

Viscoelastic and Engineering Properties of Poly(vinyl Chloride) Plasticized with Polycaprolactone-Based Polyurethanes

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Synopsis

The plasticization of poly(vinyl chloride) (PVC) by polyurethanes made from polycaprolactone (PCL) diol and *p,p'*-diphenylmethane diisocyanate (MDI) was investigated. By varying the PCL chain length and substituting with polyether chains such as poly(tetramethylene ether) (PTME) or poly(ethylene oxide) (PEO), also of various chain lengths, the efficiency of plasticization was changed. High urethane content, such as obtained with PCL-530/MDI, decreased the miscibility of the polyurethane and PVC. Plasticizing efficiency of the polyurethanes, as indicated by transparency, flexibility, and engineering properties of the blend, increased on increasing the initial PCL chain length. However, polyurethanes containing very high-molecular-weight PCL (e.g., PCL-3000) slowly crystallized from a 50:50 blend with PVC. PVC/polyurethane ratio also had a significant effect on crystallization, as indicated by the rapid crystallization of PCL-2000/MDI polyurethane when it exceeded 50 wt % in the blend. The transparency and flexibility of 50:50 blends were lowered by systematically replacing PVC-miscible PCL-2000 segments in the polyurethane with PTME-2000, PEO-200, and PEO-1500 segments. The polyurethanes became highly immiscible in PVC beyond the limiting mole fraction replacements of 0.6 for PTME-2000, 0.8 for PEO-200, and 0.4 for PEO-1500. Such chemical modification gave controlled and temperature-dependent miscibility in PVC and consequently blends with broadened glass transitions and high damping properties over a wide temperature range. Decreased miscibility in the blend gradually decreased elongation at break and tensile strength, but increased the modulus. A general correlation of the viscoelastic and tensile properties of the 50:50 blends with the weight fraction, rather than mole fraction, of the PCL content in the polyurethane composition was found; replacement of PCL beyond a limiting weight fraction by polyethers and MDI produced PVC-immiscible polyurethane. These limiting weight fractions are 0.6, 0.5, and 0.4 with PTME-2000, PEO-200, and PEO-1500, respectively, which denotes the order of decreasing miscibility of these polyurethanes in PVC. Viscoelastic and engineering properties of the blend with a particular polyurethane could also be controlled by varying the PVC/polyurethane ratio. Many of these semimiscible blends showed evidence of lower critical solution temperature (LCST) behavior at about -30°C , but complete cloud and point curves were not constructed.

INTRODUCTION

During the past decade, polymer scientists and engineers have expended considerable effort in studying polymer-polymer systems.¹ That poly(vinyl chloride) (PVC) has been the focus of attention in many such studies is not surprising because of the commercial demand for permanent plasticizers, process aids, impact modifiers, and heat distortion builders for this commodity resin. Also, PVC proves to form a uniquely large number of miscible polymer blends and has thus been the subject of extensive study with the goal of understanding the relationships between polymer-polymer miscibility and the chemical structure of the components. Examples of polymers found to be fully or highly

miscible with PVC are butadiene-acrylonitrile copolymers, ethylene-vinyl acetate copolymers, polycaprolactone, ethylene-vinyl acetate-sulfur dioxide terpolymers, and ethylene-vinyl acetate-carbon monoxide terpolymers.² Miscibility of most of these copolymers in PVC has been shown to be highly dependent on the copolymer composition.²⁻⁴

Of the above mentioned, polycaprolactone (PCL), a polyester, has been the most extensively investigated.³⁻⁶ While highly miscible in PVC, PCL exhibits slow crystallization⁴ if its concentration exceeds 40 wt %, and thus it is not completely suitable as a permanent plasticizer. One solution to this problem is to incorporate the PCL chains onto polyurethanes.⁷⁻¹⁰ Because polyurethanes can be easily modified, the relationship between the chemical structure of the polyurethanes and its miscibility in PVC can be readily studied. In this article, we will report how the level of miscibility of these polyurethanes can be successively reduced by gradual replacement of polyester (PCL) segment in the PU with polyether segments such as poly(tetramethylene ether) (PTME) or poly(ethylene oxide) (PEO). Also reported is the effect of the miscibility level in the PVC-polyurethane blends on the engineering and viscoelastic properties, with particular attention to the temperature dependence of the damping properties.

