

Dynamic Mechanical Properties of Polystyrene–Polyurethane Blends

P. S. THEOCARIS* and V. KEFALAS

Department of Engineering Sciences, The National Technical University of Athens, Athens (GR 175-10), Greece

SYNOPSIS

Four polystyrene–polyurethane mechanical blends were prepared with 5, 10, 20, and 40% thermoplastic polyurethane, respectively. Their impact properties were compared with pure polystyrene and commercial types of impact polystyrene. The rheological properties of the blends were studied with DSC and dynamic mechanical spectroscopy. It was found that addition of softer polyurethane conglomerates embedded inside the polystyrene matrix, although increasing the toughness of the blend as expected from addition of the softer particulate, also increased the glassy region of the blends by shifting their T_g s to higher temperatures. A theory based on the interaction of phases was propounded explaining this phenomenon.

INTRODUCTION

Polymeric blends consisting of a glassy matrix and a rubberlike polymeric dispersed phase are known to exhibit improved impact properties.¹ The impact strength of the otherwise brittle glassy polymers increases considerably because the rubbery phase acts as a stress concentrator and craze initiator.^{2,3} It is well known that impact strength of glassy polystyrene improves with the incorporation of polybutadiene rubber.^{1–4} This led to the commercial polymer blends called high-impact polystyrenes (HIPS). Although the actual interpolymerization blending process of the two phases plays an important role in the final properties of the material, even mechanical blending is known to improve the impact properties of the blend.⁴

In this article, typical mechanical blends were prepared from a polyurethane thermoplastic copolymer, copolymerized in the laboratory. Polyurethane rubber was used as the rubberlike dispersed phase in these blends. The mechanical and dynamic mechanical properties of polystyrene–polyurethane blends from 5–40% polyurethane content were studied.

These blends were found to have improved impact properties as a function of the polyurethane content. Moreover, the incorporation of the rubberlike polyurethane was found to contribute to an increase of the T_g of the polystyrene blends relative to pure polystyrene by several degrees centigrade.

EXPERIMENTAL

Five types of polystyrene blends, labeled A, B, C, D, and E, with different amounts of polyurethane (0, 5, 10, 20, and 40%, respectively), were prepared in an Brabender Blending machine at 180°C and 120 rpm for 4 min.

The polystyrene material used as matrix was a DOW-678 commercial grade of M_w around 180,000. The material blended was a segmented polyurethane, prepared in the laboratory, by reacting symmetric methylenediphenyl–isocyanate (MDI) with a hydroxy-terminated polyester (PE) to form a soft block segment. The polyester used was polyethylene adipate with an average molecular weight of 2,000. The resultant polymer was then extended with butanediol (BDO) to form a hard block segment. Polyurethane material was prepared with the stoichiometric amount of MDI, forming a linear type of molecule. The initial concentrations of reactants were (MDI : BDO : PE, in mol/L) 4 : 3 : 1.

* To whom correspondence should be addressed.

Pellets from the above materials were molded in flat rectangular blocks ($15 \times 15 \times 3$ cm) by a thermal press. The temperature of molding was set at 205°C and the mold was left to cool slowly down in the press. Further, the blocks from each grade were annealed well above the glass transition temperature at a temperature of 120°C for 4 h. Samples were cut to size from the blocks and annealed once more. All samples were cooled slowly through T_g at the same rate of $1^\circ\text{C}/\text{min}$ to produce the same glassy matrix conditions since different physical aging gives different thermomechanical behaviour.

Dynamic mechanical and differential scanning calorimetry tests were performed with a compound pendulum system (DuPont's Dynamic Mechanical Analyzer DMA and D.S.C. 9000). These instruments are described in detail in ref. 5.

Impact tests were performed according to Izod specifications at room temperature. The hammer release and energy measurement were done electronically on a CEAST 6545 Impact Tester.

