

Segmental Mobility in the Vicinity of T_g in PS/SBR Blends: Nanodomain Size Prediction of the Dispersed Phase

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ABSTRACT: The blends of polystyrene (PS) and styrene-butadiene rubber (SBR) are melt-blended at different ratios to form physical thermoplastic elastomers. This polymeric blend is expected to behave more or less similar to chemically synthesized block copolymers such as styrene-butadiene block copolymers (SBS). In this study, mechanical and the thermomechanical properties of this blend are investigated and compared to those of SBS copolymer. As far as morphology is considered, the blend shows a two-phase morphology with an interface, which shows very weak interactions. According to the observed morphology and the domain size of dispersed phase the blends are of good integrity. The mechanical properties of the blends confirm the integrity of the blend and effective interface stress transfer. The tensile and Izod impact properties of the blends shows improvements upon increase in SBR content of the blend. As SBR content augments the elongation at break increases, whereas tensile dissipated energy and impact resistance go through a maximum. Therefore, blend with SBR-content in 60–75% range can be considered as preferred one. In a wide range of concentration a phase inversion was observed and T_g -depression was detected also for the SBR phase. This T_g -depression was correlated to the changes in dynamics of segments (segmental mobility) near the surfaces. Using the proposed relationships between T_g -depression and the thickness of the thin films, it was tried to calculate domain size of SBR inclusions in PS matrix. A rough correlation between SBR domain sizes in SEM images and calculated thicknesses using T_g -depression in thin films was found. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Thermoplastic elastomers attracted too many technological interests.¹ These copolymers represent very unique rheological, mechanical, and physical properties.^{1–3} However, these copolymers are made via very sophisticated copolymerization reactions and procedures, which need even more specified conditions and expensive equipment and raw materials.⁴ These make these copolymers expensive and out of reach for many applications and low benefit industries. Meanwhile, polymer blends are always a nonexpensive and more feasible alternative for these chemically tailored copolymers.³ Amongst thermoplastic elastomers the three-block copolymers of styrene and butadiene and their hydrogenated forms along with their isoprene counterparts (SBS, SEBS, and SIS) are very important polymers. The microstructures of these polymers are widely investigated and well documented.⁴ Therefore, there is a wealth of knowledge on their structure. In these copolymers, the PS blocks are phase separated from PB ones. However, the chemical integrity of the chains makes the phases to remain interre-

lated.⁴ Therefore, PS inclusions (styrene monomers form 30 wt % of the total monomers in the chain) are formed in spherical shapes and act as physical crosslinking points. This makes SBS family of copolymers melt-processable upon melting PS inclusions in the same way as thermoplastic materials. However, this copolymer behaves as filled crosslinked rubbers in the solid state. Almost all block polymers are of different behavior as compared with that of the blends of polymers of their blocks.⁵ The preparation of these precisely tailored copolymers needs special equipment, reactors, and chemical. These result in limitations in production process and in augmentation of dollar/kg of the final products. As mentioned earlier, it would be economically attractive to prepare an alternative mixture of blends to compete SBS properties. Meanwhile, it is very interesting to study molecular motions in the blend and copolymer via thermomechanical measurements. This helps to tune the composition of the blend to approach as most as possible to the properties of tailored chemical multiblock copolymers.

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Table I. Physical Properties of Polymers^{8,9}

Polymer	M_w^a (g/mol)	MFI (200°C/5 kg) g/10 min	Mooney viscosity ML(1 + 4) at 100°C	Bond styrene (wt %)	Density (g/cm ³)	Solubility parameter, δ (cal/cm ³) ^{0.5}
Polystyrene	290,000	11	-	-	1.06	9.1
Polybutadiene	-	-	-	-	1.01	8.4
SBR	3×10^5 to 5×10^{5b}	-	46.0-58.8	22.2-24.5	$\sim 1.04^c$	8.45 ^d

^a GPC, in THF, Refractive Index detector, ^b IPPI rubber department, ^c http://wiki.answers.com/Q/What_is_the_density_of_Styrene-Butadiene_Rubber, ^d <http://onlinelibrary.wiley.com/doi/10.1002/macp.1967.021090119/pdf>.

