Toughened polystyrene containing block, graded block and randomized copolymers of butadiene–styrene

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During the polymerization of styrene in the presence of a block, graded block, or randomized copolymer of butadiene–styrene, new morphologies of dispersed rubber particles are observed (i.e. cylindrical-type, core-shell, lamellar). These morphologies are the result of (i) polymer–polymer interactions between the copolymer and the '*in situ*' formed polystyrene, (ii) an intramolecular phase separation within the polybutadiene and polystyrene sequences of the copolymer, and (iii) the mechanical treatment during the polymerization process. Elucidation of the structural characteristics of these morphologies has been achieved by following the phase changes during the polymerization and the changes in the intramolecular phase separation of the copolymers with respect to variation of their composition. The randomized copolymers were capable of forming toughened polystyrene blends with similar morphology to those containing polybutadiene rubber, but with enhanced adhesion between the rubber and polystyrene matrix. The structural characteristics of such randomized copolymers have been established.

(**Keywords: butadiene–styrene copolymers; toughened polystyrene; polymerization; morphology; polybutadiene**)

INTRODUCTION

Physical blending of two incompatible homopolymers produces a polyblend with inferior mechanical properties. The cause of such weak and brittle mechanical behaviour lies in the poor adhesion between the two polymer phases. Adhesion between two phases can be improved by adding block or graft polymers with blocks or segments which have the same chemical composition as those of the two homopolymers. Direct evidence of the interfacial activity of the above copolymers can be found in the production of toughened polystyrene (TPS) blends by the graft interpolymerization process[1]. The *in-situ* generated graft polymer of butadiene–styrene tends to accumulate at the interface between the polystyrene and polybutadiene, thereby providing the necessary interfacial adhesion in the TPS blend.

During the last decade, ternary and binary physical blends of polystyrene, polybutadiene with SB di- or tri-block polymers have been studied[2–5]. Some of the combinations gave products with very useful properties. It is apparent from such work that the relative composition and molecular weights of the block copolymers and of the corresponding homopolymers play a very important part in the optimization of the physical properties of the blends. The present study was directed towards the use, as rubber phase, of the graded block and randomized copolymers of butadiene–styrene described elsewhere[6]. The well-established method of preparing toughened polystyrene blends by graft interpolymerization of styrene in the presence of polybutadiene rubber[7,8] was extended to the polymerization of styrene in the presence of the above copolymers of various structures. The effect of the structure and composition of the copolymers on the morphology and mechanical properties of polyblends are examined.

EXPERIMENTAL

The graft interpolymerization process followed in this work comprised two stages. In the first (prepolymerization cycle) stage, the styrene monomer was partially polymerized in the presence of butadiene–styrene copolymer with shearing agitation until about 30% styrene conversion. In the second stage (finishing cycle) the styrene was further polymerized to high conversion in glass tubes (static bulk polymerization), or in a 5 litre stirred autoclave (dispersion polymerization).

The reactors used in the two stages, the reaction conditions, as well as the experimental methods for chemical, physical and mechanical characterization of the prepared TPS blends, have been described elsewhere[8].

The prepared TPS blends and polymerization conditions are shown in *Table 1*. The butadiene–styrene copolymers used in the preparation of the TPS blends are listed in *Table 2*. Their monomer sequence distribution can be visualized as follows:

'Tri-block polymer': (styrene)–(butadiene)–(styrene) prepared by anionic sequential polymerization.

'Graded block SBS polymer': (styrene)–(butadiene→styrene)–(styrene).

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Table 1 TPS blends containing block, graded block and randomized copolymers of butadiene–styrene

Polyblend	Type and amount of rubber[a]	Rate of agitation (RPM)	Temperature at first stage (°C)	$\bar{M}_n \times 10^{-3}$ of polystyrene matrix (g mole^{-1})	$\bar{M}_w/\bar{M}_n$	Finishing cycle
TPS-5	6.5 parts SBS	100	90	35	2.9	Static bulk
TPS-23	7 parts SB-8	250	80	75	2.8	Dispersion
TPS-29	7 parts SB-2	320	80	77	2.8	Dispersion
TPS-26	7 parts SB-4	400	80	87	2.9	Dispersion
TPS-24	7 parts SB-5	250	80	85	2.7	Dispersion
TPS-25	7 parts SB-3	320	80	83	2.7	Dispersion
TPS-35	7 parts SB-7	150	80	87	2.7	Static bulk
TPS-28	7 parts SB-6	320	80	86	2.7	Dispersion

[a] Amount of rubber is based on parts per 100 parts of styrene plus the copolymer

