

Toughened Polystyrene Containing High *cis*-1,4-Polybutadiene Rubber

K. SARDELIS, H. J. MICHELS, and G. ALLEN,* *Department of Chemical Engineering and Chemical Technology, Imperial College, London SW7, England*

Synopsis

High *cis*-1,4-polybutadiene has been used to prepare toughened polystyrene in an attempt to improve its low temperature impact properties. A range of physical and mechanical properties was obtained by keeping the amount of rubber and the polymerization conditions constant, and varying the rate of agitation in a purpose-built reactor system. Although a good balance of tensile and impact properties is obtained at room temperature, the rubber partially crystallizes when the polyblends are cooled to below -40°C . This should decrease the efficiency of rubber particles to create and terminate crazes. However, it is significant that the developed crystallinity decreases with the rubber phase volume, and is suppressed almost completely at about 21% rubber phase volume (RPV). The factors influencing the RPV are discussed, and a study of the phase inversion with three different types of rubber shows that its duration depends on the viscosity of the styrene/rubber system.

INTRODUCTION

For many years, it has been recognized that the incorporation of an elastomeric material into a brittle polymer such as polystyrene leads to reinforcement or toughening. Early attempts to blend mechanically polybutadiene with polystyrene resulted in polyblends with inferior mechanical properties, as a result of the poor adhesion between the polystyrene matrix and the dispersed rubber particles.¹

The large-scale production of TPS started with Dow's discovery of the graft interpolymerization process.² [The term "toughened polystyrene" (TPS) is used instead of "high impact polystyrene" (HIPS), which is used indiscriminately in the literature and embraces medium to super impact grades.] In this process a solution of rubber in styrene monomer is prepolymerized with shearing agitation until approximately 30% styrene conversion. Subsequent polymerization ("finishing cycle") is carried out in bulk without agitation or in suspension. The final TPS polyblend has the ability to dissipate large amounts of energy without significant decrease of the high modulus and breaking strength of the polystyrene homopolymer. The nature of the two phases present during the shearing prepolymerization cycle was later identified.^{3,4} With the introduction of transmission electron microscopy in studying polymer systems,⁵ it became clear that a TPS polyblend consists of a continuous phase of polystyrene, and a dispersed phase containing rubber particles with polystyrene occlusions.

Basic papers on TPS polyblends published in the literature deal with the formation and morphology of the dispersed rubber phase,⁶⁻¹⁰ the mechanical

* Present address: Unilever, Unilever House, Blackfriars, London EC4, England.

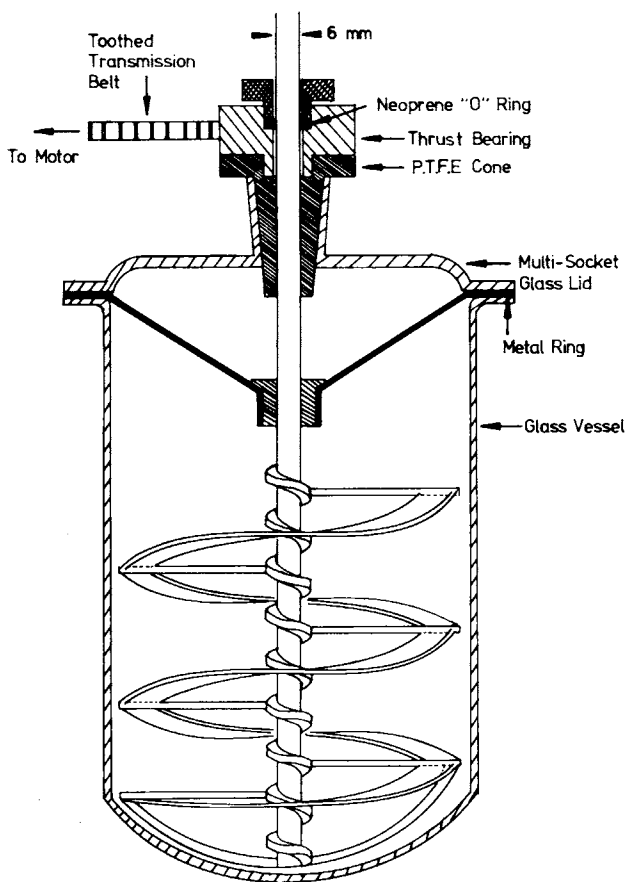


Fig. 1. First stage (prepolymerization) reactor.

loss characteristics,¹¹ and the mechanism of energy absorption during impact.^{12,13} It is apparent from this work that the polymerization conditions, the amount and type of rubber, and the morphology of the system each play a very important part in the optimization of physical properties of TPS. In all the above papers the rubber used was SBR or low *cis*-1,4-polybutadiene (LCPB), prepared anionically.

In the present study TPS polyblends containing high *cis*-1,4-polybutadiene (HCPB) were prepared in a purpose-built reactor system. Their physical and mechanical properties are examined and compared with those of TPS polyblends containing LCPB rubber. The relaxation behavior of TPS/HCPB was correlated in terms of a crystallization effect in the polybutadiene, which has not previously been reported in the literature.