RESULTS

The four blends prepared, as well as pure polystyrene, were tested in an impact machine. The results are shown in Table I, and include the impact strengths of three types of commercial HIPS for comparison. From Table I it is evident that the impact strength of polystyrene was found to increase with the incorporation of polyurethane copolymer. Satisfactory results were obtained for blends with polyurethane contents of 5–20% although the overall impact performance compared to that of HIPS was found to be an order of magnitude lower. However, mechanical blending is known to be inferior to interpolymerization blending.⁴ It is also interesting to

note that increasing the content of polyurethane over 10% resulted in a substantial reduction of the impact strength of the blends.

To understand the nature of interaction of the two blended polymers, DSC experiments were performed to obtain the equilibrium T_g s of the blends. These results are shown in Figure 1. The T_g s of the blends due to polystyrene were all found to be higher than that of the pure polystyrene (see Table I). This is an indication of some kind of interaction between polystyrene and polyurethane polymer chains.

Polyurethane as a block copolymer consists of a soft segment with T_g around -33°C and a hard segment that has a melting point T_m at around 150°C .⁶ These hard segments, which tend to act as crosslinks in thermoplastic polyurethanes, contain aromatic rings that probably interact with the polystyrene aromatic side groups, forming some kind of P-bonds, or an overall physicochemical separate phase. This kind of interaction of polystyrene with the hard segment might be responsible for the increased polystyrene peak of the blends. To investigate further the above assumption, a separate blend was produced by introducing "dicumil," a crosslinking agent for the soft segment, during mixing in the Brabender machine. No T_g shift was observed due to the crosslinking of the soft segment.

Similar observations to the above results were reported in DSC experiments conducted on ABS blends with polyurethane.⁷ An increase of the ABS T_g peak of around 5°C was reported for the blend. In addition, an increase of the polyurethane hard segment melting point T_m was reported.

To study further the micromechanical behaviour of the blends, dynamic mechanical spectroscopy was performed.

Values of storage modulus E' and $\tan \delta$ vs. temperature are shown in Figure 2 for pure matrix (0%)

Table I Average Izod Strength, the Modulus, and the T_g with DSC and DMA of Blends (A–E) is Shown with the Izod Strength for Three Commercial Types of HIPS

Sample Type	% Content of Polyurethane	Izod Strength (10^{-3} J/mm ²)	Modulus (\times MPa)	T_g DSC	T_g DMA
A	0%	0.9	3,100	92.35	96.9
B	5%	13.3	2,950	94.27	100
C	10%	27	2,820	95.57	101.1
D	20%	2	2,400	96.34	98.5
E	40%	2.7	1,970	96.34	98

Polyurethane (soft segment $T_g = -33^\circ\text{C}$, hard segment $T_m = 150^\circ\text{C}$), Mod. 9.5 MPa

Type 1 HIPS, 90; Type 2 HIPS, 52; Type 3 HIPS, 212.

