

Natural and Accelerated Weathering of Some Polyblends

D. FELDMAN, *Centre for Building Studies, Engineering Faculty, Concordia University, Montréal, Québec, Canada*

Synopsis

A weathering study has been carried out on a polyurethane elastomeric adhesive and its polyblends with the following vinyl polymers: poly(vinyl chloride), poly(vinyl alcohol), poly(vinyl acetate), and vinyl acetate–vinyl chloride copolymer. Stress–strain measurements were done on an Instron model 1125 testing machine after aging at normal room conditions, outside, and in an artificial weathering chamber. The observed modifications of the mechanical properties can be attributed to a decrease of the molecular weight of the polymers involved during the cryolysis process; this process is less significant for natural weathering than for artificial weathering. Results are discussed and conclusions drawn.

INTRODUCTION

Interest has recently been shown in incompatible polymer blends. It is expected that, if a stable mixed morphology can be maintained during the thermoplastic molding cycle, such blends could show interesting properties as well as possible lower prices. Since mixtures of polymers are usually incompatible and show phase separation, special preparation methods have to be used to obtain useful polyblends.¹

Successful blends of polyurethanes with different polymers have been known for a few years. Frisch et al.² observed single transitions from calorimetric measurements for interpenetrating network (IPN) combinations of polyurethanes and polymers such as polyester, epoxy, and polyacrylate. Electron microscopy on the polyurethane–polyacrylate IPN did not reveal any evidence of phase separation. A maximum in tensile strength at intermediate concentrations for these IPNs was believed to be the result of a high level of network interpretation.

Peterson et al.³ reported miscibility between nitrocellulose and polyester-based polyurethane.

Many studies have been made on polyurethane–poly(vinyl chloride) blends in order to verify either technological or theoretical aspects.^{4–9} Poly(vinyl chloride) blends are particularly attractive, since they combine the toughness and abrasion resistance of the polyurethane with the stiffness and high modulus of poly(vinyl chloride) and also economize on expensive polyurethane.¹

No report has been found which deals with polyurethane blends with other vinyl polymers.

With regard to the durability of the macromolecular compounds, it is well known that a large number of degradative agencies may affect them. In their applications, three are of particular importance: oxidation, heat, and light. Only a few papers deal with polymer behavior at low temperatures.^{10–13} The degra-

dation of polymers generally involves both chemical and physical processes, with the chemical reactions usually preceding the physical processes.¹⁴ While oxidative and photo effects follow a well-defined pattern in the sense that they are all closely associated with the reactivity of particular atoms and particles, thermal degradation is concerned with a wide variety of reaction types.¹⁵ As a rule, polymers that contain hydrogen are sensitive to oxidative degradation at high temperatures and during outdoor exposure.¹⁶ Studies of serviceability involve such questions as whether a given polymer (plastic, adhesive, sealant, etc.) is likely to be stable in use and to what extent the presence of additives (including another polymer) affects the weather resistance of the product.

When the changes in physical properties which occur during outdoor exposure are considered, the problem of correlation with accelerated weathering tests becomes even more complex. Not only is it necessary to take into account humidity, temperature, radiation, intensity, and wavelength, but the size and shape of the sample and the conditions under which it was prepared must also be considered.¹⁷ For these purposes, two types of weathering tests—natural weathering tests and accelerated weathering tests—have been evolved.