Table 2 Butadiene–styrene copolymers used in TPS blends

Polymer	$\bar{M}_n \times 10^{-4}$ (g mole^{-1})	$\bar{M}_w/\bar{M}_n$	Copolymer type	Total styrene content (wt%)	Block styrene content (wt%)	Polybutadiene structure (wt%) 1,2-vinyl	*cis*-1,4	*trans*-1,4
SBS[a]	11.0	1.20	Tri-block	30.0	30.0	–	–	–
SB-8[b]	32.0	1.90	Graded block SBS	38.0	25.3	5.0	21.0	34.0
SB-2	21.2	1.10	Graded block SB	41.0	33.0	5.8	20.0	32.5
SB-4	20.8	1.08	Randomized	45.7	27.7	8.1	18.7	26.0
SB-5	17.5	1.18	Randomized	44.3	24.8	9.6	19.8[c]	25.1[c]
SB-3	19.5	1.19	Randomized	45.8	12.4	18.7	15.4[c]	22.2[c]
SB-7	21.9	1.13	Randomized	28.6	11.5	8.5	24.7	41.3
SB-6	23.8	1.10	Randomized	29.6	9.7	9.3	22.4	41.7

[a] SBS Manufactures by Shell Co., under the tradename Cariflex TR-1101

[b] SB-8 Supplied by S. L. Aggarwal, General Tire and Rubber Co.

[c] Styrene content and polybutadiene microstructure were obtained by 300 MHz ^{1}H n.m.r., values marked ([c]) have been determined by i.r

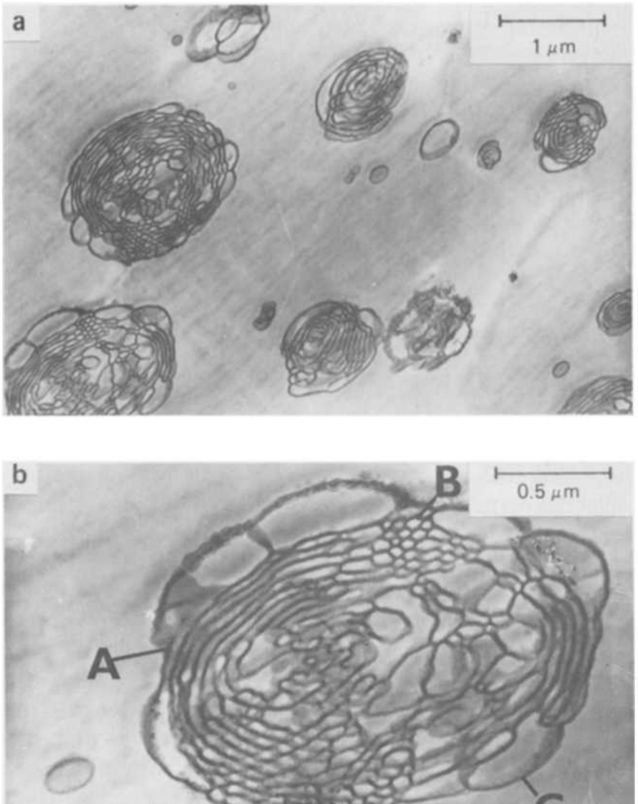

Figure 1 Transmission electron photomicrographs of TPS-5 containing a tri-block SBS polymer (Cariflex TR-1101) as rubber phase

'Graded block SB polymer': (butadiene)–(butadiene→styrene)–(styrene). The latter two being prepared by anionic copolymerization of butadiene and styrene mixture. Initially the middle block is richer in butadiene with a gradual change in composition until eventually it becomes richer in styrene. Incremental addition of polar compounds decreases the length of polybutadiene and polystyrene sequences of the graded block SB polymer, and the structure of the copolymers so obtained (designated '*randomized*' in this work) is best represented as (butadiene→styrene) (styrene). A further increase in the relative amount of polar compound can lead to a completely random copolymer. The detailed preparation and properties of the above copolymers are described elsewhere[6].

RESULTS AND DISCUSSION

Morphology

TPS blends containing block or graded block polymers of butadiene–styrene. Figure 1 shows a morphology of rubber particles dispersed in a continuous polystyrene matrix as observed for sample TPS-5 containing a tri-block SBS polymer. For each of these particles the ultramicrotome sections show three substructures: (i) a striped pattern of alternating bands of polystyrene and polybutadiene (area A), (ii) domains of polystyrene arranged in a hexagonal array (area B) and (iii) larger domains of polystyrene between polybutadiene bands (area C). Since a block polymer adopts different domain structures (depending on its composition) the areas A, B indicate that the above particles are composed of