EXPERIMENTAL

All the TPS polyblends were prepared with the graft interpolymerization process. The reactor system shown in Figure 1 was used during the prepolymerization stage. The vessel consisted of a 2-L cylindrical glass flask, fitted with a Quickfit four-socket glass lid. It was heated by means of an 800-W electrical

heating tape, wound round its outer surface. The temperature was controlled by a Skil Serie 9 temperature control unit, commanded by a Cr/Al thermocouple for which the leads passed through the hollow stirrer shaft. The helical ribbon agitator was made of stainless steel, fitted with a reverse pitch, center-mounted screw, and having a clearance of 3.5 mm with the wall of the vessel. The stirrer was equipped with a motor speed control and connected to a power measuring system. The following ingredients were used at the prepolymerization stage: 0.05 parts benzoyl peroxide, 0.05 parts dicumyl peroxide, 0.1 part of 2,6-di-*tert*-butyl-*p*-cresol, 0.05–0.08 parts of *tert*-dodecyl mercaptan. The styrene was used as supplied and in all cases homogeneous solutions were obtained without any noticeable insoluble gels.

In the early stages of the work the prepolymerized syrup was transferred into long glass tubes. The tubes were sealed under nitrogen, placed in an oven, and subjected to the following temperature program: 72 h at 90°C, 24 h at 125°C, and 5 h at 150°C. The solid blocks were then granulated and dried in a vacuum oven at 60°C for about 3 days. Later, a 5-L stirred autoclave was used. The syrup was suspended in water containing 0.07% PVAc, 0.02% sodium dodecyl benzene sulfonate, and 0.1% sodium chloride. The partially polymerized styrene was further polymerized to high conversion, under pressure in the stirred autoclave ($p \approx 100$ psig) with the following heating program: 1.5 h at 120°C, 3 h at 130°C, and 4 h at 140°C.

Rubber phase volume determinations were carried out according to the method of Keskkula and Turley.¹⁴

A "Zeiss Epival" interference microscope (Carl Zeiss Jena, Ltd.) was used in the shearing mode to follow the phase morphology during the prepolymerization stage. In this way it was possible to establish the time of phase inversion, the structure, and the size of the dispersed rubber phase. TEM micrographs of the TPS polyblends were taken by the same procedures described elsewhere.¹⁵

Dynamic mechanical measurements were carried out with the Rheovibron DDV-II viscoelastometer from compression moulded sheets (200°C) at a fixed frequency of 11 Hz.

Izod impact strength and stress-strain measurements were taken in accordance with ASTM-D 256-73 and ASTM-D 638-77a methods, respectively. The impact testing machine has been described elsewhere.¹⁶

TABLE I
TPS Polyblends Containing HCPB and LCPB as Rubber Phase^a

Polyblend	Type and amount of rubber ^b	Chain transfer agent ^c	Rate of agitation (rpm)	Temperature of first-stage (°C)	Finishing cycle
TPS-16	7 parts LCPB	0.08	150	80	Static-bulk
TPS-21	7 parts LCPB	0.05	250	80	Suspension
TPS-17	7 parts HCPB	0.08	150	80	Static-bulk
TPS-18	7 parts HCPB	0.08	180	80	Static-bulk
TPS-34	7 parts HCPB	0.05	200	80	Static-bulk
TPS-22	7 parts HCPB	0.05	250	80	Static-bulk

^a LCPB is a low *cis*-1,4-polybutadiene manufactured by ISR Co. under the trade name Intene 55 $\overline{M}_n = 160,000$ g mol⁻¹; HCPB is a high *cis*-1,4-polybutadiene manufactured by Shell Co. under the trade name Cariflex BR-1220 $\overline{M}_n = 120,000$ g mol⁻¹.

^b The amount of rubber is based on parts per 100 parts of styrene + rubber.

^c The amount of chain transfer agent is based on parts per 100 parts of styrene + rubber.

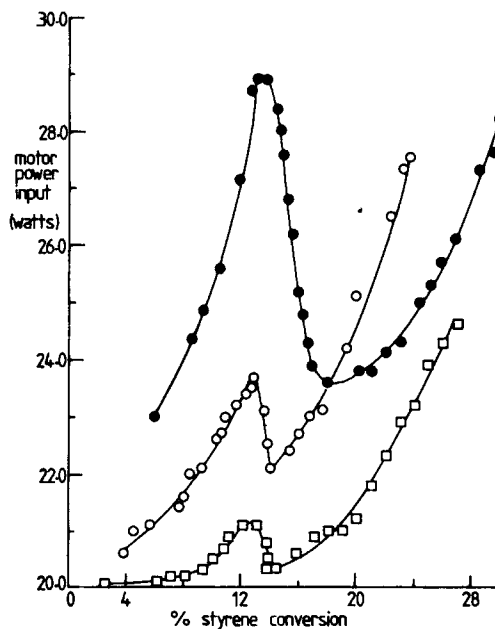


Fig. 2. Phase changes in the polymerization of styrene in the presence of different rubbers. Rubber content 7%; rpm = 250. (O) TPS-21: LCPB, $\overline{M}_n = 160,000 \text{ g mol}^{-1}$; (\square) TPS-22: HCPB, $\overline{M}_n = 120,000 \text{ g mol}^{-1}$; (\bullet) TPS-23: SB-8, $\overline{M}_n = 320,000 \text{ g mol}^{-1}$.