It is amongst the objectives of this article to assess the possibility of making a blend of PS and SBR behaving in a similar way as SBS does. Little research has been devoted to study the blend of PS and SBR.^{6,7} It seems that the business of high impact PS (HIPS) and PS-based block copolymers hindered people to discover other forms of toughened PS. According to these investigations this blend shows an upper critical solution temperature (UCST) behavior with an M-shape curve of two peaks. The density and solubility parameters of the parent polymers of SBR are reported in Table I. It means that at high temperatures these polymers become compatible. Some of their blends show two T_g s and some other show only one T_g in DSC measurements, which is dependent on the molecular weight of polymers. However, thermomechanical measurements indicated two distinct T_g s for all their blends. Therefore, the thermomechanical properties seem to be a more sensitive technique to detect interphase interactions and to compare each phase physical properties in SBS and PS/SBR blend.

A noticeable point about SBS is that all its blocks are amorphous and this point can be used to compare the copolymer thermomechanical response with that of the blend. The glass transition temperature and the shape of $\tan \delta$ curve can be used to interpret the interphasic interactions and the behavior of each phase in the copolymer and in the blend. The changes in mechanical relaxation ($\tan \delta$ curve changes) of the applied stress with changes in composition could be attributed to changes in segmental mobility of the chains in the vicinity of glass transition temperature.

The main subject of this article is to investigate the thermomechanical and physical properties and morphology of PS/SBR blends and compare in some aspects with those of SBS tri-block copolymer. The novelty of this work lies in the observation that the T_g of the SBR phase changes with composition of PS/SBR blend, relating this T_g -depression to the changes in dynamics of SBR inclusions and finding a way to use these changes to estimate the thickness or domain size of the SBR inclusions as dispersed phase.

Table II. Tensile Properties of SBR/PS Blends

SBR/PS blend	80/20	75/25	70/30	65/35	60/40	50/50	40/60	30/70	0/100
Elastic modulus (MPa)	23.63	50.46	70.45	109.74	134.79	549.36	532.	600.32	641.39
Elongation at break (%)	52.64	47.35	33.82	39.87	37.15	12.95	11.62	18.78	5.48
Dissipated energy (J)	1820.1	2461.9	2681.123	4193.6	4626.0	4379.5	3251.95	8457.08	1911.9

EXPERIMENTAL

Materials

Polystyrene (PS) (1440 grade from Tabriz Petrochemical Company, Iran) and SBR (1500 grade from Bandar Imam Petrochemical Complex, Iran) were used for blend preparation. Some available structural parameters are provided in Table I. The reference copolymer (SBS) from Kraton company (1101 grade) was used and its properties are reported in Table I.

Procedures

PS and SBR were melt blended in an internal mixer (Haake buckler) at 160°C and 40 rpm for 5 min without addition of any stabilizing agent. The composition of the blends is reported in Tables II and III. The prepared blends and pure PS and SBS were molded to sheets between the platens of a laboratory hot-press under a pressure of 150 bar and at 180°C. The molded sheets were cut into DMTA sample tests. DMTA tests were carried out in a temperature range between -100 and 130°C at a frequency of 10 rad/s and a heating rate of 3°C/min using dual-cantilever fixtures on a PL instrument. For scanning electron microscopy a small piece of the original blends obtained from the internal mixer was taken and cryogenically broken in liquid nitrogen. The fracture surface of samples was gold coated and viewed using a Cambridge scanning electron microscope (SEM, Stereoscan model S-360) without etching. The tensile tests were carried on a Santam universal testing machine (model STM-20) at room temperature (25°C) and 30% humidity with a gauge of 50 mm and at a crosshead speed of 50 mm/min. Three samples were tensiled and the average of them was reported. The Izod impact test was carried out on the samples at room temperature using a Zwick impact tester (5102 model, full capacity: 4 J). At least four samples were impacted and the average was reported.

RESULTS AND DISCUSSION

Morphology

The morphology of the PS/SBR blends is dependent on the composition. The minor phase is always dispersed in the major phase. These two polymers are partially miscible and because of

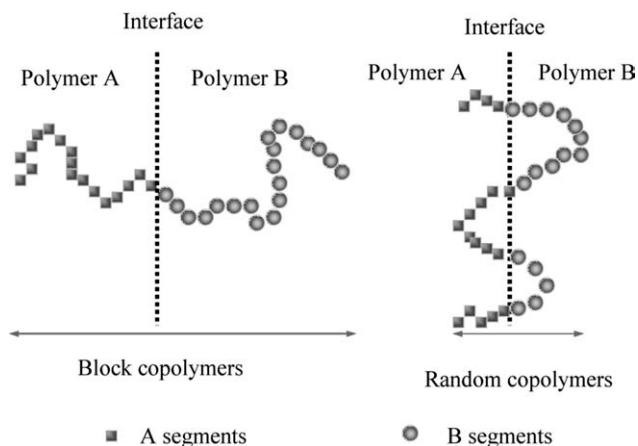


Figure 1. Schematic representation of the position of different copolymers at interface.