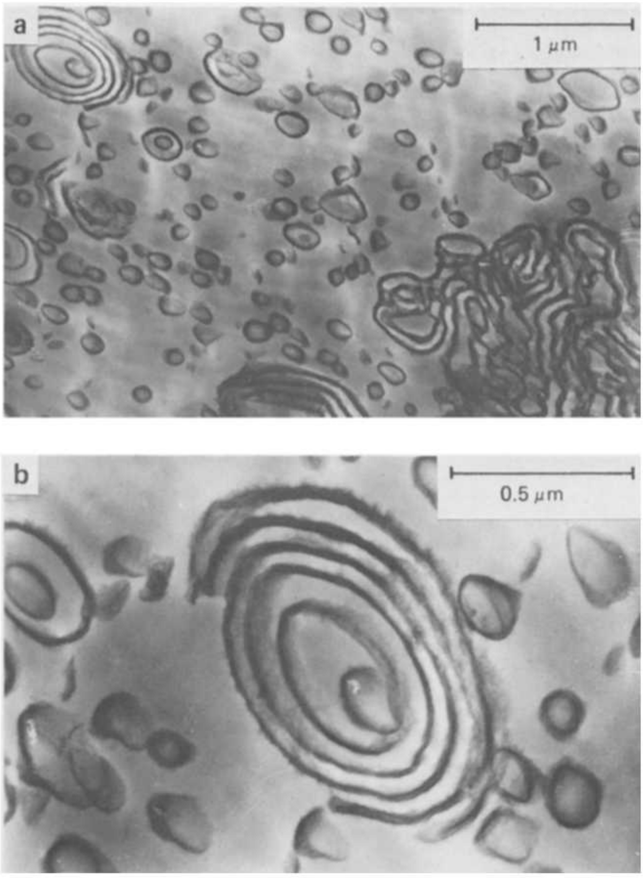

Figure 2 Transmission electron photomicrographs of TPS-23 containing a graded block SBS polymer (SB-8) as a rubber phase

cylindrical polystyrene domains embedded in polybutadiene. This is supported by measurements of the diameter of the suggested cylinders (D_s), the distance between the axes of two adjacent cylinders (d_{int}) in area B, and by substituting these values in the formula:

$$\phi = 0.91\left(\frac{D_s}{d_{int}}\right)^2$$

which gives the volume fraction of polystyrene. In the present case where $D_s = 300$ Å, $d_{int} = 500$ Å, the above formula gives $\phi = 0.32$ which is very near to the volume fraction of the polystyrene in the block polymer ($\sim 30\%$). The formation of these 'cylindrical-type' dispersed rubber particles can be explained as follows: the solution of the tri-block SBS polymer in styrene is clear (styrene is a non-selective solvent), but when some of the styrene is polymerized, the solution becomes turbid, showing macroscopic phase separation. Inoue *et al.*[9] have pointed out that when solvent was evaporated from block polymers in toluene, there was a critical concentration C^* (about 10%) at which each segment of the block polymer underwent phase separation, and aggregated into characteristic micelles. This is similar to the behaviour of soap molecules in aqueous solution at the critical micelle concentration. Considering the styrene monomer as a casting solvent, the polymerization process can partly be treated as similar to the solvent casting process, i.e. cylindrical polystyrene micelles are formed as styrene is depleted by polymerization. However, one has also to take into account that the formation of polystyrene in the polymerizing solution of the tri-block SBS polymer in styrene takes place in parallel with the formation of the micelles. The polystyrene formed *in situ* has a higher molecular weight ($\bar{M}_n \simeq 35\,000\,\mathrm{g\,mole^{-1}}$) than the polystyrene block of the SBS ($\bar{M}_n \simeq 16\,500\,\mathrm{g\,mole^{-1}}$). In these circumstances it is expected that the polystyrene will form a separate phase[9]; thus the block polymer behaves as if it was incompatible with the progressively formed polystyrene homopolymer. Hence, there are two phases:

(i) a continuous phase of SBS block polymer (with the polystyrene sequences in the form of cylindrical micelles) in styrene; and

(ii) a dispersed phase of polystyrene in styrene.

As more styrene is converted to polystyrene, the second phase increases in volume and phase inversion takes place, which in the experiment was assisted by agitation. Hence, the rubber particles formed at phase inversion show the state of the phase system immediately before the inversion, i.e. cylindrical micelles of polystyrene containing regimes of occluded polystyrene homopolymer. As the polymerization progresses, the mixture becomes very viscous and there is no further change in these rubber particles.

Figures 2 and *3* show the morphology of the dispersed particles corresponding to polyblends TPS-23, TPS-29 containing the graded block SBS polymer (SB-8), and the graded block SB polymer (SB-2), respectively. Both Figures show the same 'shell–core' dispersed rubber particles structure, although in *Figure 2* there are particles showing an 'onion' structure.