EXPERIMENTAL

Materials

The PVC used in this study was a BF Goodrich product with an intrinsic viscosity of 0.96 dL/g and the molecular weight averages, M_n 52,000 and M_w 110,000. The PVC was stabilized with 2% by weight of stannous octoate (TM-181 of Cincinnati Milacron) along with 0.2% by weight of a sterically hindered phenol (Irganox 1076, Ciba-Geigy).

The diols and the diisocyanate used for the synthesis of the polyurethanes were procured from Polyscience Inc. The purity of *p,p'*-diphenylmethane diisocyanate (MDI) was 99.4% with respect to isocyanate content, while the para-para and ortho-para isomer contents were 98.4 and 1.5%, respectively. The diols were of commercial quality.

Synthesis of Polyurethanes

Four sets of polyurethanes were synthesized by bulk polymerization, and in each synthesis an equimolar proportion of total diol to diisocyanate was maintained. This assured a small excess of hydroxyl functionality in the reaction mixture because the MDI was slightly less than difunctional.

(1) To optimize the diol molecular weight for subsequent studies, PCL diols of different molecular weights, MW 530, 1250, 2000, and 3000, were polymerized. In one synthesis with PCL-530, a 20% excess of MDI was employed, giving a crosslinked product. Polyurethanes were also synthesized from PTME-2000 and PEO-200 diols.

To synthesize the polyurethanes, weighed amounts of diol were placed in tin containers and dried at 120°C in a vacuum oven for 6 h to remove moisture (about 1%). Equimolar amounts of MDI were then added to the heated diols and mixed

well. MDI generally dissolved easily in the hot diols, but in some cases a slight heating of the cans ensured proper mixing. About 0.1% of catalyst TM-181, a stannous alkoxy compound, was added and the mixture was stirred vigorously until the reaction slowed, whereupon the containers were capped and placed in a 120°C oven for 3 h.

Since the blend of PCL-2000/MDI polyurethane and PVC was found to impart optimum properties both with respect to plasticization and long-term permanency, PCL-2000 diols was always used as one component in the synthesis of all the co-polyurethanes described below.

(2) In the second set, a series of polyurethanes was prepared with PCL-2000 and poly(tetramethylene ether) diol (PTME-2000 diol), MW 2000, in the following molar ratios: 1:0, 0.8:0.2, 0.6:0.4, 0.4:0.6, 0.2:0.8, and 0:1. The diols were completely miscible in each other, and the polymerization procedures were as above.

(3) In a third series, PCL-2000 diol was systematically replaced with poly(ethylene oxide) diol (PEO-200 diol), MW 200, giving mole ratios of 0.6:0.4, 0.4:0.6, 0.2:0.8, and 0.1:0.9. The mole ratios corresponded to 6.3, 13.0, 28.6, and 46.4 wt %, respectively, of PEO-200. Since PEO-200 diol is a liquid which evaporates rapidly at 120°C, it was dried separately overnight at 90°C under vacuum. The PCL-2000 diol was dried as usual at 120°C in the tin container and cooled. The proportionate amount of dried PEO diol was then weighed into this container. The mixture was slowly heated, a molar proportion of MDI was added, and stirring was continued until the MDI dissolved. The rest of the polymerization procedure was as described above. Polyurethane with PEO-200 diol only was synthesized with a PEO/MDI ratio of 1:0.95 to avoid crosslinking due to the slight evaporation of PEO-200 diol during reaction.

(4) To determine the effect of polyether molecular weight, a fourth series of polyurethanes was synthesized in which PCL-2000 diol was successively replaced with PEO-1500 (MW 1500). Mole ratios of PCL-2000:PEO-1500 were 0.9:0.1, 0.8:0.2, 0.7:0.3, 0.6:0.4, and 0.4:0.6, which correspond to 7.6, 15.8, 24, 33, and 53 wt %, respectively, of PEO-1500 content in the polyurethane, excluding the MDI. Since PEO-1500 is a waxy solid, the synthetic procedures were as described in the first series.

Characterization of Polyurethanes

Infrared spectra of some of the polyurethanes were taken to check for the absence of free isocyanate group to assure complete reaction. The intrinsic viscosities of the polyurethanes in THF at 30°C were measured and are reported in Table I. Viscoelastic and tensile properties of the polyurethanes were determined to find the effect of compositional variation on these properties.