RESULTS AND DISCUSSION

The prepared TPS polyblends, their ingredients, and their polymerization conditions are listed in Table I. The molecular weights of the polystyrene matrix of the copolymers were $\overline{M}_n \approx 80,000 \text{ g mol}^{-1}$ and $\overline{M}_w \approx 220,000 \text{ g mol}^{-1}$.

Phase Changes during the Prepolymerization Stage

Phase changes were followed with the interference microscope and by direct measurement of the electrical power input to the stirrer motor with a watt meter, while keeping the agitation rate constant and the mechanical losses at a minimum. Figure 2 shows the phase changes in the polymerization of styrene in the presence of different type and molecular weight rubbers, recorded in terms of motor power input vs. styrene conversion. Phase inversion takes place between the maximum and the minimum of the curves, which have the same general shape. The rubber particles come into existence at the phase inversion point.¹⁷ Keeping the amount of rubber, the agitation rate, and the polymerization conditions constant, the phase inversion always starts at approximately the same styrene conversion while its duration depends on the viscosity of the system. In TPS-23 containing a graded triblock SBS polymer (SB-8), $\overline{M}_n = 320,000 \text{ g mol}^{-1}$ ¹⁵ inversion takes place within a range of about 5% styrene conversion. On the other hand, in TPS-21 containing LCPB rubber, $\overline{M}_n = 160,000 \text{ g mol}^{-1}$, phase inversion is fast within the range of 1%.

These results show clearly that an attempt to improve the impact strength by increasing the amount of rubber in the initial solution will make phase in-

TABLE II
Effect of Agitation Rate on Rubber Phase Volume (RPV)

Polyblend	Agitation rate (rpm)	Particle size distribution (μm)	Rubber content (%)	Rubber phase volume (%)	Rigid phase volume PS (%)
TPS-16	150	3.0-45.0	7	28.0	72.0
TPS-21	250	2.0-18.5	7	23.0	77.0
TPS-17	150	2.5-35.0	7	29.2	70.8
TPS-18	180	2.5-35.0	7	28.0	72.0
TPS-34	200	2.0- 8.5	7	26.0	74.0
TPS-22	250	2.0- 6.0	7	21.5	78.5

version more difficult, and would require efficient and costly stirrers. In high viscosity rubber solutions lower polymerization rates could be more helpful towards completion of the phase inversion. As has been shown in the published literature, and will be discussed in the next paragraphs, the advantage of the graft interpolymerization method is that occluded polystyrene can increase the rubber phase volume (rubber + polystyrene occlusions), producing different levels of impact strength for the same initial amount of rubber.

Factors Influencing the Rubber Phase Volume (RPV)

Rubber phase volume studies were carried out on TPS polyblends containing LCPB and HCPB as rubber phase. Table II shows the effect of agitation rate on rubber phase volume. The rubber particles size, rubber phase volume, and agitation rate are interrelated; rubber phase volume and rubber particles size are decreased by increasing the agitation rate. Similar results were observed by Wagner and Robeson¹⁸ in TPS polyblends containing LCPB as rubber phase.

Better understanding of the correlation between rubber phase volume, rubber particles size, and agitation rate is obtained from the use of various microscopic techniques. In Figures 3 and 4, the polyblends have the same rubber content of LCPB or HCPB, and rubber phase volume decreases with increase of agitation rate. As a result, smaller amounts of polystyrene are occluded within the rubber membranes. Interference microscopy has shown¹⁷ that the reduction of rubber phase volume occurs immediately after the phase inversion by the dispersion and rupture of the rubber membranes.

A comparison of the pairs TPS-16, TPS-17 and TPS-21, TPS-22, respectively (Table II and Figs. 3 and 4) shows that, for the same agitation rate, the rubber particles size and rubber phase volume depend on the type of rubber. This can be explained as arising from the higher solution viscosity of LCPB than of HCPB rubber in styrene. As is shown in Figure 2, the higher the viscosity of the rubber solution in styrene, the longer the duration of the phase inversion process and the more difficult for this to be accomplished. Therefore, the resulting rubber particles are larger, the system is more viscous, and it becomes more difficult to rupture their membranes by shearing.