The present report deals with such types of tests made on polyblends of a

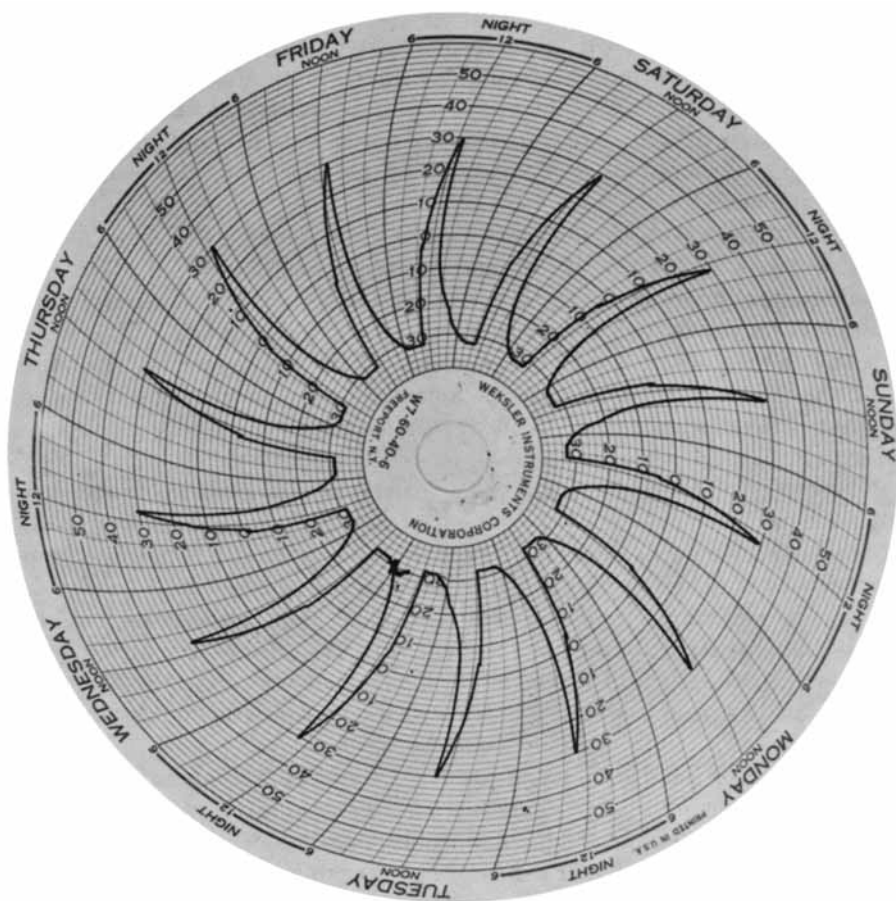


Fig. 1. Graph of the temperature variation during 1 week of accelerated weathering.

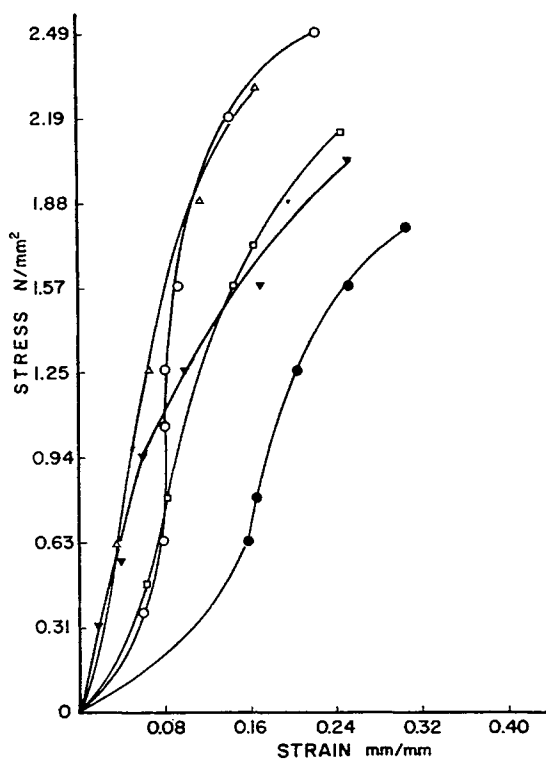


Fig. 2. Stress-strain curves of series A specimens: California redwood substrates. (○) PU, (Δ) PU + PVC, (□) PU + PVA, (●) PU + VAc-VC copolymer, (▼) PU + PVAc. Testing temperature = 22°C, crosshead speed = 10 mm/min, chart drive = 20 mm/min.

polyurethane adhesive and some vinyl polymers. The best known polyurethanes result from coupling a hydroxyl-terminated polyester or polyether with a polyfunctional isocyanate. Ester links are known to be susceptible to acid- and base-catalyzed hydrolysis, whereas ether links are not.