Blending

Five grams each of PVC and the polyurethanes were dissolved in about 100 ml THF. The solvent was initially removed by evaporation in a laboratory hood and finally dried in a vacuum oven at 80°C to yield thin films. Residual solvent was removed from the film by passing it through the heated (85–90°C) two-roll mill. The blend was pressed into a 1.4-mm-thick sheet in a hydraulic press at

TABLE I
Intrinsic Viscosity of Polyurethanes in THF at 30°C

Diol used	Intrinsic viscosity (dL/g)
PCL-530	0.75
PCL-1250	0.66
PCL-2000	0.53
PCL-3000	0.49
PTME-650	1.13
PTME-2000	0.72
PCL-530 (excess MDI)	Insoluble
PCL-2000/PTME-2000 (0.8:0.2)	0.69
PCL-2000/PTME-2000 (0.6:0.4)	0.83

150°C for 5 min. Melt blending of the two polymers on the mill at 130–140°C yielded equivalent blends but with somewhat more oxidative degradation, as evidenced by color development.

Characterization of the Blends

The viscoelastic properties of the plasticized PVC samples were carried out with du Pont's Dynamic Mechanical Analyzer, model 981 (DMA) over a temperature range of -60 to +60°C and to +110°C in some instances. In all the blends studied here, the $\tan \delta$ values fell off continuously well below 0.01 with temperature after reaching T_g . However, to avoid overcrowding in the figures, some of these values have not been shown, and the curves have not been extended downward.

The tensile properties were determined with an Instron tensile tester, model TM-S, following ASTM D638-77a procedure using microtensile test specimens with a gauge length of 2.3 cm and a crosshead speed of 1.27 cm/min. Both the viscoelastic and engineering properties were determined within two weeks after the preparation of the blend.

RESULTS AND DISCUSSION

Polyurethanes Containing a Single Diol

Table I shows that as the molecular weight of the starting diols was increased, the intrinsic viscosity of the polyurethane decreased. For this reason, an off-stoichiometric reaction with PCL-530 was run to check on the effects due only to polyurethane molecular weight. This product was crosslinked but could be blended by milling.

As expected, blending PVC with 100 pph polyurethanes based on PCL-1250, -2000, and -3000 produced transparent, one-phase blends resulting in soft plasticized products. The polyurethane containing PCL-530 gave a somewhat cloudy blend, though only a single glass transition temperature was noted for all PCL-based polyurethane blends with PVC (Fig. 1). When observed over a period of seven to eight months, 50:50 blends containing PCL-3000 polyurethane slowly became cloudier and stiffer, while blends containing PCL-1250 and PCL-2000 polyurethanes remained unchanged. The ester chain length of the

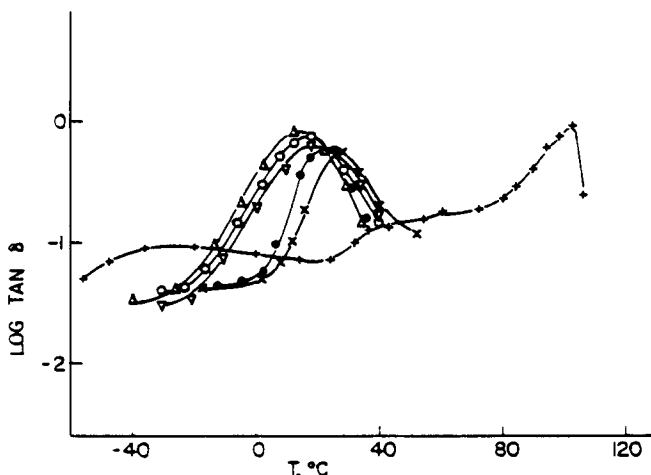


Fig. 1. Damping behavior of blends of PVC with 100 pph polyurethanes synthesized from PCL diols of different molecular weights. MW of PCL: (\times) 530; (\bullet) 530, crosslinked; (∇) 1250; (\circ) 2000; (Δ) 3000; (+) PTME-2000.

PCL-3000 is evidently sufficiently long to permit crystallization from the blend, as has been observed with PVC/PCL mixtures.⁵

The molecular weight of the polyurethane had little effect on miscibility, as is apparent from the nearly identical damping curves (Fig. 1) for blends containing polyurethanes prepared from PCL-530, but with different molecular weight, one of which is crosslinked. In general, for all these blends, T_g decreased while the peak damping values increased in order of the diol molecular weight. This indicates more miscibility and consequent plasticization in that order, which is expected from the higher miscibility of the polyester segment with PVC relative to the aromatic urethane segments.