Dynamic Mechanical Properties

For blends of incompatible polymers the mechanical response reflects mo-

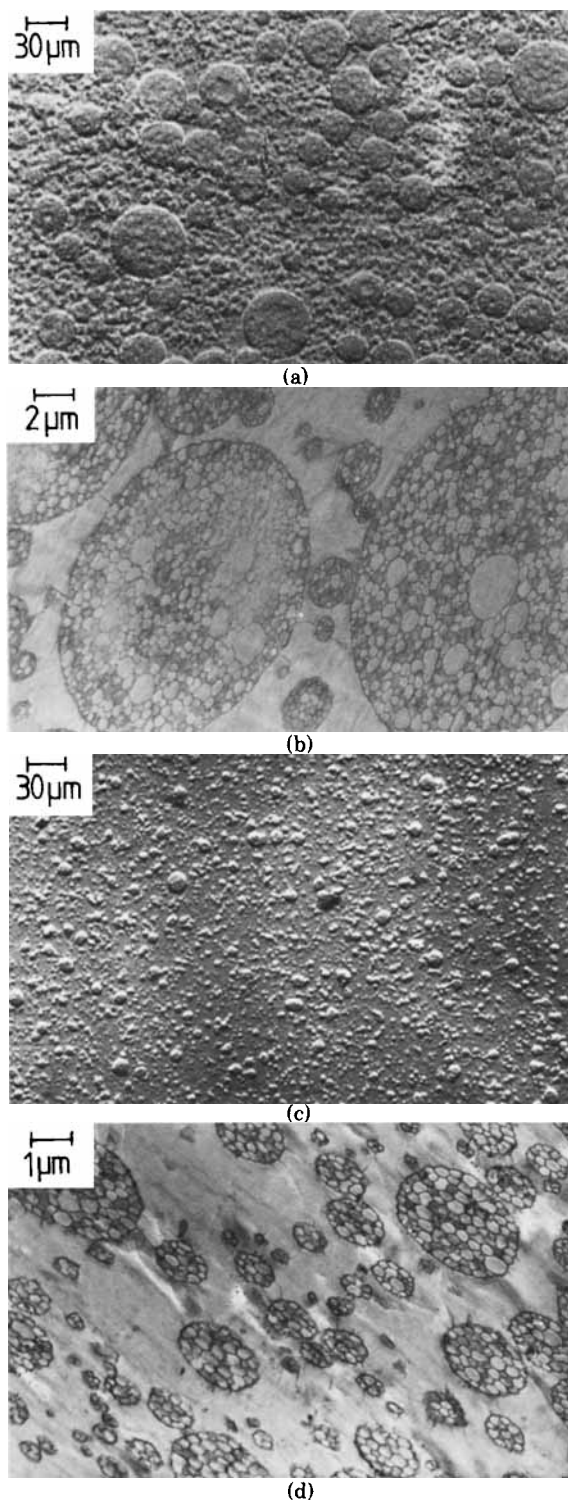
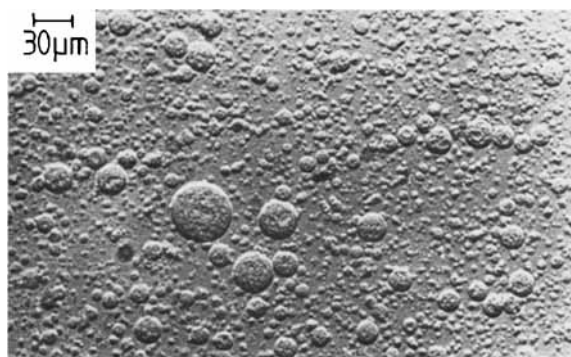
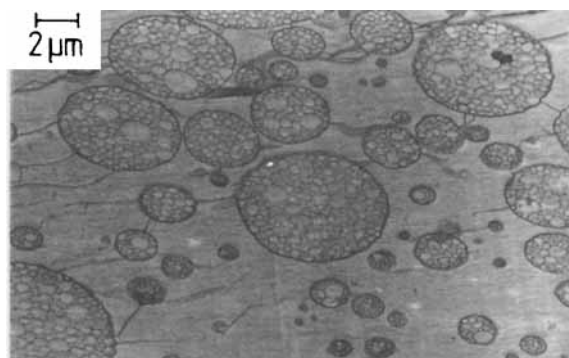


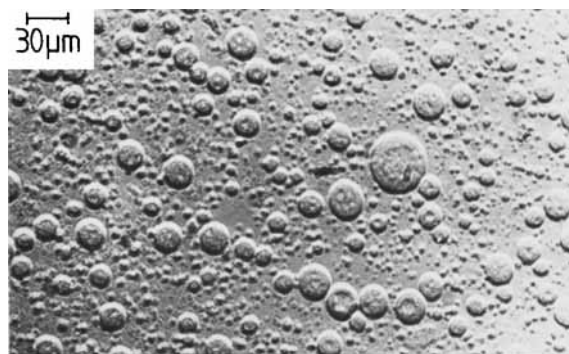
Fig. 3. TPS blends containing LCPB as rubber phase: (a), (b) TPS-16: RPV = 28%; (c), (d) TPS-21: RPV = 23%; (a), (c) interference shear photomicrographs; (b), (d) TEM photomicrographs.