Athey¹⁸ studied the effects of the humidity on both ester- and ether-based polyurethanes. The polyether-based urethane shows no change in tensile strength after 18 months at 100% relative humidity and 15°C. The polyester-based polymer, on the other hand, loses 90% of the tensile strength. At 50°C in water, the polyether material retains 70% of its tensile strength after six months, whereas the polyester system loses all tensile strength.

EXPERIMENTAL

In previous reports,^{10,11} the behavior of some modified polyurethane adhesives at low temperatures was studied. An extensive knowledge of material property variations with weathering is especially important for engineering materials when subject to Canadian climatic conditions. In the present article, the natural and accelerated weathering of some polyurethane blends with vinyl polymers, such as poly(vinyl chloride), poly(vinyl acetate), poly(vinyl alcohol), and vinyl acetate-vinyl chloride copolymer, was investigated. The materials used were

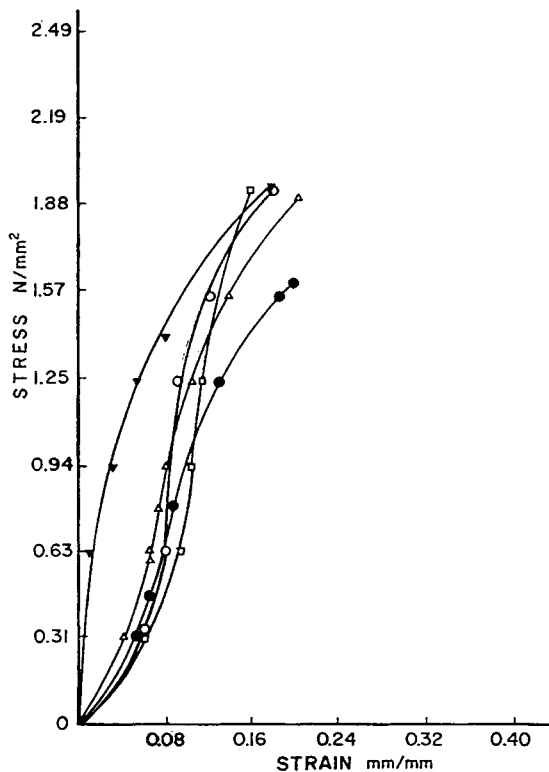


Fig. 3. Stress-strain curves of series A specimens: Portland cement mortar substrates. (○) PU, (△) PU + PVC, (□) PU + PVA, (●) PU + VAc-VC copolymer; (▼) PU + PVAc. Testing temperature = 22°C, crosshead speed = 10 mm/min, chart drive = 20 mm/min.

commercial grades of castable two component polyurethane (PU) (Reichhold Chemicals Ltd.); poly(vinyl chloride) (PVC) (103E-PF-7 Resin, BF Goodrich); poly(vinyl acetate) (PVA_c) (Mowilite 30, Hoechst); poly(vinyl alcohol) (PVA) (Anachemia); vinyl acetate-vinyl chloride copolymer (VAc-VC copolymer) (Hostaflex M131, Hoechst). Each of these four vinyl polymers, in powder state, was used and mixed with the polyol component before the preparation of the polyurethane elastomeric system. Usually, a dispersion was observed. Taking into account the problem of incompatibility, the mixing was always conducted with care in order to obtain good interpenetrating network systems.

Specimens of 13/13/50 mm were prepared according to ASTM C-719-72 and C-736-72. Each specimen was essentially a bead of polyurethane adhesive or polyblend cast between two prismoidal pieces of substrates made either of Portland cement mortar or California redwood. Before the application of the polymeric system, the substrate was prepared as follows: cement pieces were oven-dried to constant weight, while the wood pieces were brushed clean to remove dust and dirt.

After curing (50–70 s) at room temperature, the specimens were subjected to three different conditions:

(A) The first series was maintained six months at room temperature (22°C) and 20–50% relative humidity.