To study the effect of PVC/polyurethane ratio on miscibility, PCL-2000 polyurethane was blended with PVC in different proportions. It was noted that clear and transparent blends were obtained until the polyurethane content exceeded 50 wt %. The flexibility of the blend, which is a rough indication of the extent of plasticization, gradually increased with polyurethane content up to this limiting ratio. These blends were stable; no crystallization of polyurethane from the blend occurred over a period of seven to eight months. When blends were prepared with polyurethane contents higher than 50 wt %, immediate crystallization was noticed and the blend continued to stiffen with time. The tensile properties of these blends will be discussed later.

While the polyurethanes with PCL diol gave flexible plasticized products with PVC, polyurethanes prepared from PTME and PEO diols gave opaque, stiff, two-phase blends with two glass transition temperatures. The PEO-200/MDI polyurethane, especially, was highly crystalline and highly immiscible in PVC.

Polyurethanes Containing Two Diols

Since the polyurethane derived from PCL-2000 give a miscible blend while those derived from PTME-2000 and PEO-200 yield immiscible blends with PVC, copolyurethanes were synthesized with a varying proportion of PCL-2000/

PTME-2000, PCL-2000/PEO-200, and PCL-2000/PEO-1500 diols to study their miscibility with PVC and to measure the viscoelastic and engineering properties of the blends.

Viscoelastic Properties of 50:50 Blends of PVC and PCL/PTME Polyurethanes

As the PCL segment in the polyurethane is replaced by PTME segments, the copolyurethanes become more amorphous as indicated by lower modulus and higher elongation to break of pure polyurethanes (note the points on the right-hand side of Figs. 11 and 13). The intrinsic viscosity of the polyurethanes increased with increased PTME content (Table I), holding the stoichiometry constant.

The transparencies and the flexibilities of the 50:50 blends of these polyurethanes with PVC decreased with increased PTME content. However, a single T_g was noted in the blends based on polyurethanes containing up to 60 mol % PTME, as can be readily observed from the damping curves in Figure 2. With 80 mol % PTME content, the polyurethane became immiscible with PVC, yielding cloudy, brittle blends with two T_g 's. The damping response (Fig. 2) indicates significant damping over a broadened temperature range with increased PTME content; this effect has been plotted in Figure 4. (For convenience, the damping range in this work was defined as the temperature range over which $\tan \delta$ exceeds 0.1.) The broadening of the $\tan \delta$ curve and the increase in T_g (Fig. 2) with increasing PTME content is due to the gradual decrease of the solubility of the polyurethane in PVC and an increase in the temperature dependence of the solubility. In support of the latter, we note in Figure 3 the increase in modulus for several of the blends starting around -30°C . This is perhaps due to a phase separation (LCST) process commonly found in polymer-polymer systems,¹¹ and it was further supported by observing a decrease of opacity of the blend with decreasing temperature. Behavior of this type could be useful in

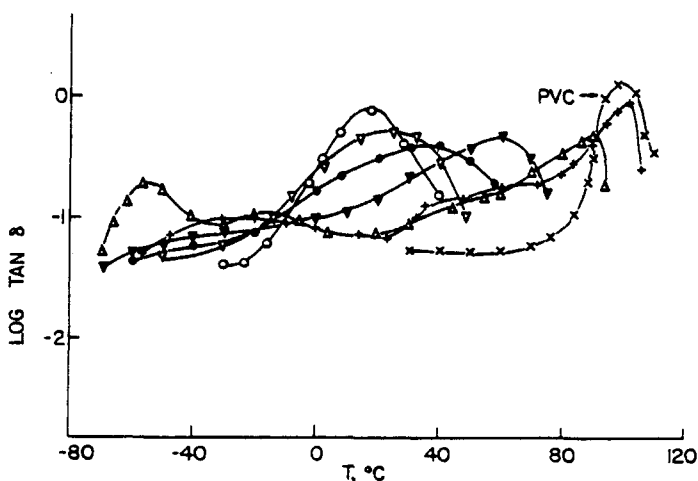


Fig. 2. Damping behavior of blends of PVC with 100 pph polyurethanes synthesized from mixtures of PCL and PTME diols. PCL/PTME ratio: (○) 1:0; (▽) 0.8:0.2; (●) 0.6:0.4; (▼) 0.1:0.6; (△) 0.2:0.8; (+) 0:1.