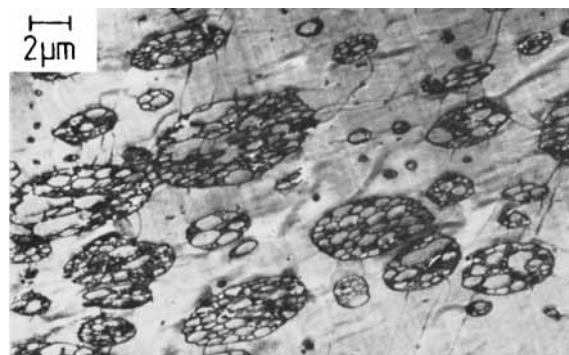
(a)



(b)



(c)



(d)

Fig. 4. TPS blends containing HCPB as rubber phase. (a), (b) TPS-17: RPV = 29.2%; (c), (d) TPS-18: RPV = 28.0%; (e), (f) TPS-22: RPV = 21.5%; (a), (c), (e): interference shear photomicrographs; (b), (d), (f): TEM photomicrographs.

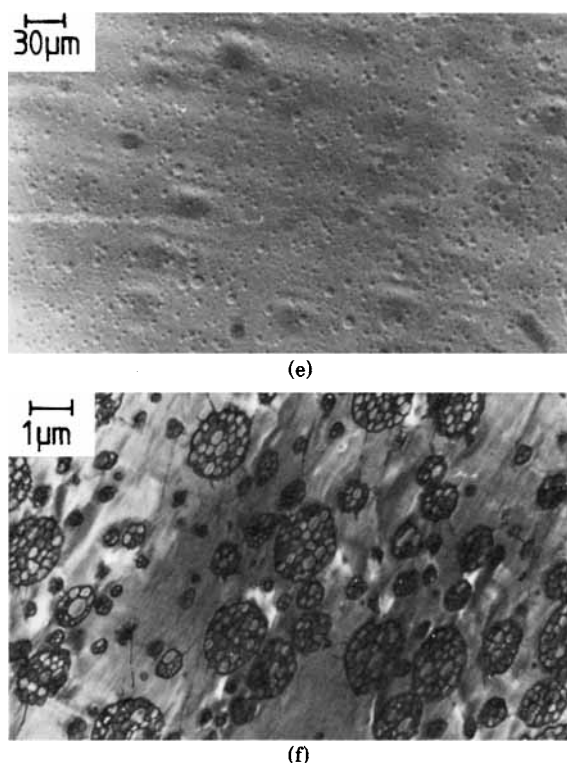


Fig. 4 (continued from previous page.)

lecular relaxation processes characteristic of each component and new or modified relaxation processes characteristic of the blend. These new or modified processes arise, for example, from intermolecular mixing or constraint of chain movement at the interface between matrix and dispersed particles.

TPS polyblends show two prominent loss peaks, one at low temperature which is due to the glass transition of the rubber (e.g., -78°C for LCPB and -98°C for HCPB), and one at high temperature which is due to the glass transition of the matrix (e.g., $+100^{\circ}\text{C}$ for polystyrene). The present studies have mainly concentrated on the rubber transition region, since the polystyrene transition is less affected.

TPS Polyblends Containing LCPB as Rubber Phase

Figure 5 shows the effect of rubber phase volume on the storage modulus (E'), loss modulus (E''), and loss tangent ($\tan \delta$) of TPS polyblends containing LCPB as rubber phase. The damping peak height and the area under the peak decrease with decreasing rubber phase volume. Similar behavior is shown by the loss modulus. On the other hand, the fall in storage modulus in the vicinity of the rubber damping peak is less, and its level above the rubber glass transition increases with decreasing rubber phase volume. Since the amplitude of the dynamic transition of a component in a polyblend is directly related to the relative

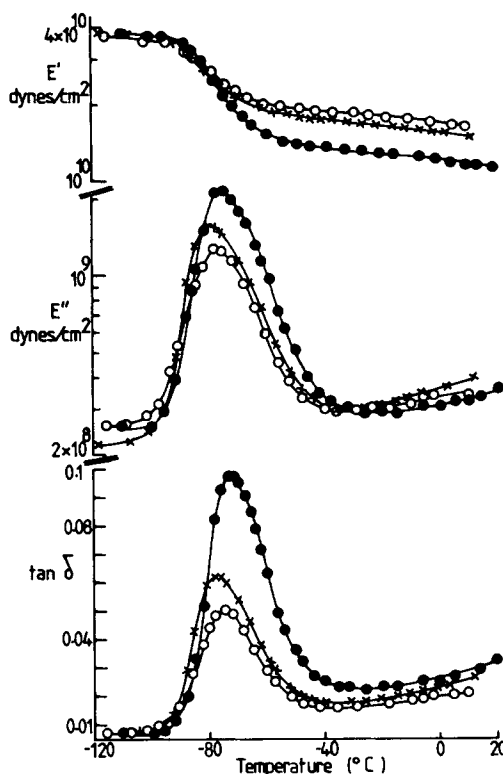


Fig. 5. Effect of LCPB rubber phase volume (RPV) on dynamical mechanical properties of TPS. Rubber content 7%. (●) TPS-16: RPV = 28%; (○) milled TPS-16: RPV = 17%; (x) TPS-21: RPV = 23%.