The formation of the above particles can also be explained along the same lines as for TPS-5. However, the

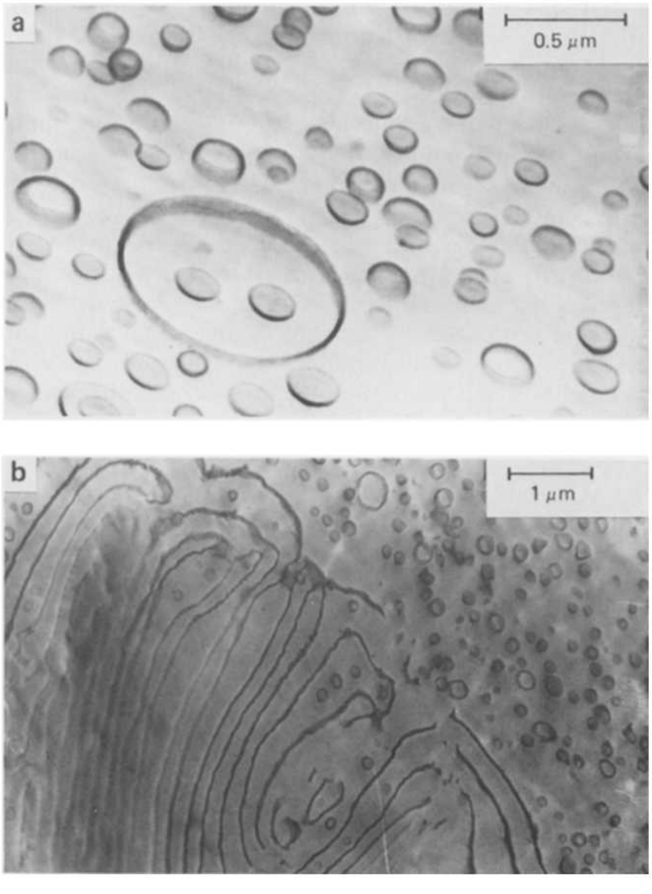

Figure 3 Transmission electron photomicrographs of TPS-29 containing a graded block SB polymer (SB-2) as rubber phase

polystyrene generated *in situ* has a molecular weight $\bar{M}_n \simeq 75\,000\,\mathrm{g\,mole^{-1}}$ which is very similar to the molecular weight of the polystyrene block of the copolymers (PS block of SB-2: $\bar{M}_n \simeq 70\,000\,\mathrm{g\,mole^{-1}}$, SB-8: $\bar{M}_n \simeq 80\,000\,\mathrm{g\,mole^{-1}}$). Thus the polystyrene is solubilized in the corresponding domains of the block polymers. Based on their composition, the copolymers SB-2, SB-8 in the polymerized styrene solution, are expected to form cylindrical polystyrene micelles: block styrene contents for SB-2, SB-8 are 33% and 25% respectively. Through solubilization by polystyrene homopolymer, these micelles are progressively transformed to the lamellae shown in *Figure 3b* which apparently has survived the shearing agitation. As more styrene is converted to polystyrene the polystyrene domains of the lamellae expand until the lamellae break by shearing agitation at about 14% styrene conversion. This phase change has been followed by monitoring the electrical power input to the stirrer motor at constant RPM, (Figure 2, ref. 8). Subsequently, the block polymer molecules form the 'core–shell' structure. The formation of the 'onion' structure observed in the case of the graded block SBS polymer (SB-8) can be understood by considering the presence of polystyrene end sequences of each molecule in either side of the polybutadiene domains of the lamellae structure.

By polymerization of styrene in the presence of a triblock SBS polymer (25% styrene), Aggarwal *et al.*[10] obtained a lamellar structure in the absence of shearing agitation, instead of 'cylindrical type' rubber particles expected from the block polymers' composition.

Therefore, it is understood that during polymerization of styrene in the presence of butadiene–styrene block polymer (20–30% styrene content), cylindrical polystyrene micelles are formed early in the reaction. If solubilization of the '*in situ*' formed polystyrene occurs in the corresponding domains of the block polymer, a lamellar structure will progressively develop. The lamella is an intermediate state in the following transformation:

$$\begin{array}{c} \text{cylinders} \rightarrow \text{lamellae} \rightarrow \text{spheres} \\ \text{(PS)} \quad \text{(PS, PB)} \quad \text{(PB)} \\ \xrightarrow{\hspace{3cm}} \\ \text{PS homopolymer} \end{array}$$

In the *absence* of shearing agitation, the transformation stops at the lamellar boundaries due to the high viscosity of the system. On the other hand, *with* shearing agitation the lamellae break, leading to the formation of the 'core–shell' structure.