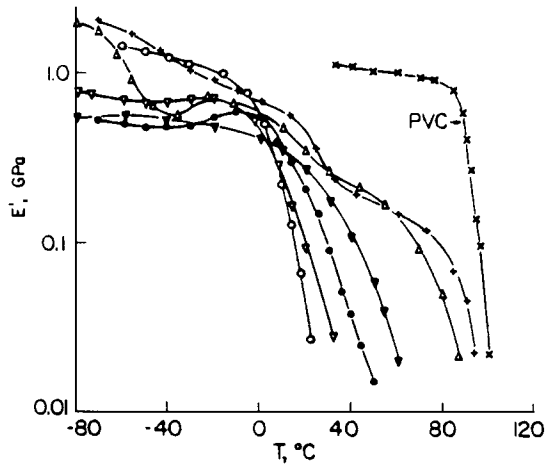


Fig. 3. Storage modulus–temperature relationship in blends of PVC with 100 pph polyurethanes synthesized from a mixture of PCL and PTME diols. PCL/PTME ratio: (O) 1:0; (∇) 0.8:0.2; (●) 0.6:0.4; (▼) 0.1:0.6; (Δ) 0.2:0.8; (+) 0:1.

plasticized systems because of the wide damping range produced by the temperature-dependent solubility of the plasticizers.¹²

Viscoelastic Properties of Blends with Different PVC/Polyurethane Ratios

Three sets of polyurethanes with 0, 0.2, and 0.4 mole fraction PTME content in the diol mixture were blended with PVC at different weight ratios. The important viscoelastic properties of the blends have been summarized in Figures 5 and 6. (Individual damping curves for these PVC/PU blends have not been shown here.) Interestingly, the two peaks in Figure 5 indicate that higher damping ranges are obtained when PVC/polyurethane ratios are either high or very low. This is probably due to the large difference in T_g values of the individual polymers and the slow rate of the temperature-dependent phase separation process when the concentration of either of the polymers is low. Figure 5 also shows that for any PVC/polyurethane ratio, a greater damping is obtained with greater PTME content in the polyurethane, although the peak $\tan \delta$ values are compromised somewhat in the process (Fig. 6). T_g values of all such blends,

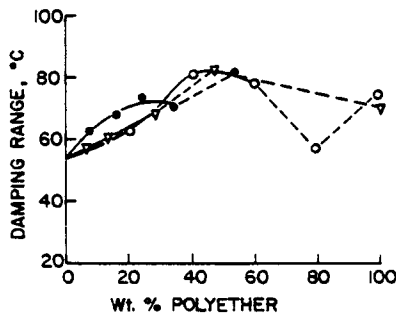


Fig. 4. Effect of polyurethane composition on the damping range for blends of PVC with 100 pph polyurethanes (calculated from width of damping curve at $\tan \delta = 0.1$): (O) PTME-2000; (∇) PEO-200; (●) PEO-1500; (---) two phases; (—) one phase.

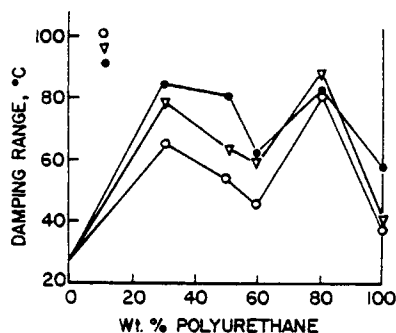


Fig. 5. Variation of damping range for PVC/polyurethane blends with polyurethane content using PCL/PTME polyurethanes (damping range was calculated as in Fig. 4): PCL/PTME ratio: (○) 1:0; (▽) 0.8:0.2; (●) 0.6:0.4.

as expected for miscible systems, lie between those of pure PVC and pure polyurethane (Fig. 6).