quantity of the component itself,¹⁹ the above effects can be explained by the decrease of the dispersed rubber phase (rubber plus occluded polystyrene) undergoing modulus relaxation. Wagner and Robeson¹⁸ noticed that the rubber glass transition $(\tan \delta)_{\max}$ shifts to lower temperatures with decreasing rubber phase volume. They attributed this shift to a decrease in grafted polystyrene. However, a recent publication¹¹ shows a shift of the rubber glass transition to lower temperatures in TPS polyblends having the same levels of grafting and crosslinking. Therefore, there is evidence to explain on better grounds the rubber glass transition shift. Cooling the TPS polyblends, a state of triaxial tension is expected in each particle as a result of the different thermal expansion coefficients of rubber phase and polystyrene matrix.²⁰ This tension results in an increase in rubber free volume and therefore in a decrease of the glass transition temperature. Since smaller rubber particles could support a more intense triaxial tension²¹ and, furthermore, a decrease in rubber phase volume corresponds to a decrease in rubber particles size (shown earlier), a progressive increase in rubber free volume is expected. Hence, the progressive shift of the rubber glass transition to lower temperatures with decreasing rubber phase volume is explained.

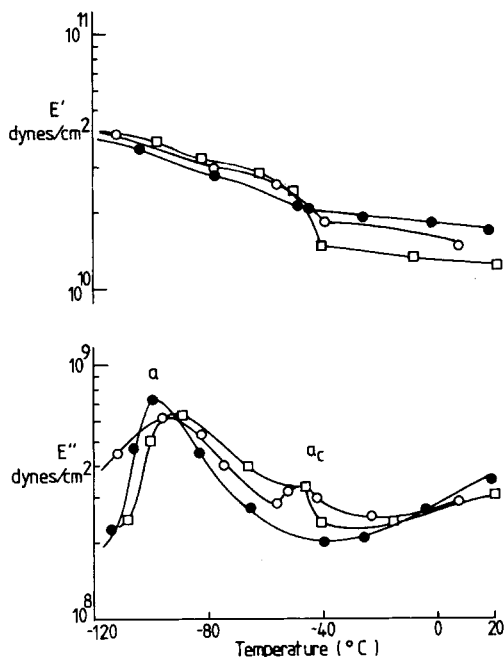


Fig. 6. Effect of HCPB rubber phase volume (RPV) on α_c and α transitions. Rubber content 7%. (●) TPS-22: RPV = 21.5%; (○) TPS-34: RPV = 26.0%; (□) TPS-17: RPV = 29.2%.

TPS Polyblends Containing HCPB as Rubber Phase

Figure 6 shows the dynamic mechanical properties of TPS polyblends containing HCPB as rubber phase. All polyblends show two loss modulus peaks at approximately -86 – 90°C and -40°C , respectively. The storage modulus also shows two increases at the above temperatures. The higher temperature relaxation is a crystallization peak, detected as the sample is cooled from above room temperature. A similar crystallization peak has been detected by cooling a sample on a differential scanning calorimeter (Perkin-Elmer DSC-2B). Furthermore, Collins and Chandler²² have noticed a similar peak by cooling a sample of HCPB in a DSC. This relaxation, called the α_c transition, is attributed to molecular motions within the crystalline phase.²³ The lower temperature relaxation is the glass transition (α transition) caused by the micro-Brownian motion of the noncrystalline regions under the structural restraint of the neighboring molecular chains in the crystalline regions.

The level of the storage modulus between room temperature and α_c transition in the polyblends of Figure 6 increases as a result of the reduction of rubber phase volume. At -40°C (α_c transition) the storage modulus increases very rapidly as the rubber crystallizes. The magnitude of the modulus rise increases with increasing rubber phase volume. Crystallinity modifies the modulus curve by at least two mechanisms. First, the crystallites act as crosslinks by tying segments of many molecules together. Second, the crystallites have very high moduli compared with the rubbery amorphous parts, so that they behave as rigid fillers in an amorphous matrix.²⁴

The developed crystallinity has also a great effect on the glass transition (α -transition). The height of the glass transition peak (E''_{max}) decreases as the rubber

