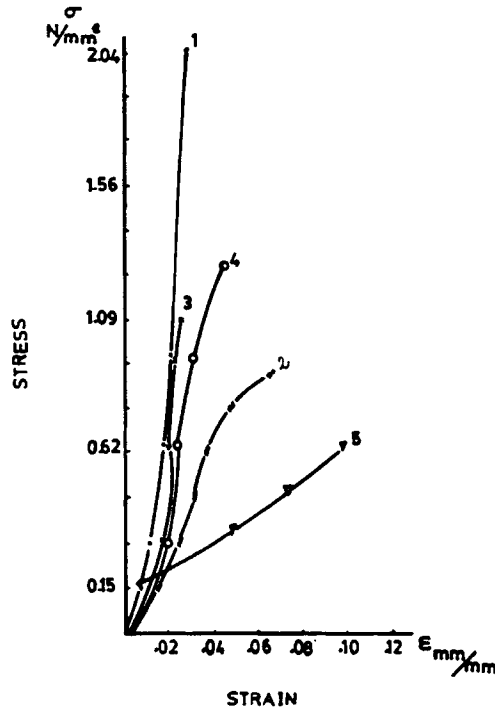
Fig. 5. Stress–strain curves of specimens made of PU—silicone polyblends at different ratios; substrate: Portland cement mortar. Curve 1—control specimen, PU, series A; curve 2—PU series B; curve 3—PU—silicone, ratio 2:1, series B; curve 4—PU—silicone, ratio 1:1, series B; curve 5—PU—silicone, ratio 1:2 series B.

In all cases the same polyurethane (Reichhold Chem., Ltd.) was used; it was made with a diolpolyether and diphenylmethanediisocyanate (MDI) in the ratio 1:1 by weight, and is usually used as an adhesive.

Polyurethane–Silicone Blends

The second component of the polyblend was a weatherproofing poly(organosiloxane) sealant (Silpruf, General Electric Co.) with good resistance to degradation caused by ultraviolet light, serviceability through a wide temperature range, and reliability.

The polyblends were prepared with a view to improving the flexibility and weatherability of PU. They were prepared with these two polymers at the weight to weight ratios of 2:1, 1:1, and 1:2. The silicone polymer 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 ASTM C-719-72 and C-736-72. They were a 50 × 12.5 × 12.5 mm bead of PU, silicone, or their polyblend cast between two prismoidal substrates made either of aluminum, Portland cement mortar, or California redwood. Before the application of the polymeric system the substrate was prepared as reported previously.[6,7]

After curing 24 h at room temperature the specimens were subjected to two different conditions:
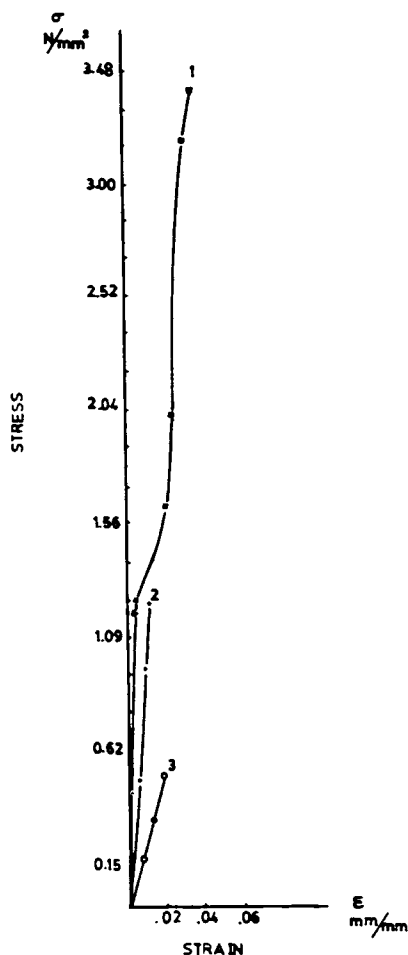
Fig. 6. Stress–strain curves of specimens made of PU—silicone polyblends at different ratios, substrate: aluminum. ·Curve 1—control specimen PU, series A; curve 2—PU—silicone, ratio 1:1, series B; curve 3—PU—silicone, ratio 1:2, series B.

(A) The first series was maintained before testing 5 weeks at room temperature (22°C) and 20–50% relative humidity (RH).

(B) At the same time the second series was cycled between −23°C and +23°C in a dark cooling chamber at a rate of 3.87 cycles/24 h. The temperature variation during 1 week of accelerated weathering is shown in Figure 1. Each sample of this series was subjected to 139.5 cycles.