TPS blends containing randomized copolymers of butadiene–styrene. Figure 4 shows the morphology of the dispersed rubber phase of TPS-26, TPS-24 and TPS-25 blends containing the randomized copolymers of ST:BD$\simeq$45:55 composition. A detailed examination of these structures in *Figure 4b* shows aggregates of 'core–shell' subparticles between polystyrene occlusions. In *Figure 4a* these subparticles are also shown to form large clusters. In a TPS blend containing polybutadiene rubber these subparticles are stabilized via the '*in situ*' formed graft butadiene–styrene copolymer. The size of the aggregates depends upon the shearing agitation during the prepolymerization stage[8,12]. In the present TPS blends the styrene content of the copolymers (~45%) is increasingly randomly distributed within the polybutadiene sequences, along SB-4 to SB-3 (*Table 2* indicates that the degree of randomness increases going down from SB-4 to SB-3). The bulky phenyl side group of the styrene units are expected to hinder sterically the grafting reaction, hence the formation of the '*in situ*' graft copolymer decreases from SB-4 to SB-3. Therefore, in TPS-6, containing the SB-4 copolymer, the subparticles are stabilized to a greater extent (*Figure 4a*) than in TPS-24 and TPS-25 which contain the SB-5 and SB-3 respectively (*Figures 4b* and *c*). The large polystyrene occlusions are formed as a result of coalescence between the subparticles.

The lack of influence of the graft copolymer was demonstrated by an inter-comparison of the stability of emulsions in samples of a series taken from the reactor (2–10% styrene conversion). Samples containing these

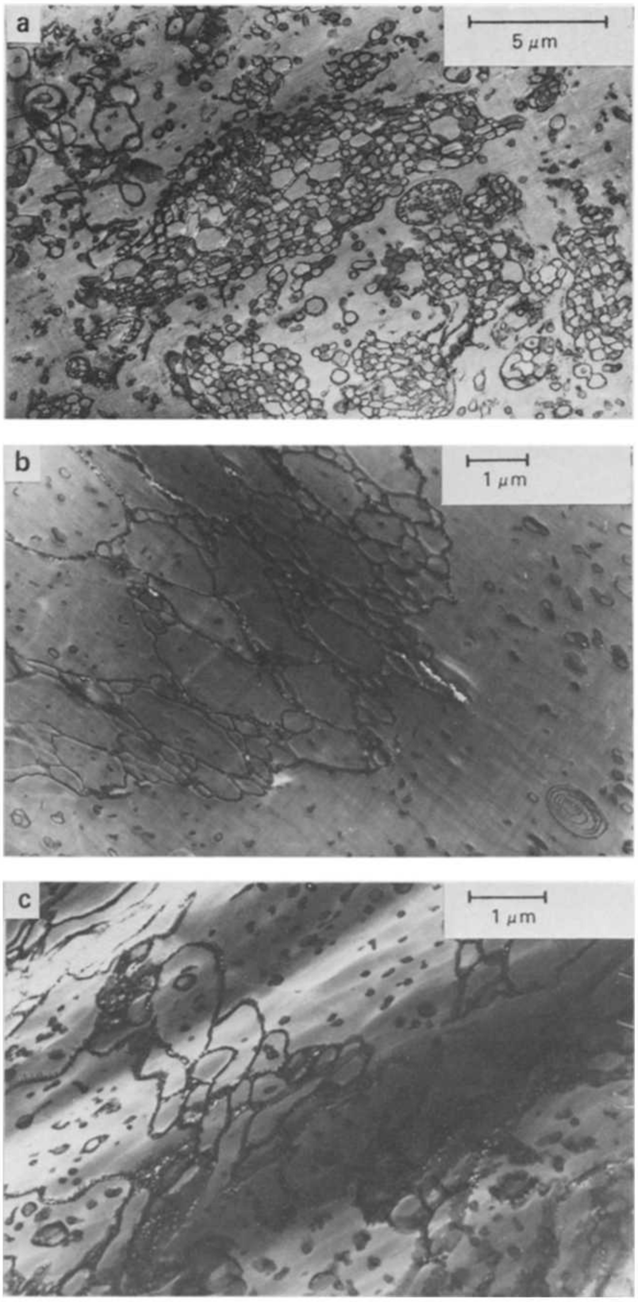

Figure 4 Transmission electron photomicrographs of TPS blends containing the randomized copolymers of ST:BD$\simeq$45:55 composition. (a) TPS-26:SB-4; (b) TPS-24:SB-5; (c) TPS-25:SB-3

randomized copolymers were demixed after approximately one day, while samples containing polybutadiene were stable more than nine days.