short styrenic segments of the SBR, some interactions and limited miscibility is expected for this blend (Table I). As compared in Figure 1, at the interface of the blend some extent of interdiffusion is probable. Consequently, in the case of partially miscible blends a thick interphase is formed instead of interface as compared with the case of immiscible blends (Figure 2). In Figures 3–8 the evolution of the morphology of different

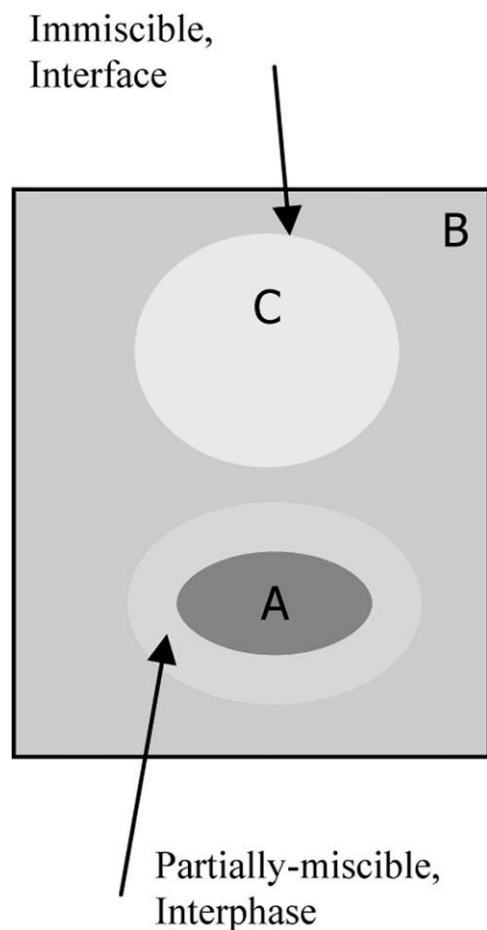


Figure 2. Formation of interphase in the case of partially miscible blends.

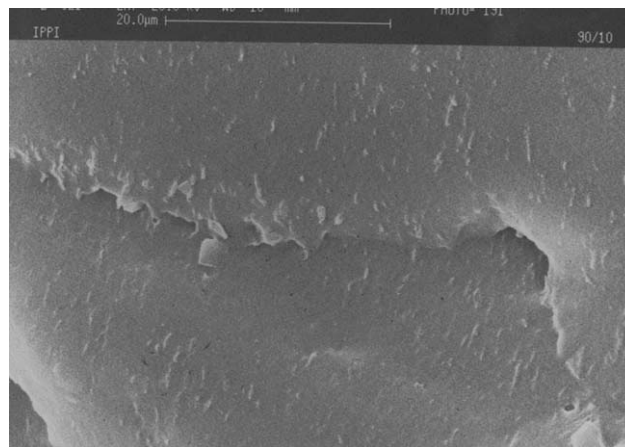


Figure 3. Morphology of SBR/PS 90/10 blend.

compositions of PS/SBR blend is illustrated. As seen, for high SBR content this copolymer assumes the matrix role and at low concentration it converts to the dispersed phase. This is also observable that the phase conversion or cocontinuity of the phases happens around 50% SBR concentration. According to these figures, one may expect the core-shell morphology for this blend. The absence of roundness of the dispersed phase witnesses the formation of the interphase.