In all our experiments the effects of normal conditions or of the accelerated weathering were established by changes in the tensile stress–strain relationship. The tests were done on a Instron model 1125 testing machine at 22°C, 50 mm/min chart speed, and 10 mm/min cross head speed. The tensile stress–strain diagram describes the amount of force needed to stretch a sample to varying elongations. It can be used as a relative measurement of stiffness.
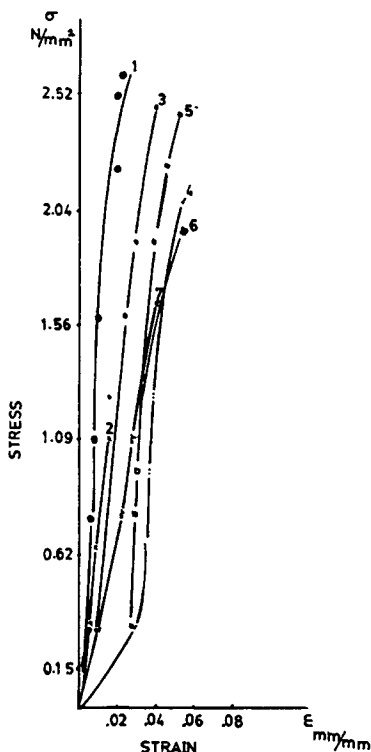
Fig. 7. Stress–strain curves of specimens made of fiber-reinforced PU; substrate: California redwood. Curve 1—control specimen unreinforced PU; series A; curve 2—unreinforced PU, series B (156 cycles between −30°C and + 30°C); curve 3—glass-fiber-reinforced PU, 2.43% fibers, series A; curve 4—glass-fiber-reinforced PU, 4.76% fibers, series A; curve 5—glass-fiber-reinforced PU, 2.43% fibers series B; curve 6—glass-fiber-reinforced PU, 4.76% fibers, series B; curve 7—cellulose-fiber-reinforced PU, 2.43% fibers, series A.

Fiber-Reinforced Polyurethane

Glass fibers, or in some cases cellulosic fibers, were mixed with the polyurethane system to establish their influence on the mechanical properties of these materials.

The amounts of fibers were 2.43% or 4.76% for glass-fiber-reinforced specimens and 2.43% for cellulose-fiber-reinforced samples. No coupling agent was used.

Specimens were prepared and tests were done as in the case of polyblends.

Plasticized Polyurethane

Dibuthylphthalate (DBP) was used as a plasticizer for PU in different amounts up to 30%; DBP was chosen because of its solubility parameter $\delta = 9.3$ (cal/cm^3)$^{1/2}$, which is very close to that of polyurethane $\delta = 10$ (cal/cm^3)$^{1/2}$.[8]

The plasticizer was first mixed with the polyether, then blended with MDI, and poured between the substrates. In this particular case no samples were cycled in the artificial weather chamber. All specimens were kept for 5 weeks at 22°C and 20–50% RH.
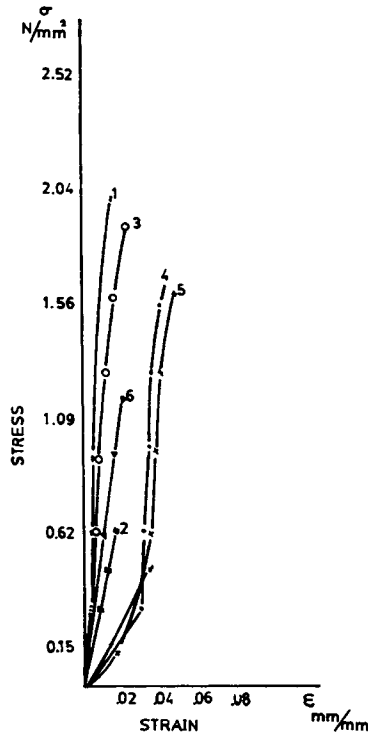
Fig. 8. Stress–strain curves of specimens made of fiber-reinforced PU; substrate: Portland cement mortar. Curve 1—control specimen, unreinforced PU, series A; curve 2—unreinforced PU, series B (156 cycles between −30°C and + 30°C); curve 3—glass-fiber-reinforced PU, 2.43% fibers, series A; curve 4—glass-fiber-reinforced PU, 4.76% fibers, series A; curve 5—glass-fiber-reinforced, 4.76% fibers, series B; curve 6—cellulose-fiber-reinforced PU, 2.43% fibers, series A.

RESULTS AND DISCUSSIONS

Tensile stress–strain diagrams averaged for 5–10 successful tests are presented in the Figures 2–14. Because of substrate failure (especially Portland cement mortar) in the Instron, many more specimens were cast than are shown in the figures.