The polystyrene end blocks of the copolymers do not mix with the polystyrene matrix. Instead, as *Figure 4a* shows, they form separate domains embedded in the polybutadiene sequences. Hence they do not contribute to the stability of the subparticles as might have been expected.

The structures of TPS-28 and TPS-35 blends containing the randomized copolymers SB-6 and SB-7 of ST:BD $\simeq$ 30:70 composition, are shown in *Figure 5*. Since the styrene content is low, grafting efficiency increases; the '*in situ*' formed graft copolymer stabilizes the subparticles which form similar aggregates with the ones prepared from polybutadiene rubber[8]. In TPS-35, the polystyrene block of copolymer SB-7 also forms separate domains embedded in the polybutadiene (*Figure 5b*). The submicron aggregates in *Figure 5a*, which are smaller overall than those of *Figure 5b*, are the result of intense shearing agitation of the former during the prepolymerization.

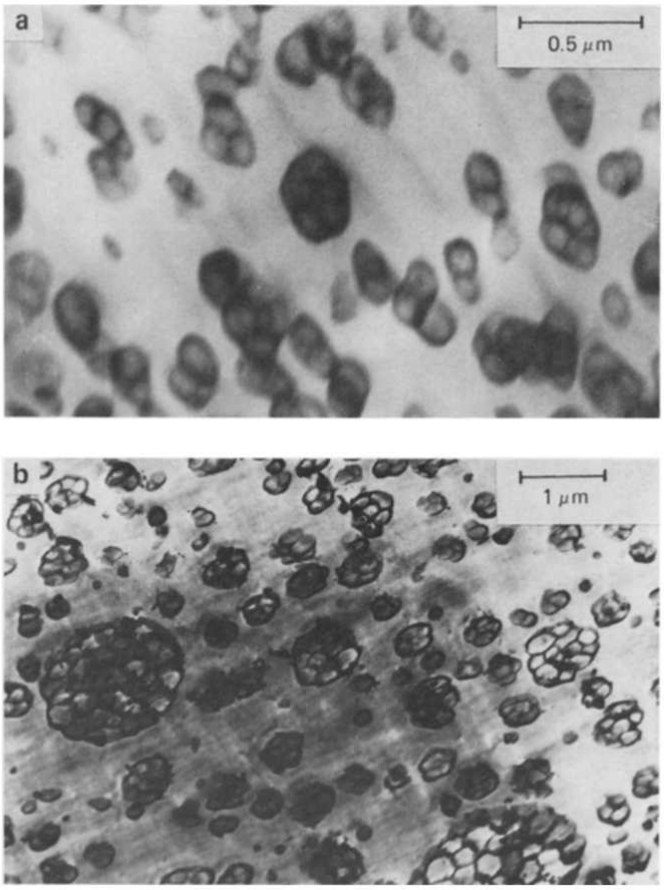

Figure 5 Transmission electron photomicrographs of TPS blends containing the randomized copolymers of ST:BD $\simeq$ 30:70 composition. (a) TPS-28:SB-6; (b) TPS-35:SB-7

Dynamic mechanical properties

Dynamic mechanical data for TPS blends containing the ST:BD $\simeq$ 45:55 composition randomized copolymers are presented in *Figure 6*. The low temperature loss peaks are due to the glass transition of the polybutadiene sequences of the copolymers on which styrene units are distributed randomly. Since the degree of randomness in the copolymers increases along SB-4 to SB-3 the loss modulus peaks of the corresponding TPS-26 to TPS-25 blends move towards higher temperature.

Following the decrease in rubber phase volume (*Table 3*), the storage modulus E' increases and the area under the loss modulus peaks decreases along TPS-26 to TPS-25. Since the amplitude of the dynamic transition of a component in a polyblend is directly related to the relative quantity of the component itself[15], the above effects are explained by the decrease of the dispersed rubber phase (rubber plus occluded polystyrene) undergoing modulus relaxation. Similar effects have been observed in TPS blends containing polybutadiene[8].