Mechanical Properties

The tensile properties of the SBR-rich blends are reported in Table II to investigate the compatibility of the components. Although the SEM micrographs represent good interphase adhesion the mechanical data are reported to confirm this claim. Figure 9 shows a change in the breaking behavior of the blend with increase in SBR content. As compared with pure PS the presence of the SBR in blend results in changing brittle to ductile stress–strain behavior. This confirms the homogeneity of the blend and a good interfacial stress transfer between the phases. This finding is in good agreement with the data already reported in Ref. 10. A 30 time decrease in elastic modulus of the SBR/PS 80/20 as compared with that of the pure PS (Table II). At the first glance, it could mislead us to the lost of integrity of

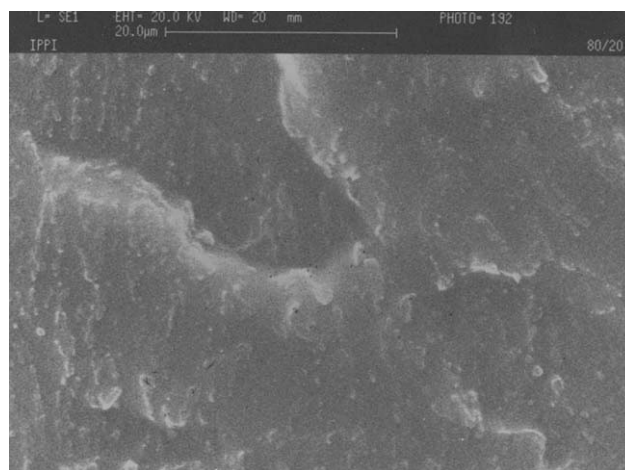


Figure 4. Morphology of SBR/PS 80/20

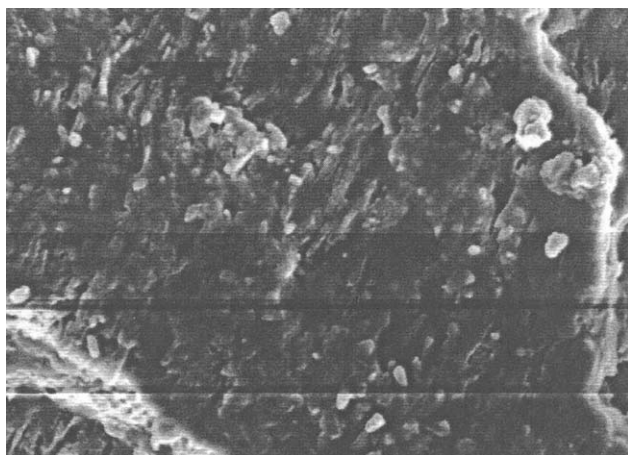


Figure 5. Morphology of SBR/PS 70/30 blend.

the blend. However, checking the percentage of elongation at break and the energy of the rupture reveals that the component of the blends intimately adhere together and blends are very far from the heterogeneity.

The results of Izod impact test on the samples is reported in Table III. Because of the fact that preparation of pure SBR specimens is not possible, only the blends and pure PS were impacted and the results reported in Table III. The impact resistance of pure PS is very low. As clearly seen in the table with a decrease in SBR content the impact resistance of the blends passes through a maxima in case of SBR/PS 70/30 blend. According to the reported mechanical properties the blends with a SBR-content around 60–75 wt % can be considered as good candidates for replacing SBS in certain applications such as bitumen modification in paving and roofing membranes. This composition is very close to the composition of the SBS block copolymers in which the copolymer chains bear around 15% of PS at each end. This means 30% PS segments per chain and 70% polybutadiene segments imbedded in between two PS segments. It has to be also noted that there exist around 23% styrene monomers in SBR chains, which provide the blends with the necessary interactions.

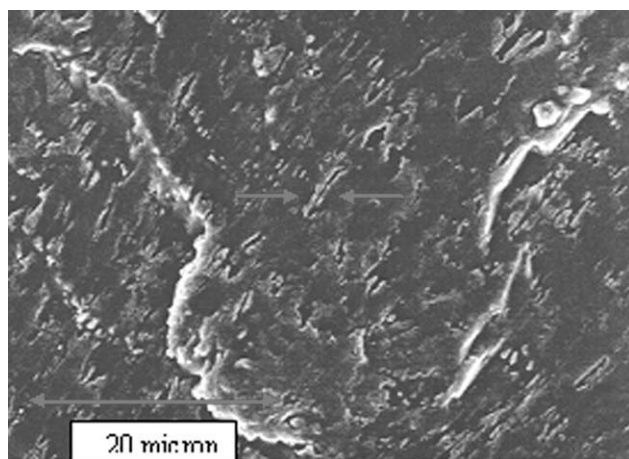


Figure 6. Morphology of SBR/PS 60/40 blend.