Polyurethane–Silicone Blends

The stress–strain curves obtained in the case of specimens of series A prepared with the silicone polymer only are shown in Figure 2; as may be observed, this polymer is characterized by a high strain and tensile stress.

The best adhesion of this sealant was obtained in the case of California redwood as substrate.

The frequent thermal variations (thermal shock) received by this polymer during the artificial weathering had little influence on the mechanical properties, as shown in Figure 3. The very good thermal behavior of this group of polymers at high and low temperature is well known. The changes recorded may be a result of the weakness of the intermolecular bonds. This favors microbrownian movements, which increase the flexibility of the chains.

Silicones harden and become brittle when progressively cooled, but generally remain more flexible to lower temperatures than organic elastomers.
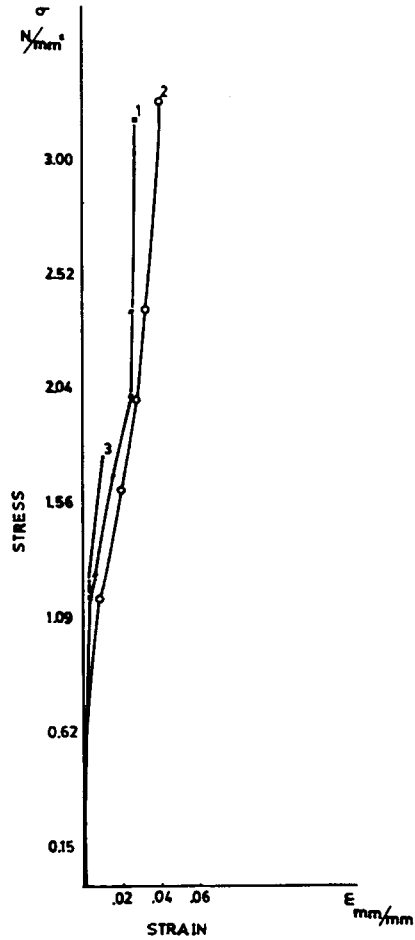
Fig. 9. Stress–strain curves of specimens made of fiber-reinforced PU; substrate: aluminum. Curve 1—control specimen, unreinforced PU; curve 2—glass-fiber-reinforced PU, 4.76% fibers, series A; Curve 3—cellulose-fiber-reinforced PU, 2.43% fibers, series A.

The behavior of PU—silicone blends in series A and B conditions is shown in Figures 4–6. During the mixing of the polyurethane components with silicone it is possible to form organ–silicone–polyurethane block copolymers of the following microstructure:

$$-[-O-(CH_2)_m-OCH_2-(\underset{\underset{R'}{|}}{\overset{\overset{R'}{|}}{Si}}-O)_n-CH_2O-(-CH_2-)_m-O-CO-NH-R-NH-CO-]_p-$$
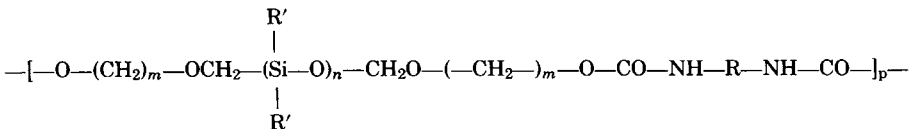
where R is an aliphatic group; R' is an alkyl or phenyl group. This chain is more flexible than PU and more sensitive to thermal shock than silicone.

Polyblends with certain amounts of silicone were used for bonding various materials such as: California redwood, Portland cement mortar, and aluminum.