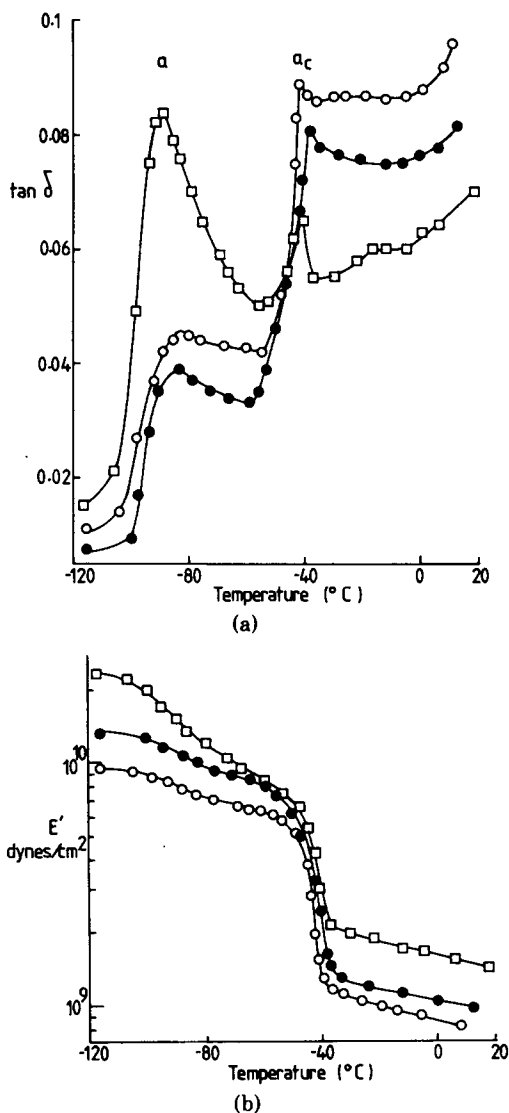


Fig. 7. Effect of crystallinity on the dynamic mechanical properties of three gel phases isolated from polyblends of decreased rubber phase volume. Rubber content 7%. (●) TPS-17: RPV = 29.2%; (○) TPS-18: RPV = 28.0%; (□) TPS-22: RPV = 21.5%.

phase volume increases, contrary to the observed behavior of polyblends containing LCPB in Figure 5.

Because of the similar reaction conditions, the level of crosslinking for each polyblend can be assumed to be the same; it is therefore proposed, on the basis of the above results, that for some reason crystallinity increases with increase of rubber phase volume. The decrease of the height of the glass transition peak (E'_{\max} in Fig. 6) is then explained as a consequence of the inhibiting effect of crystallites on the motion of segments in the amorphous region; hence, the amount of energy dissipated as heat progressively decreases with increasing rubber phase volume.

To demonstrate further the effect of crystallinity on the relaxation behavior of the above TPS/HCPB polyblends, the dynamic mechanical properties of the gel phases (crosslinked rubber and occluded polystyrene) were investigated. Figure 7 shows the storage moduli (a) and loss tangents (b) of three gel phases isolated from three polyblends with decreasing rubber phase volume. The storage modulus shows two steps, a very steep one at -40°C as the rubber crystallizes and a less steep one at -90°C due to the glass transition. The magnitude of the modulus rise at -40°C is greater for the gel phase isolated from the polyblend containing the largest rubber phase volume (hence, the increased amount of occluded polystyrene). These results are in good agreement with the storage modulus rise of the actual TPS/HCPB polyblends in Figure 6. It should be pointed out that the increase of occluded polystyrene in the gel phase leads to reinforcement of the rubber matrix. Thus at room temperature the modulus of the gel phase is expected to increase progressively. The gel phases of TPS-17 and TPS-18 follow the above pattern; on the other hand, the gel phase of TPS-22 with the least amount of occluded polystyrene shows the highest room temperature modulus. The reason for this deviation is not readily apparent.

The inhibiting effect of crystallites on the motion of segments in the amorphous regions is apparent from the loss tangent curves. $\tan \delta$ at -40°C decreases steeply, especially for the gel phase with the largest amount of occluded polystyrene (gel phase of TPS-17). The height of the glass transition decreases as the amount of occluded polystyrene increases.

Following from the above discussion, the question may be raised, how the variation of rubber phase volume influences the degree of crystallinity. This can possibly be explained as a result of strain-induced crystallization. When these polyblends are molded and cooled, the continuous polystyrene phase becomes glassy at about 90°C . On further cooling a state of triaxial tension must develop in each rubber particle if adhesion and crosslinking requirements are met. Cooling the polyblends to subzero temperatures, the triaxial tension intensifies further. However, increasing the rubber phase volume, the interfacial area between the polystyrene and rubber (including that interfacial area within the occluded particles) increases; hence a larger area of the rubber is under triaxial tension. The molecules of high *cis*-1,4-polybutadiene can then be preferentially aligned along the stretch directions, inducing additional crystallinity.