(B) The second series was kept in a dark cooling chamber with a repetitive

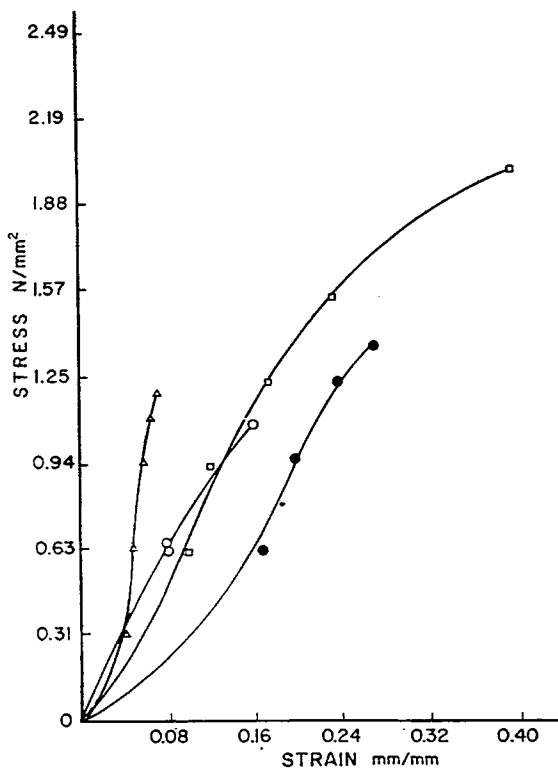


Fig. 4. Stress-strain curves of series B specimens: California redwood substrates. (O) PU, (Δ) PU + PVC, (\square) PU + PVA, (\bullet) PU + VAc-VC copolymer. Testing temperature = 22°C, crosshead speed = 10 mm/min, chart drive = 20 mm/min.

temperature program of 2 cycles/24 h, in the temperature range -30 to $+32^\circ\text{C}$. The relative humidity was kept between 62 and 68%. A graph of the temperature variation during one week of accelerated weathering is shown in Fig. 1. Each sample was subjected to 156 cycles.

(C) Another series was kept outside in downtown Montreal for six months, from January to July, 1980. The lowest temperatures reached in this time were between -19 and -23°C on January 24 and February 3. The highest temperatures were registered on 24–25 June, and they were between 30 and 31°C .

RESULTS AND DISCUSSION

The effect of accelerated and natural weathering on the specimens was established by tensile strength tests. Stress-strain curves averaging over 5–10 tests are presented in Figs. 2–7.

With regard to series A, in the case of wood (Fig. 2) as well as in that of cement mortar (Fig. 3), strain values in general are higher for polyblends than for PU; the stress is a little higher for PU specimens in the case of wood substrate. Generally, in more than 80% of the tests, adhesive properties have been superior to cohesive properties; i.e., substrate pieces have been broken and the bead of the polymer or polyblend has remained unmodified.