For California redwood substrates the PU—silicone blend stress–strain curves presented in Figure 4 were obtained. It may be seen from these data that, as
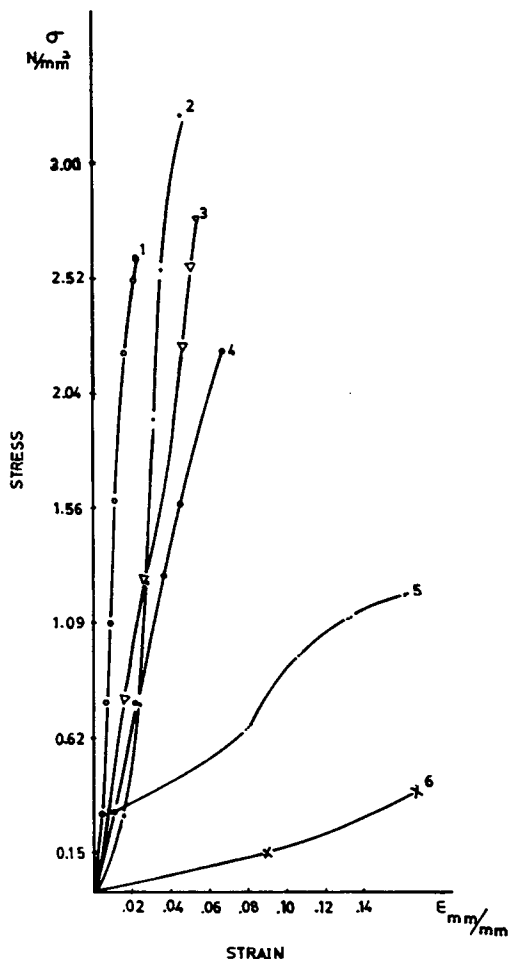
Fig. 10. Stress–strain curves of specimens made of DBP-plasticized PU; substrate: California redwood.   Curve 1—control specimen, unplasticized PU, series A; curve 2—PU + 4.76% DOP, series A; curve 3—PU + 9.09% DBP, series A; curve 4—PU + 13.04% DBP series A; curve 5—PU + 20% DBP, series A; curve 6—PU + 30% DBP series A.

a consequence of the temperature variation during the artificial weathering, a cryolysis process similar to that discussed before[7] occurs, which influences both the stress and the strain.   It may be also observed that an increase of the amount of silicone causes a decrease of the tensile stress of the polyblends and an increase of their strain.   Similar comments may be made in the case of other supports: Portland cement mortar (Fig. 5) and aluminum (Fig. 6).

The stress decreases dramatically in the case of aluminum substrates.   The adhesion of PU towards aluminum decreases with an increase of the quantity of silicone.

Considering the microstructure of these two polymers, there was no reason to consider them compatible or to expect spectacular improvements of all the properties.
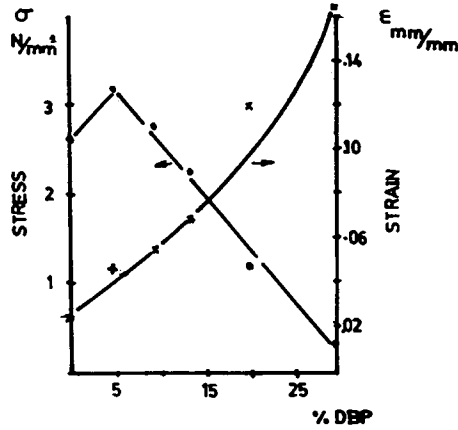
Fig. 11. Tensile stress and strain variation of DBP-plasticized PU depending on the amount of plasticizer; substrate: California redwood.

Fiber-Reinforced Polyurethane

For this series of experiments, we used glass or cellulose fibers with a length distribution in the range of 10–15 mm.   Some results are presented in Figure 7 for California redwood and Figure 8 for Portland cement mortar substrates.

At 2.43% glass fibers, the tensile stress is similar to that of unreinforced PU, but the strain is a little higher.   When we rise the amount of glass fibers to 4.76%, the tensile stress decreases to 19% of that of neat PU, but the strain is better.   As may be seen from curve 7 (Fig. 7), in the case of cellulose fibers the stress decreases dramatically because of their mechanical resistance, which is smaller than that of glass fibers.

After artificial weathering, the properties of glass-fiber-reinforced PU are
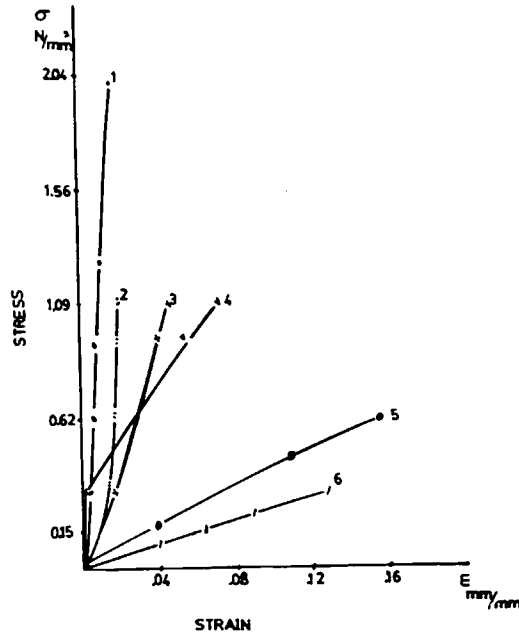