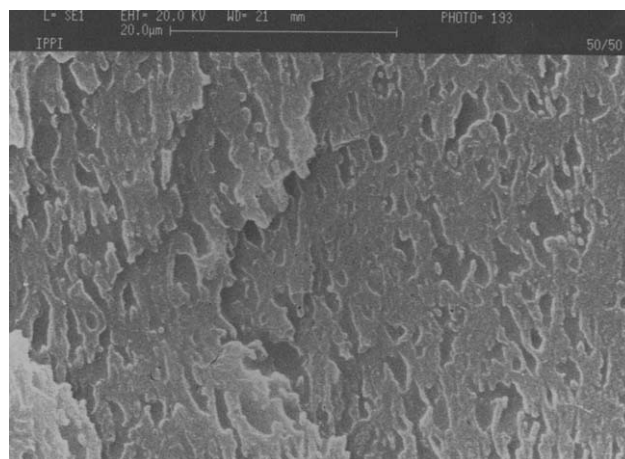


Figure 7. Morphology of SBR/PS 50/50 blend.

According to the observed morphology of the blends (Figures 3–8) it is expected that an increase in PS content results in more separated and noninterconnected SBR particles in PS matrix. This results in a brittle material at high PS contents, meanwhile, in vicinity of concontinuous phase composition the impact properties passes through a maximum.

Thermomechanical Analysis

The thermomechanical properties at constant frequency were measured in a wide range of temperature which covers T_g s of both phases. Since PS, SBR, and SBS are totally amorphous polymers and copolymers. The only transition traced in the curves is glass transition temperature. As observed in Figure 10 and as expected PS and SBR only show one T_g , which are located around 105 and -27°C , respectively. Meanwhile, the SBS which is a tri-block copolymer shows two distinct T_g s around 100 and -67°C . In spite of the nonbonded chemical structure of physical blend of PS and SBR one may expect a similar thermorheological behavior of this blend. In Figure 11 the thermorheological properties of different compositions of this blend. As seen, two T_g s are observable in these curves. As considered with curve of SBS, a higher T_g for PS phase and also

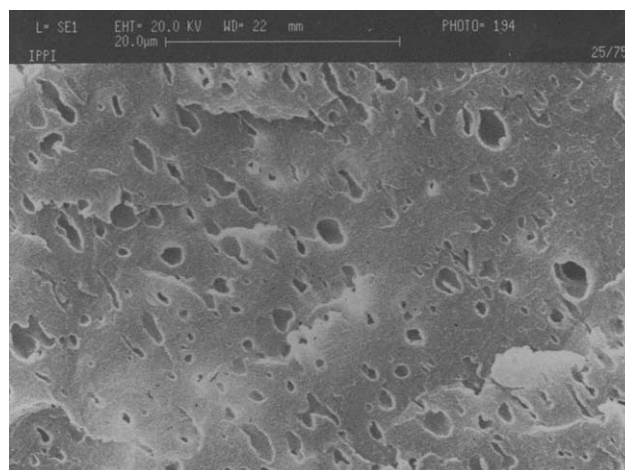


Figure 8. Morphology of SBR/PS 25/75 blend.

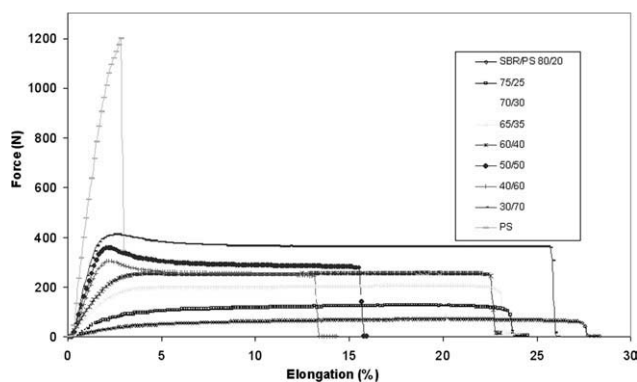


Figure 9. Stress–strain behavior of pure polystyrene and its blends with styrene-butadiene random copolymer.

a 10° depression for T_g of SBR phase with the blend composition. Another observation is the changes in the shape of the PS peak in high temperature region. Because of formation of an interphase a wide peak is also observable at medium temperatures.