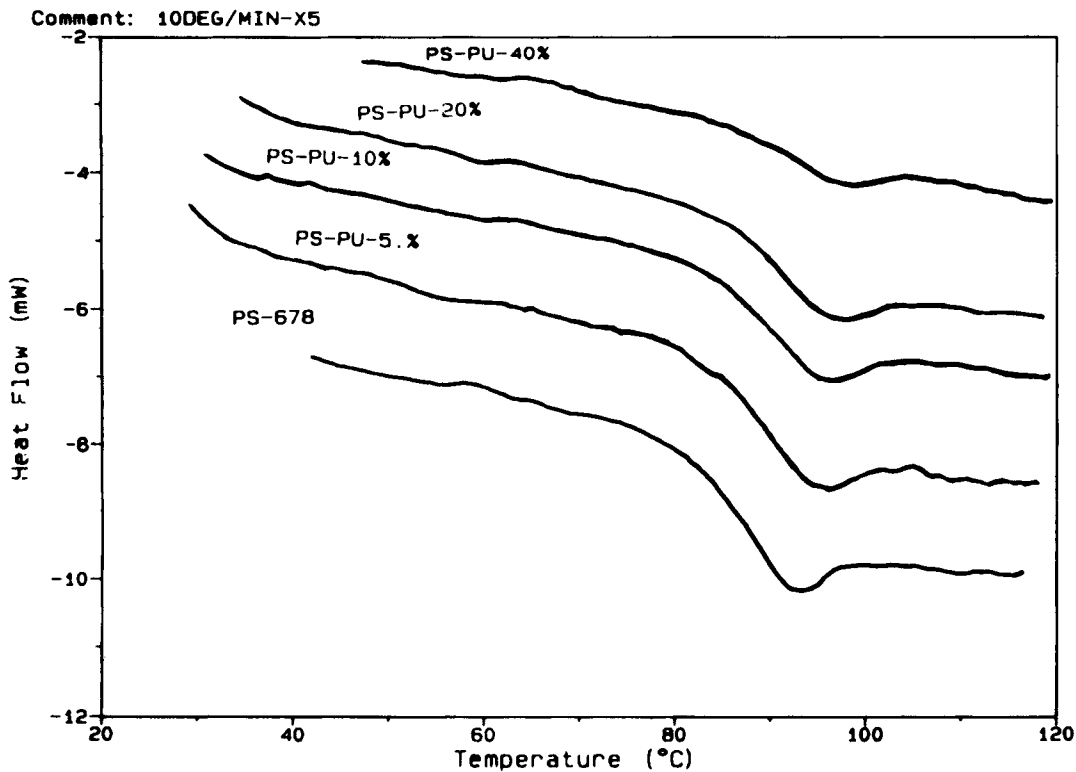


Figure 1 Heat absorbed at constant pressure vs. temperature of four types of polystyrene-polyurethane blends and polystyrene matrix material.