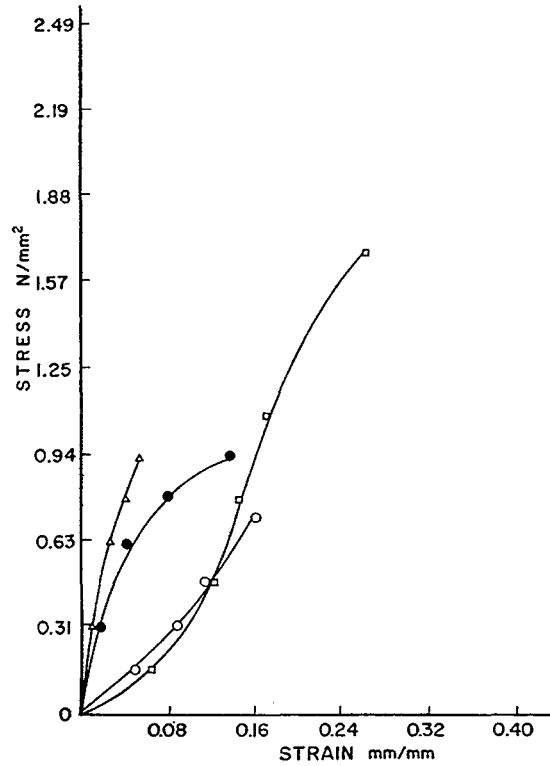


Fig. 5. Stress-strain curves of series B specimens: Portland cement mortar substrates. (O) PU, (Δ) PU + PVC, (\square) PU + PVA, (\bullet) PU + VAc-VC copolymer. Testing temperature = 22°C, crosshead speed = 10 mm/min, chart drive = 20 mm/min.

The magnitude of the tensile stress values decreased in the following manner:

In the case of wood substrates:

$$\text{PU} > \text{PU} + \text{PVC} > \text{PU} + \text{PVA} > \text{PU} + \text{PVAc} > \text{PU} + \text{VAc-VC copolymer}$$

the case of cement mortar substrates:

$$\text{PU} = \text{PU} + \text{PVA} = \text{PU} + \text{PVAc} > \text{PU} + \text{PVC} > \text{PU} + \text{VAc-VC copolymer}$$

The weakest blends were those made with PU and VAc-VC copolymer. Results obtained for series B tests are presented in Figs. 4 and 5.

Changes in both tensile stress and strain, as a result of accelerated weathering, are very important. The tensile stress decreased in all cases except the PU + PVA blend. This polyblend also showed the highest strain.

In the case of wood substrates, the magnitude of the strain decreased as follows:

$$\text{PU} + \text{PVA} > \text{PU} + \text{VAc-VC copolymer} > \text{PU} > \text{PU} + \text{PC}$$

In the case of mortar cement substrates,

$$\text{PU} + \text{PVA} > \text{PU} > \text{PU} + \text{VAc-VC copolymer} > \text{PU} + \text{PVC}$$

These modifications in mechanical behavior may be due to a cryolysis (me-

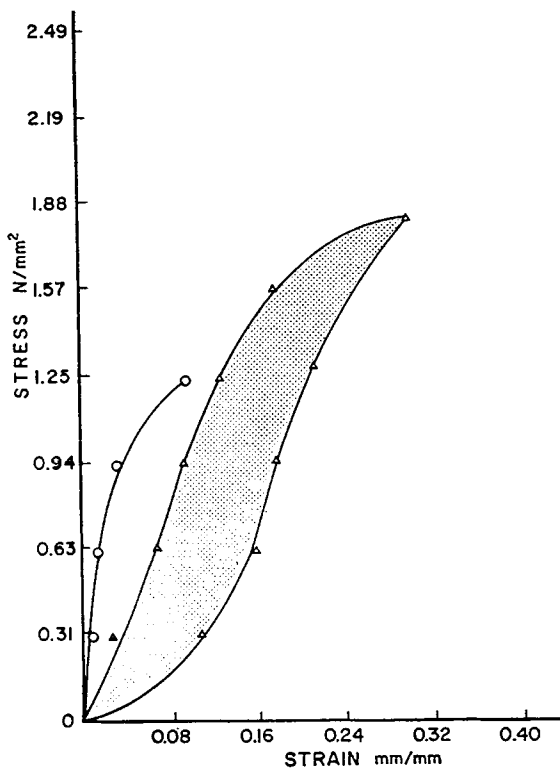


Fig. 6. Stress-strain curves of series C: polyurethane elastomeric adhesive. (O) Cement mortar, (Δ) wood. Testing temperature = 22°C, crosshead speed = 10 mm/min, chart drive = 20 mm/min.

chano-chemical degradation during cryolytic cycle freeze-thaw) process in the intramolecular bonds of the polymer chains. Another possibility is a decrease in the number of hydrogen bonds (which involve urethane groups). Polyurethane modifications are especially referred to because they were the major components in all mixtures.