The T_g of the PS is more or less intact with changes in blend composition. However, the very broad peak at medium temperatures and in neighboring of PS phase peak can be considered as an evidence for formation of the interphase while the core of PS domains remains untouched by SBR chains. Meanwhile, the SBR domains are severely affected by PS and interphase domains. This is witnessed by depression of the low temperature glass transition of the blend, which belongs to the SBR phase.

Before trying to account for these observations, it is of value to review the origin of glass transition temperature and the parameters effective on it and operative mechanisms at T_g . As a matter of fact, the glass transition temperature (T_g) marks the onset of segmental mobility for a polymer. Below T_g , the polymer segments do not have sufficient energy to move past one another, materials behave as a glass, and if the material is stressed, the only reversible response can be for bond angles and distances to be strained, since no large movements of the segments are possible. Above T_g , the segments rearrange to relieve an externally applied stress, which results in heat flow. That is, as temperature increases, certain numbers of carbons in polymer chain backbone (a segment) starts to move at T_g .^{8,9,11–13} The following factors affect T_g : bond interaction, molecular weight, functionality, branching, and chemical structure. All these factors affect the position of T_g .

Table III. The Izod Impact Properties of SBR/PS Blends

SBR/PS blend	80/20	75/25	70/30	65/35	60/40	50/50	40/60	30/70	0/100
Impact resistance (J/M)	99.90 ± 3.40	165.91 ± 19.32	218.93 ± 4.53	198.43 ± 8.06	151.69 ± 11.23	74.18 ± 2.09	91.53 ± 11.76	57.76 ± 5.50	15.29 ± 0.36
Mode of failure	No break	No break	No break	No break	No break	Break	break	break	break

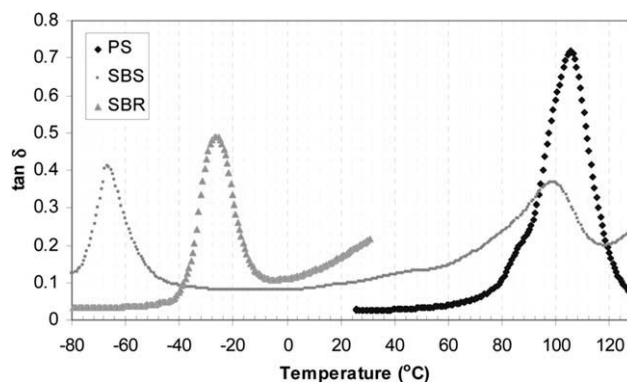


Figure 10. Thermomechanical curves of PS, SBR, and SBS.

The translational, rotational, and vibrational energies of the polymer molecules increase on heating. That is, segmental mobility changes as temperature of the sample passes through its T_g . It is found in a multilayer polymer film that changes in T_g of the components follow this equation¹⁴:

$$T_{g,i} = \frac{(d - d_I)}{d} T_{g,i}^o + \frac{d_I}{d} T_{g,I}$$

where i represents component, $T_{g,i}^o$ = glass transition temperature of i -component, $T_{g,I}$ = glass transition of interphase, d = average layer thickness and d_I = interphase thickness (equilibrium inter-penetration depth ~ 10 nm)

$$d_I = \frac{2b}{(6\chi)^{0.5}}$$

b = statistical segment step length. This equation is of too many parameters and can not be used easily.

For PS, near a free surface the followings are observed¹⁵:

T_g -depression and a lower resistance to indentation of chains compared to bulk properties.

These are due to enhanced segmental mobility of chains near a surface, resulted from a higher free volume available. Anisotropy of this region accounts for this observation. Consequently, a chain segment of a certain length starts to move at a lower temperature, which results in a lower T_g . It is also showed that the dynamics of polymer segments near the surfaces is faster than that of the polymer segments in bulk.^{16,17} The same could be true for an immiscible or partially miscible blend. In thin polymer films thinner than 50 nm it was observed that their T_g