Fig. 12. Stress–strain curves of specimens made of DBP-plasticized PU; substrate Portland cement mortar;   Curve 1—control specimen, unplasticized PU, series A; curve 2—PU + 4.76% DOP, series A; curve 3—PU + 9.09% DBP, series A; curve 4—PU + 13.04% DBP series A; curve 5—PU + 20% DBP, series A; curve 6—PU + 30% DBP series A.
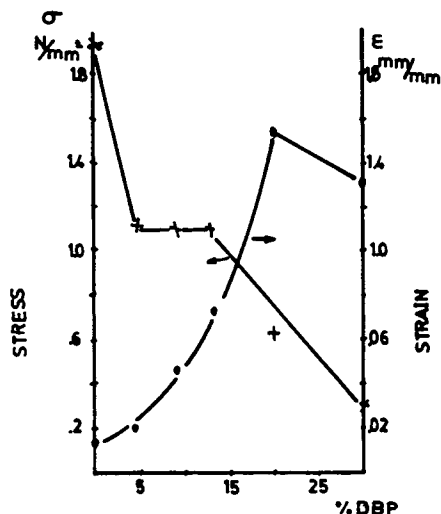
Fig. 13. Tensile stress and strain variation of DBP-plasticized PU depending on the amount of plasticizer; substrate: Portland cement mortar.

almost unchanged, in contrast to the stress of unreinforced PU specimens, which decreases by more than 50%.

Similar results were obtained in the case of specimens made with Portland cement mortar as the substrate (Fig. 8).

The decrease of the tensile stress of the PU unreinforced samples, artificially aged, was greater than 60%.

From Figure 9 we may observe that no improvement of the PU adhesive mixed with glass or cellulose fibers was obtained when used to join aluminum substrates.

Plasticized Polyurethane

Polyurethane—DBP systems were used with all the above substrates.

With wood (Figs. 10 and 11) we obtain a slight increase of the stress at low amounts of DBP (up to 9%); at higher quantities the tensile stress decreases, as was expected the strain increases with the amount of DBP.

The tests made with Portland cement mortar substrates (Figs. 12 and 13) show lower tensile stresses in the case of plasticized PU, and a continuous increase of the strain, similar to the wood samples, as the content of DOP is raised. For the range between 4% and 13% DOP almost the same tensile stresses were obtained. Similar results are obtained with aluminum (Fig. 14). During the experiments no DBP exudation was observed.

CONCLUSIONS

(1) The elastic properties of PU—silicone polyblends increase and the tensile stress decreases with the amount of silicone.

(2) The presence of glass fibers in an amount of about 4% improves substantially the stability of reinforced PU during artificial weathering. No improvement was observed in the case of cellulosic fibers.

(3) In small quantities, DOP may improve PU adhesion to wood. Increasing the amount of DOP in PU improves the elastic properties of the system.

(4) The deterioration of the properties during artificial weathering may be explained by the decrease of the molecular mass as a result of a cryolitic process which affects the PU partner especially.
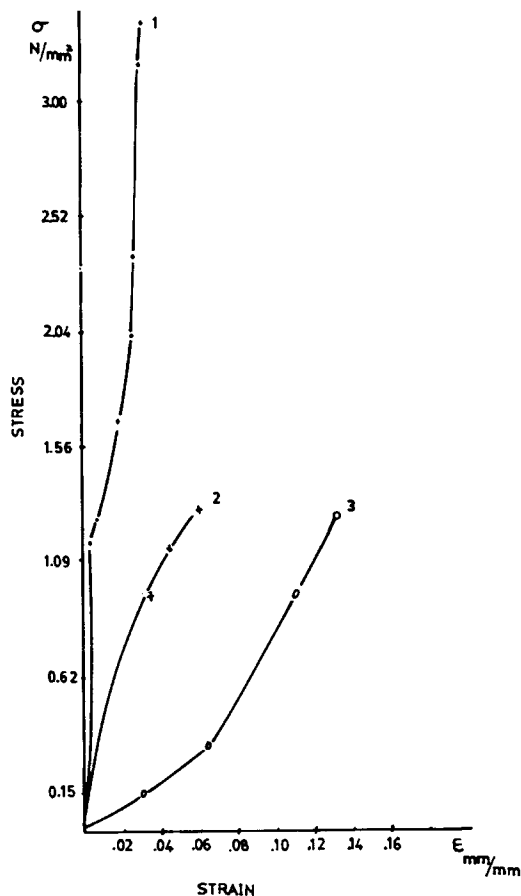
Fig. 14. Stress–strain curves of specimens made of DBP-plasticized PU; substrate: aluminum. Curve 1—unplasticized PU, series A; curve 2—PU + 13.04% DBP, series A; curve 3—PU + 20% DBP, series A.

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