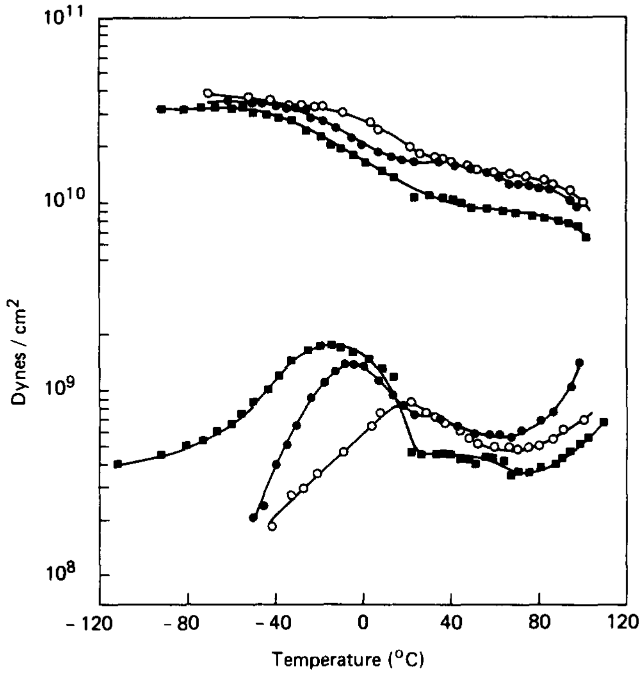

Figure 6 Dynamic mechanical data of TPS blends containing the randomized copolymers of ST:BD $\simeq$ 45:55 composition. (a) TPS-26:SB-4 (■); (b) TPS-24:SB-5 (●); (c) TPS-25:SB-3 (○)

Table 3 Tensile properties and impact strength of TPS blends containing graded block and randomized copolymers of butadiene–styrene

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-5	6.5 parts SBS		–	–	–	4.3
TPS-23	7 parts SB-8		2235	29.7	3.4	3.2
TPS-29	7 parts SB-2		2383	17.2	0.7	2.7
TPS-26	7 parts SB-4	31.0	1323	21.3	15.0	5.5
TPS-24	7 parts SB-5	24.0	1650	24.5	12.0	3.4
TPS-25	7 parts SB-3	22.0	1733	27.6	6.3	3.2
TPS-35	7 parts SB-7	20.0	1858	29.3	10.0	6.5
TPS-28	7 parts SB-6	18.0	2363	23.7	1.5	3.0
TPS-21	7 parts LCPB	23.0	1520	18.4	20.0	8.6

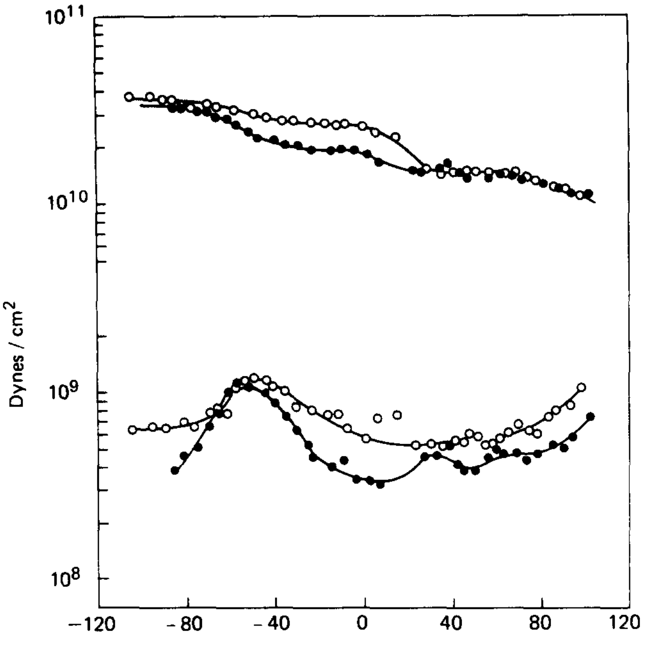

Figure 7 Dynamic mechanical data of TPS blends containing the randomized copolymers of ST:BD $\simeq$ 30:70 composition. (a) TPS-28:SB-6 (○); (b) TPS-35:SB-7 (●)

The broadening of the loss modulus peaks is the result of molecular relaxation processes of the copolymers, and of modified relaxation processes characteristic of the blends. The dynamic mechanical measurements of the above copolymers have shown[6] broad rubber transition regions (except SB-5) due to variation in the intramolecular composition distribution, i.e. molecular chain segments of various composition pass through their glass transition each at their characteristic temperature. As for the modified relaxation processes, on cooling the TPS blends a state of triaxial tension is expected in each aggregate of subparticles as a result of different thermal expansion coefficients of rubber phase and polystyrene matrix[13]. This tension results in an increase in rubber free volume, and varies with the size of the rubber aggregates, i.e. the smaller rubber aggregates can support a more intense triaxial tension[14]. Due to irregular shape and wide size distribution of the aggregates in *Figure 4*, a variation in free volume is expected, leading to broadening in the rubber transition. TPS-26 containing the randomized copolymer SB-4 shows a shoulder in its loss modulus peak between temperatures +30°C and +70°C. Dynamic mechanical measurements of SB-4 have also shown[6] a broad loss modulus peak at this temperature range, attributed to the polystyrene end block of the copolymer having low molecular weight. As is shown in *Figure 4a*, these polystyrene blocks form separate domains embedded in the polybutadiene. Hence they do not contribute in the interfacial adhesion between the polystyrene matrix and the rubber subparticles.