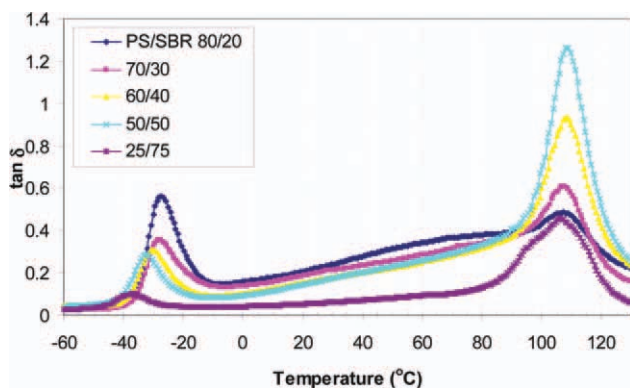


Figure 11. Thermomechanical behavior of PS/SBR blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

depress below their bulk value. The glass transition temperature of the thin film can be estimated the following empirical equation¹⁶:

$$T_g(d) = T_g(\infty) \left[1 - \left(\frac{A}{d} \right)^\delta \right]$$

where $T_g(\infty)$ is the bulk density of the polymer and $A = 3.2 \pm 0.6$ and $\delta = 1.8 \pm 0.2$ for PS. This equation can be rearranged to obtain an equation to calculate the thickness of the thin films $\zeta(T)$:

$$\zeta(T) = A \left(1 - \frac{T}{T_g(\infty)} \right)^{-\frac{1}{\delta}}$$

Accordingly, any reduction in T_g is a clear evidence for enhancements in the segmental mobility of the corresponding phase. In PS/SBR system, on the particle's surface the SBR segments senses less restrictions to move as particles become finer and as a consequence of increase in interface area more freedom to move become available to SBR chains. Therefore, smaller particle show lower T_g . Because of the fact that the blends are phase separated, the nature of the matrix (brittle or ductile) does not affect this phenomenon too much.

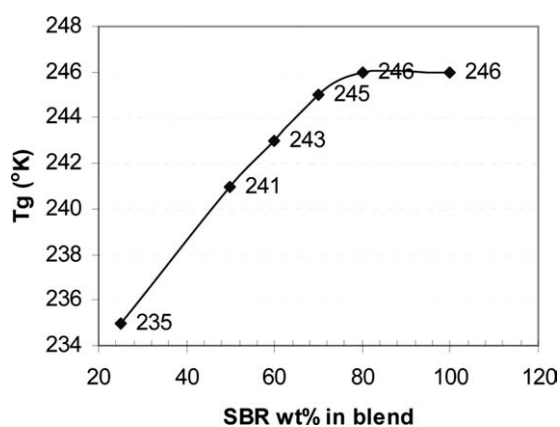


Figure 12. The changes in the T_g of the blends with composition.

Table IV. The T_g -Depression and Domain Thickness of the Blends with $A = 3.2$ and $\delta = 1.8$

SBR content (%)	100	80	70	60	50	25
PS content (%)	0	20	30	40	50	75
$\zeta(T)$ (nm)	-	-	68	37	27	17

The T_g depressions for the blends, which is extracted from the curves in Figure 11 are summarized in Figure 12. This is inferred from the data that the SBR segments are of enhanced mobility as compared with those in bulk state. The corresponding SBR domain thicknesses are calculated and reported in Table IV. It shows that in the blends also the domains of SBR in presence of PS can be considered as thin films. Once the data of SBR domain thickness are compared with the domains sizes of SBR in SEM micrographs (Figures. 5–8), a good correlation is found between the calculated thicknesses and observed domain thicknesses. However, this correlation can be improved by using the exact fitting parameters. Therefore, it is concluded that these equations can be used for the blends whenever a T_g -depression is observed and this enables us to estimate the domain size of the blends. This is of a special interest for the blends with low contrast in microscopic techniques.

CONCLUSION

Blending polymers together results in a mixture, which can be used to replace some copolymers. Blending PS and SBR produces a mixture, which is in some aspect similar to SBS block copolymer. The tensile properties of the blends revealed very large differences between these properties of the blends and those of the pure PS. The pure PS showed a brittle behavior whereas the blends behaved ductile. This improves formation of a strong interphase in the case of the blends. Meanwhile, the morphology of the blend investigated by SEM backs this conclusion. The mechanical properties of the blend were improved upon increasing SBR content; however, impact resistance passes through a maximum. These data suggest a blend with 60–75 SBR-content as optimized one. The thermomechanical behavior of this blend is very similar to that of SBS. For this blend it was observed that the glass transition temperature of SBR is depressed with increasing PS content, whereas that of PS phase remains intact but the shape of the peak changes. Because of creation of interface and interphase upon blending, the SBR chain's segmental mobility increases as PS contents increase. Extent of this T_g -depression was correlated to the domain size of the dispersed SBR phase. The calculated domain sizes are in a relatively good agreement with SEM observations.

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