Viscoelastic Properties of 50:50 Blend of PVC and PCL/PEO Polyurethanes

The PEO-200/MDI polyurethane is highly crystalline and highly immiscible with PVC. However, a limited replacement of PCL by PEO-200 diol produces polyurethanes which are very good plasticizers for PVC. The 50:50 blends of these polyurethanes in PVC are transparent, when initially prepared, even upon increasing the PEO content to a molar PCL/PEO ratio of 0.2:0.8, corresponding to 29 wt % PEO-200. Some cloudiness was noted in the blend made with this polyurethane. The flexibility of the blends, however, decreased with increased PEO content. Though the blends were transparent initially, they became opaque over a period of three to four months, with the degree of opacity increasing with PEO content. This was probably due to the slow crystallization of PEO-200 segment, and was further confirmed with PCL-2000/PEO-1500 polyurethanes which gave initially opaque blends with PVC, the opacity increasing with the PEO-1500 content in the polyurethane. In this case, the limiting molar PCL/PEO ratio of 0.6:0.4 corresponds to 33 wt % PEO-1500.

The loss tangent and storage modulus of the blends containing PCL/PEO-200

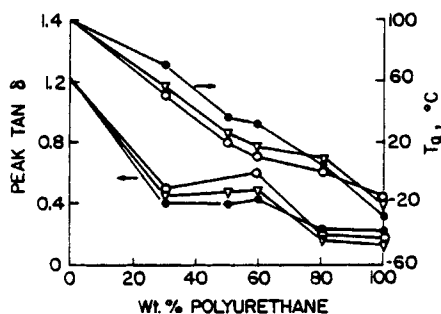


Fig. 6. Variation of peak $\tan \delta$ and T_g values with polyurethane content of PVC/polyurethane blends, the polyurethanes being synthesized from PCL and PTME diols using the ratios shown. Peak $\tan \delta$ is the maximum value of $\tan \delta$ in the temperature range studied. PCL/PTME ratio: Same notation as in Fig. 5.

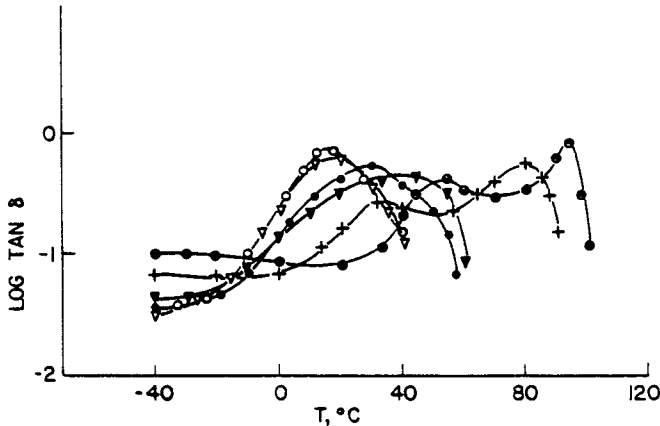


Fig. 7. Damping behavior of blends of PVC with 100 pph polyurethanes synthesized from mixtures of PCL and PEO diols: PCL:PEO ratio: (○) 1:0; (▽) 0.6:0.4; (●) 0.4:0.6; (▼) 0.2:0.8; (+) 0.1:0.9; (⊖) 0:1.

polyurethanes have been plotted in Figures 7 and 8. As with PCL/PTME polyurethanes, the temperature range of damping broadens (Fig. 7) with increased PEO-200 content up to the limiting ratio; increased PEO-200 content beyond this ratio produces polyurethanes which are immiscible in PVC. Identical behavior (figures not included) are also noted for blends containing PCL/PEO-1500 polyurethanes, except that the limiting mole fraction is 0.4, vs. 0.8 for PCL-200.

Damping ranges for the blends have been shown in Figure 4 as a function of weight fraction, rather than mole fraction, of polyether diol content in the diol mixture, which correlates better both the viscoelastic and engineering properties. It is seen from Figure 4 that the damping range increased most rapidly with polyether substitution in the order PEO-1500 > PEO-200 = PTME-2000. The limiting polyether content at which the polyurethane became immiscible in PVC decreased in the order PTME-2000 > PEO-1500 > PEO-200. The limiting polyether content was expected to be higher with PEO-200 than with PEO-1500;

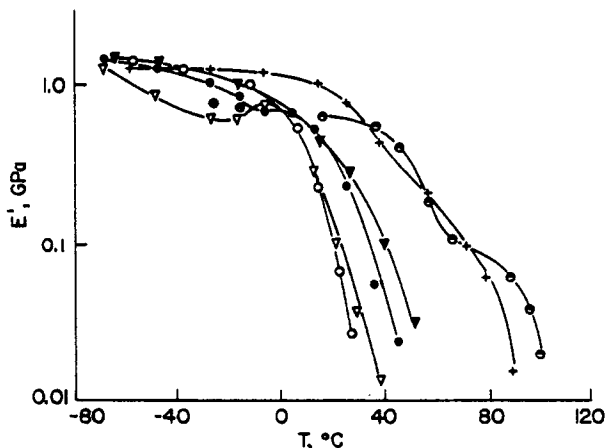


Fig. 8. Storage modulus-temperature relationship in blends of PVC with 100 pph PCL/PEO polyurethanes. PCL:PEO ratio: same notation as in Fig. 7.