Mechanical Properties

Table III shows the tensile properties and impact strength of TPS polyblends containing LCPB or HCPB as rubber phase. The introduction of the rubber (within Young's modulus typically of 20 MN m^{-2}) in the glassy polystyrene (Young's modulus typically 3000 MN m^{-2}) leads to reduction in the modulus of the prepared TPS polyblends. The reduction of the Young's modulus follows the increase in the rubber phase volume, in agreement with the dynamic mechanical data discussed in the preceding section. The tensile strength increases due to the decrease in the volume of the softer and weaker rubber phase. The elongation decreases with decreasing rubber phase volume while the impact strength is not influenced very much. Turley and Keskkula¹¹ found that elongation and impact strength decrease proportionally with rubber phase volume. They explained this behavior as a result of less crazes development by small

TABLE III
Tensile Properties and Impact Strength of TPS Polyblends Containing LCPB or HCPB as Rubber Phase

Polyblend	Type and amount of rubber	Rubber phase volume (%)	Young's modulus (MN/m ²)	Tensile strength (MN/m ²)	Elongation (%)	Impact strength (kJ/m ²)
TPS-16	7 parts LCPB	28.0	1310	20.3	28.0	7.9
TPS-21	7 parts LCPB	23.0	1520	18.4	20.0	8.6
TPS-17	7 parts HCPB	29.2	1380	19.9	45.0	9.9
TPS-18	7 parts HCPB	28.0	1385	20.3	45.0	10.0
TPS-22	7 parts HCPB	21.5	1725	22.5	13.0	10.0
Styron 457 ^a	? LCPB		1827	18.6	35.0	7.3

^a Styron 457 is a high impact grade polystyrene prepared by Dow Chemical Co.

particles compared to large ones. However, Wagner and Robeson,¹⁸ examining polyblends with larger range of rubber phase volumes, found that impact strength and elongation pass through a maximum at about 22% RPV. Since the rubber toughening mechanism is still under examination, further work could lead to more positive results.

CONCLUSIONS

The present study shows that TPS polyblends containing high *cis*-1,4-polybutadiene (HCPB) show a good balance of tensile and impact properties. However, the crystallinity developing at -40°C as the samples are cooled from above room temperature and the consequent hardening of the rubber particles are expected to give poor low temperature impact properties, i.e., the efficiency of rubber particles to create and terminate crazes decreases. It is significant that crystallinity can be decreased by decreasing the rubber phase volume.

We wish to thank General Electric Corporate Research and Development, Schenectady, N.Y., for financial support, and ICI Petrochemicals and Plastics Division for the donation of the autoclave. We also wish to thank Dr. D. J. Walsh for helpful discussions, and Mr. N. A. H. Salpadorou for carrying out the electron microscopic work.

References

1. D. J. Angier and E. M. Fettes, *Rubber Chem. Technol.*, **38**, 1164 (1965).
2. J. L. Amos, *Polym. Eng. Sci.*, **4**, 1 (1974).
3. G. E. Molau, *J. Polym. Sci. A*, **3**, 4235 (1965).
4. G. E. Molau and H. Keskkula, *J. Polym. Sci. A-1*, **4**, 1595 (1966).
5. K. Kato, *Polym. Eng. Sci.*, **7**, 38 (1967).
6. B. W. Bender, *J. Appl. Polym. Sci.*, **9**, 2887 (1965).
7. G. F. Freeguard and M. Karmarkar, *J. Appl. Polym. Sci.*, **15**, 1649, 1657 (1971).
8. J. D. Moore, *Polymer*, **12**, 478 (1971).
9. H. Keskkula, S. G. Turley, and R. F. Boyer, *J. Appl. Polym. Sci.*, **15**, 351 (1971).
10. J. Silberberg and C. D. Han, *J. Appl. Polym. Sci.*, **22**, 599 (1978).
11. S. G. Turley and H. Keskkula, *Polymer*, **21**, 466 (1980).
12. C. B. Bucknall, *J. Mater.*, **4**, 214 (1969).
13. C. G. Bragaw, *Adv. Chem. Ser.*, **99**, 86 (1971).
14. H. Keskkula and S. G. Turley, *J. Polym. Sci., Polym. Lett. Ed.*, **7**, 697 (1969).
15. K. Sardelis, H. J. Michels, and G. Allen, to appear.

16. E. Plati and J. G. Williams, *Polymer*, **16**, 915 (1975).
17. K. Sardelis, Ph.D. thesis, University of London, 1981.
18. E. R. Wagner and L. M. Robeson, *Rubber Chem. Technol.*, **43**, 1129 (1970).
19. R. A. Dickie, *J. Appl. Polym. Sci.*, **17**, 45 (1973).
20. R. H. Beck, S. Gratch, S. Newman, and K. C. Rusch, *J. Polym. Sci., Polym. Lett. Ed.*, **6**, 707 (1968).
21. J. A. Schmitt, *J. Polym. Sci. C*, **30**, 437 (1970).
22. E. A. Collins and L. A. Chandler, *Rubber Chem. Technol.*, **39**, 193 (1966).
23. M. Takayanagi, *Mem. Fac. Eng. Kyushu Univ.*, **23**, 41 (1963).
24. L. E. Nielsen, *Mechanical Properties of Polymers and Composites*, Marcel Dekker, New York, 1974, Vol. 1, p. 54.

Received January 17, 1983

Accepted April 25, 1983