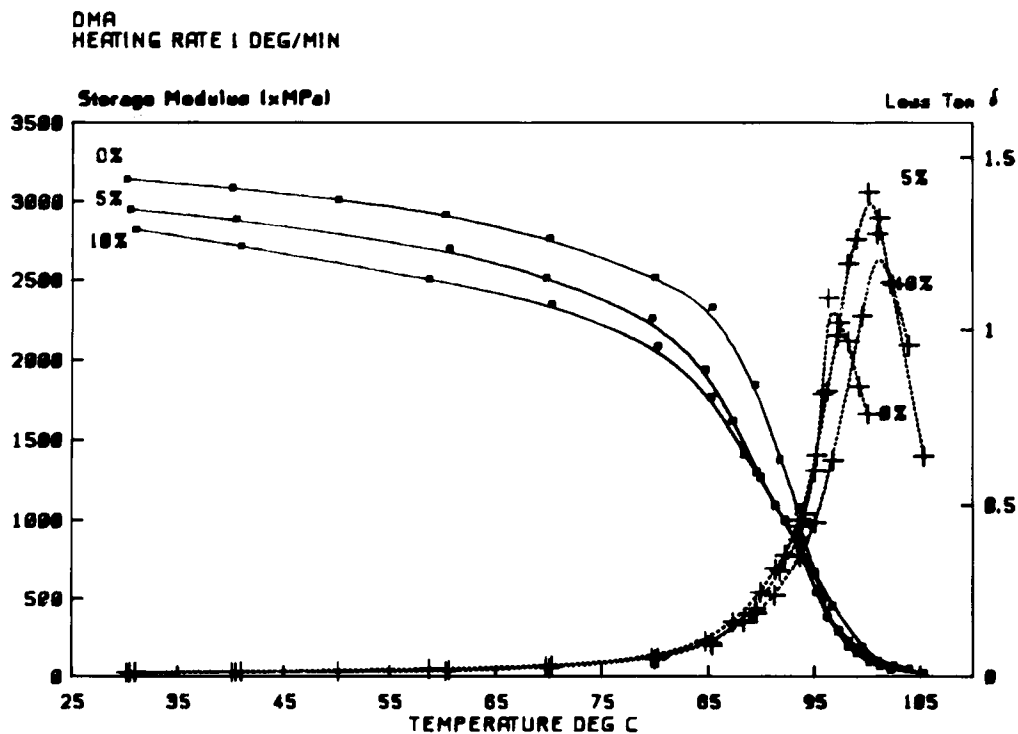


Figure 2 Storage modulus and loss tan δ vs. temperature for two types (5, 10%) of polystyrene-polyurethane blends, as well as pure polystyrene matrix.

and blends containing 5 and 10% polyurethane copolymer. The modulus of elasticity in the glassy state for the two blends is shown to decrease with increasing polyurethane content. This result is expected because the material incorporated has a lower modulus by three orders of magnitude.⁸ However, in the transition region the moduli of the two blends tend to approach the modulus of pure polystyrene. It is of interest to note that the modulus of the 10% polyurethane blend crosses over that of the 5% percent blend. Further, the T_g s of the two blends are shown to be slightly higher than the T_g of the pure matrix (see also Table I).

This type of behaviour has been even more evident with commercial HIPS.⁹⁻¹¹ The effect was attributed to the fact that as the rubbery plateau region is approached the effective crosslink density of the blend remains larger than the corresponding entanglement crosslink density of the pure polystyrene matrix. For HIPS, this phenomenon was attributed to the additional chemical grafting of the polystyrene matrix to the rubber phase.^{4,10} However, in this case of mechanical blending, the particular physicochemical morphology is not known and the reasons for this shift are not yet very clear. However, it is possible that P-bonds act as effective crosslinks

forming a separate physicochemical interphase around the rubber particles.

In Figure 3, values of storage modulus, E' , and $\tan \delta$ vs. temperature are shown for the matrix (0%) and the other two blends containing 20 and 40% polyurethane copolymer. The modulus of elasticity again is shown to decrease with polyurethane content as expected. However, for blends with high percentages of polyurethane (20% and 40%), the glass transition region is shown to be lower than that of the 5 and 10% blends. The 40% blend has approximately the same T_g as the pure matrix.

This result is indicated indirectly in the DSC measurements, where the characteristic transitions at the respective T_g s of the materials tested are smoother than the respective transitions for lower concentrations (5 and 10%) of polyurethane. One possible explanation for this phenomenon is that at higher polyurethane contents mechanical mixing cannot produce enough dispersion of the rubber phase, and thus large portions of the polyurethane do not interact with polystyrene chains. These large regions of occluded polyurethane do not affect the DSC measurement, which is sensitive only to the polystyrene chain mobility and nature of the physicochemical region around the rubber occlusions at