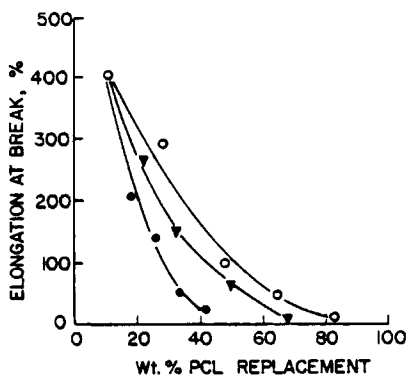


Fig. 9. Variation of elongation at break of 50:50 PVC/polyurethane blends with weight percent PCL replacement (by PTME + MDI or PEO + MDI) in the polyurethane: (○) PCL/PTME; (▼) PCL/PEO-200; (●) PCL/PEO-1500.

however, the opposite values, as obtained here, could be accounted for by the unequal weight fraction of MDI in the two sets of polyurethanes. Indeed, by considering the amount of PCL replaced in the polyurethane by both polyether and MDI ("PCL replacement"), this discrepancy was removed.

In two instances (40 and 60 mol % PEO), blends containing PCL/PEO polyurethanes also showed a modulus increase at subambient temperatures (Fig. 8); a similar behavior has been noted above for blends containing PCL/PTME polyurethanes (cf. Fig. 3).

Tensile Properties

The tensile properties of the 50:50 blends of PVC with both PCL/PTME and PCL/PEO polyurethanes were studied as a function of the molecular composition of the polyurethane. The results are plotted in Figures 9 and 10. With increased PCL replacement, the elongation at break and tensile strength fell off while the modulus increased. These results were expected from the changes in the miscibilities of the blends. It may also be noted from Figures 9 and 10 that the rate of decrease of tensile properties with respect to the weight percent PCL replaced follows the order of PEO-1500 > PEO-200 ≥ PTME-2000. As has been observed in the previous sections, the damping range also follows the same order, and this obviously represents the inverse order of miscibility in the blend.

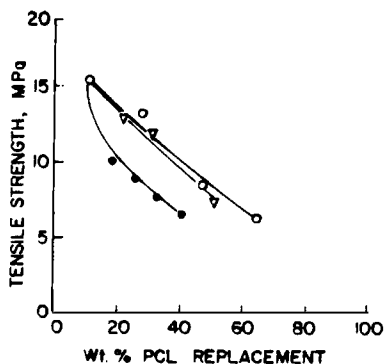


Fig. 10. Variation of tensile strength of 50:50 PVC/polyurethane blends with weight percent PCL replacement in the polyurethane: (○) PCL/PTME; (▼) PCL/PEO-200; (●) PCL/PEO-1500.

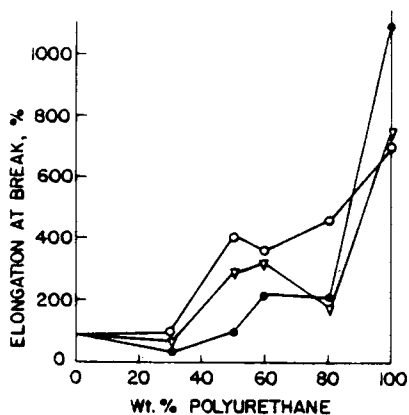


Fig. 11. Dependence of elongation at break on polyurethane content for blends of PCL/PTME polyurethanes with PVC. PCL/PTME ratio: (○) 1:0; (▽) 0.8:0.2; (●) 0.6:0.4.