In *Figure 7* the blends TPS-28 and TPS-35 containing the ST:BD $\simeq$ 30:70 composition randomized copolymers show transition regions at lower temperatures than the previous blends due to their low styrene content. TPS-35 also shows a small loss peak around 40°C, due to the polystyrene end block of SB-7 copolymer[6]. The smaller area under the rubber loss modulus peak of TPS-28 *versus* TPS-35 is due to the relatively small rubber phase volume (*Table 3*) of the former.

Following from the above discussion, a TPS blend containing randomized copolymers of ST:BD $\simeq$ 30:70 composition shows similar morphology and dynamic mechanical properties as the one containing polybutadiene. However, for good interfacial adhesion the polystyrene block of the randomized copolymer has to be mixed with the polystyrene matrix; it is therefore necessary to have similar molecular weights. Preparation methods for such randomized copolymers are described elsewhere[6].

Mechanical properties

Table 3 lists the tensile data and impact strength of TPS blends containing the butadiene–styrene copolymers. A TPS blend containing polybutadiene is also included for comparison.

The values of elongation and impact strength of TPS-23, TPS-29 indicate that these blends, containing the graded block polymers, show brittle fracture. There is no stress whitening on the fractured specimens, indicating that the 'core–shell' and 'onion' structures fail to initiate crazes in the polystyrene matrix. Craze formation is responsible for the toughening mechanism of TPS blends since the impact or stress energy is consumed in the plastic deformation of the matrix. Particles larger than one micron and good interfacial adhesion are the required conditions for the formation of crazes[16]. The interfacial adhesion between the 'core–shell' subparticles and polystyrene matrix is very good since the polystyrene block of the graded block polymers SB-2 and SB-8 is compatible and is mixed with the polystyrene matrix (discussed in the Morphology section). Therefore, the failure of the above TPS blends is explained as a result of the submicron dimension of the 'core–shell' structures.

'Impact fractures' specimens of TPS-5 containing the triblock SBS polymer revealed a white region only around the notch tip. This indicates that crazes have been initiated and that their further propagation towards a crack was not stopped by these rubber particles. The low molecular weight of the polystyrene matrix, and the low interfacial adhesion between the matrix and the 'cylindrical-type' particles must have caused this failure behaviour; as was discussed earlier, the matrix is incompatible with the polystyrene block of the tri-block SBS polymer.

In TPS-26 to TPS-25 blends containing the ST:BD $\simeq$ 45:55 composition randomized copolymers, the increase of Young's modulus follows the reduction of 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. At the same time the elongation and impact strength decrease proportionally with rubber phase volume. Although these polyblends show better tensile properties than the ones containing the block polymers, they still fail to match the impact behaviour of TPS blends containing polybutadiene. The mechanical failure is due to the irregular shape of rubber aggregates and the low interfacial adhesion in these blends, i.e. incompatibility between the polystyrene end block of the randomized copolymer with the polystyrene matrix, and absence of graft copolymer. Between the TPS blends containing the

ST:BD$\simeq$30:70 randomized copolymers, TPS-28 shows poor tensile and impact properties due to the submicron particles dimension. On the other hand, TPS-35 shows high tensile strength and good elongation and impact strength. These properties can further be improved by matching the molecular weights of the polystyrene matrix and the polystyrene block of the randomized copolymer.

CONCLUSIONS

The dispersed rubber particles of a TPS blend containing conventional block or graded block polymers of butadiene–styrene display partly the morphology that the block polymer would be expected to adopt at that composition, i.e. cylinder, lamellae. Elsewhere the morphology is modified by the '*in situ*' generation of polystyrene homopolymer. However, if solubilization of the polystryene homopolymer occurs in the corresponding domains of the block polymer, a 'lamellae' or 'core–shell' structure is observed in the absence or presence of shearing agitation respectively. These toughened polyblends with the 'cylindrical' or 'core–shell' dispersed rubber particles do not match the mechanical performance of those containing polybutadiene. The composition, structure and molecular weight of the polystryene end block of the randomized copolymer appear to influence the morphology and mechanical properties of the TPS blends. A randomized copolymer with a random block composition of ST:BD$\simeq$30:70 or less is desirable for good impact properties at low temperatures. A TPS blend containing such a randomized copolymer shows similar morphology with the one containing polybutadiene. For improved mechanical properties the polystyrene end block of the randomized copolymer should have the same molecular weight as the polystryene matrix.

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