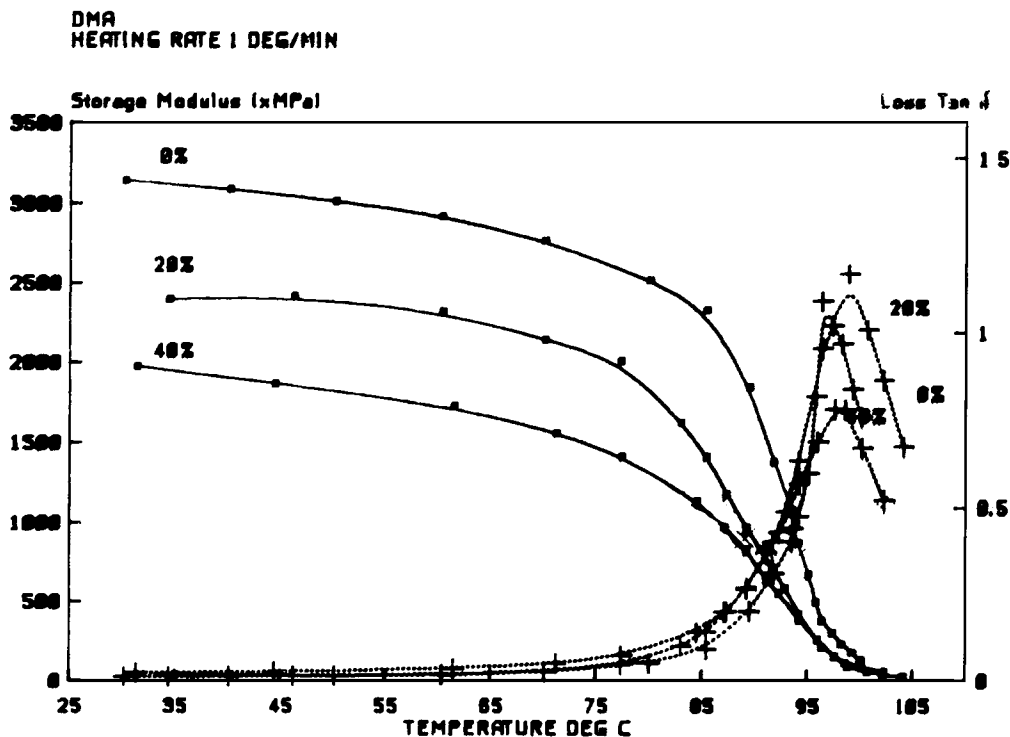


Figure 3 Storage modulus and loss $\tan \delta$ vs. temperature for two types (20, 40%) of polystyrene-polyurethane blends, as well as pure polystyrene matrix.

the particular temperature. On the contrary, the dynamic mechanical resonance is more sensitive to the overall mechanical behaviour of the two phases and the way they interact elastically.

If large regions of occluded polyurethane exist, it is expected that impact strength will be lowered due to large stress concentrations that result in catastrophic failure. It is of interest to note that the 20 and 40% blends showed a marked reduction in their impact strengths along with the T_g reduction (see Table I).

CONCLUSIONS

Blends of polystyrene with thermoplastic polyurethane as a dispersed phase showed improved impact strength compared to that of pure polystyrene.

The materials produced confirm the general rule that the incorporation of a rubber phase into a glassy matrix improves impact strength. However, optimization of these types of composites is needed by controlling homogeneity, particle size, and particle rigidity. Better results could possibly be obtained by trying to control the above factors if mixing in solution.

REFERENCES

1. J. Mann and G. R. Williamson, *Physics of Glassy Polymers*, Applied Science Publishers, London, 1973, p. 454.
2. C. B. Bucknall, *J. Mater.*, **4**(1), 214 (1969).
3. R. P. Kambour, *Appl. Polym. Symp.*, **7**, 215 (1968).
4. E. R. Wagner and L. M. Robeson, *Rubber Chem. Tech.*, **43**, 1129 (1970).
5. E. A. Collins, J. Bares, and F. W. Billmeyer, *Experiments in Polymer Science*, Wiley Interscience, New York, 1973.
6. J. M. Buist, *Developments in Polyurethanes*, Applied Science Publishers, London, 1978.
7. W. J. Farrissey, H. W. Bonk, R. S. Drzal, and C. N. Georgacopoulos, North Haven Laboratories, Dow Chemical U.S.A., Report, Polyurethanes World Congress, 1987.
8. P. S. Theocaris, *Advances in Polymer Science*, Springer-Verlag Berlin, Heidelberg, 1985, Chap. 6, p. 66.
9. V. Kefalas, P. S. Theocaris, and E. Kontou, *Polym. Composites*, **9**(3), 229-236 (1988).
10. P. S. Theocaris, V. Kefalas, and G. Spathis, *J. Reinfor. Plast. Composites*, **7**(1), 66-71 (1988).
11. P. S. Theocaris and V. Kefalas, *Rheologica Acta*, **24**(4), 405-409 (1988).

Received July 24, 1989

Accepted November 27, 1990