It is well known that in polymers submitted to a cryolytic treatment in a freeze-thaw cycle, forces develop which lead to the mechanical degradation of macromolecular chains, usually by the decrease of their molecular weight. In the presence of water, the mechanical factor which initiates the degradation process results from the forces which arise from the pressure exerted on the polymer chains due to the development of ice crystals.

Recently, Schollenberger and Dinbergs¹⁹ have demonstrated the dependence of the mechanical properties of polyurethanes on their molecular weight. As in this case, the tensile strength decreases and the tensile strain increases when the molecular weight decreases.

The higher values of tensile stress for PU + PVA polyblends may be due to some supplemental interactions between the hydroxylic groups of PVA and various PU functional groups or with groups formed during cryolytic degradation. The lower flexibility of PU + PVC polyblends may arise from the well-known rigidity of PVC chains caused by strong dipole forces and hydrogen bonds.

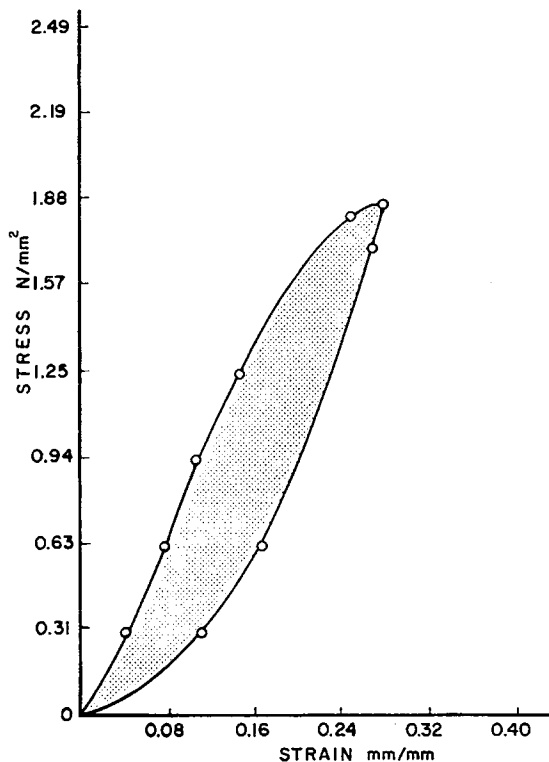


Fig. 7. Stress-strain curves of series C: polyurethane and poly(vinyl acetate) polyblend; California redwood substrates. Testing temperature = 22°C, crosshead speed = 10 mm/min, chart drive = 20 mm/min.

Some results of the natural weathering series are presented in Figs. 6 and 7.

Important modifications of the stress-strain properties of PU may be seen with both wood and cement mortar substrates. The decreases in tensile strength is higher in the case of cement mortar (Fig. 6). Because of the large spread of the results obtained with wood, the area which includes the family of respective curves is represented. The flexibility of these specimens are higher than that of PU from series A. This may also be explained by a decrease in the molecular weight due to cryolysis. In series C, it seems that the degradation process was less important than for the case of artificially forced weathering, although the specimens were in direct contact with rains, snow, sunshine, and winds. However, low and high temperatures and thermal shock were also less significant.

If one compares the PU + PVAc polyblend (Fig. 7) with the results of series A, it shows little modification of the stress-strain behavior after six months of natural weathering.

CONCLUSIONS

After six months at room temperature, the polyblends of a polyurethane adhesive and vinyl polymers such as PVC, PVA, and PVAc show little change in stress-strain behavior. Changes were observed in the case of the PU and VAc-VC copolymer polyblend.

In the case of artificial weathering the best results were obtained with the PU + PVA polyblend; this may be due to some supplemental interactions between the hydroxylic groups of PVA and various PU functional groups. The decrease in the mechanical properties of the specimens kept in artificial weathering conditions is explained by the decrease in molecular weights as a result of a cryolytic process.

This degradation process was less important for samples exposed to natural weathering conditions. The PU + PVAc polyblend shows little modification in stress-strain curve after six months of natural weathering.

Other studies for proving the cryolysis process are in progress.

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