The MDI weight fractions in the PCL-2000/PTME-2000, PCL-2000/PEO-200, and PCL-2000/PEO-1500 polyurethanes are significantly different and depend on the diol molar ratios in the polyurethanes. As we have noted with single diol systems, the decreased MDI content in PCL/MDI polyurethanes obtained by raising the PCL molecular weight increases the miscibility of the polyurethane in PVC and changes the mechanical properties of the blend. In the case of the copolyurethanes, the amount of PCL which can be replaced and still maintain substantial miscibility (limiting PCL replacement) depends on the type of polyether; the values are 60, 50, and 40 wt % for PTME-2000, PEO-200, and PEO-1500 polyethers, respectively. This trend is in agreement with the changes in tensile properties of the blend as discussed earlier.

The effect of PVC/polyurethane ratio on the tensile properties of the blends has been studied for PCL/PTME polyurethanes; the results are presented in Figures 11, 12, and 13. The elongation at break decreases with increasing PTME content at any PVC/polyurethane ratio. With fixed PCL/PTME ratio, the elongation at break shows a mild maximum at around the 50:50 blending ratio of polyurethane in PVC. If elongation at break is taken as an index of the plasticizing action of the polyurethane, then the optimum PVC/polyurethane

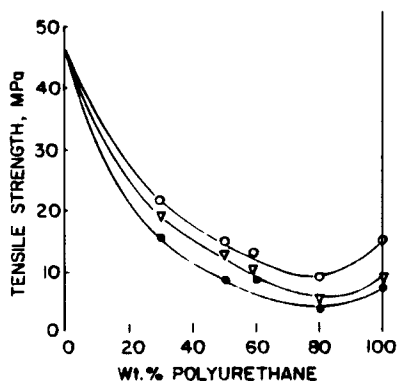


Fig. 12. Dependence of tensile strength on polyurethane content for blends of PCL/PTME polyurethanes with PVC. PCL/PTME ratio: same notation as in Fig. 11.

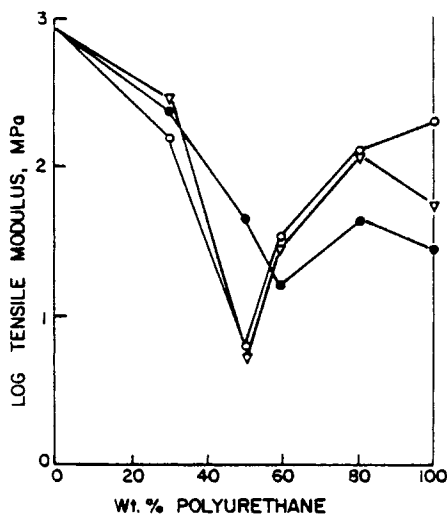


Fig. 13. Dependence of modulus on polyurethane content for blends of PCL/PTME polyurethanes with PVC. PCL/PTME ratio: same notation as in Fig. 11.

ratio with PCL-2000 polyurethane is very close to 50:50 (Fig. 11), and the optimum ratio shifts toward higher polyurethane content as the PTME content in the polyurethane is increased. As the polyurethane content of the blend is increased, the blend's tensile strength drops (Fig. 12). The values generally lie between the tensile strengths of the pure polymers, with a mild minimum at very high polyurethane content. For a particular PVC/polyurethane ratio, tensile strength decreases with increased PTME content in the polyurethane, as expected from the decreased miscibility. Figure 13 shows the results of modulus of the blend against PVC/polyurethane ratio; as expected from the reverse of Figure 11, a minimum in all these curves is noted.

CONCLUSIONS

The miscibility of PCL/MDI polyurethanes in PVC can be increased by decreasing the MDI content, i.e., by increasing the PCL chain length. However, polyurethanes containing high-molecular-weight PCL slowly crystallize from the 50:50 blend; the rate of crystallization also depends on PVC/polyurethane ratio. Successive replacement of PCL-2000 segment by polyether produces polyurethanes with decreased miscibility in PVC. This limited and temperature-dependent miscibility of the blend broadens the glass transition and consequently imparts high damping over a wide temperature range. In general, the viscoelastic and engineering properties of the 50:50 blends correlate with the weight percent PCL in the polyurethanes for both PCL/PTME and PCL/PEO polyurethanes. As indicated by these properties, the miscibility of the polyurethanes in PVC depend on the type of polyether and its molecular weight. Viscoelastic and engineering properties of the blend can also be varied by changing the PVC/polyurethane ratio. At intermediate polyether content, the blends behaved in a fashion suggesting an LCST of around -30°C .

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