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Influence of Molecular Weight and Composition on the Morphology and Mechanical Properties of SBS–Polystyrene–Mineral Oil Blends

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ABSTRACT: The relationship between the tensile properties and morphology of styrene–butadiene–styrene (SBS)–mineral oil–polystyrene blends has been evaluated. The SBS–mineral oil system (Kraton D2104, 21 wt % total styrene content, Shell Chemical Co.) exhibits a morphology of polystyrene spheres in a continuous butadiene–oil matrix, and the mechanical properties are characteristic of a cross-linked rubber. When the mineral oil is removed, the polystyrene domains become cylindrical and the mechanical properties correspondingly show increased stresses and a reduced ultimate elongation. Monodisperse polystyrene was blended into the SBS–mineral oil system: mineral oil is solubilized exclusively into the butadiene phase of the copolymer and the SBS–mineral oil–homopolymer blends seem to behave similarly to SBS–homopolymer blends. As the total styrene content is increased through blending, a transition from a spherical to cylindrical styrene domain morphology is observed. Higher styrene content blends also exhibited yielding and necking, which are indications of polystyrene domain continuity. The solubility limit of the homopolystyrene in the copolymer morphology was dependent on homopolymer molecular weight. Only the lowest molecular weight polystyrene blend showed no evidence of homopolymer segregation at the highest total styrene content (40 wt %). For polystyrene molecular weights greater than the styrene block length of the copolymer, the solubility limit was significantly reduced. The dependence of mechanical properties on homopolymer molecular weight and morphology is more sensitive than has previously been observed.

Introduction

Block copolymers are an important class of polymeric materials and as a result have been studied extensively.[2] Additives are often used to alter the properties or improve the processability of the copolymers. The types of additives include other polymers, resins, and extender oils. A number of studies have examined the effects of mixing homopolymers into block copolymers as a way to modify the properties of the pure copolymer.[3-11] For example, the addition of polystyrene into a styrene–butadiene–styrene (SBS) block copolymer can improve the mechanical properties and abrasion resistance of the material. Mineral oil is another type of additive used to improve the processing behavior of the copolymer. Since this additive is present in many of the finished products, it is important to understand how this affects the properties and morphology of the copolymer as well as SBS–polystyrene blends. In addition, by altering the component compositions, blending with mineral oil may be an effective way to achieve desired properties or modify the morphology of a block copolymer. In order to understand how blending leads to material property changes, it is important to examine how the morphological structure of the blend is affected and to examine the relationship between microscopic structure and macroscopic properties of the material. In the present study we have examined how the addition of polystyrene into an SBS copolymer mixed with mineral oil influences the mechanical properties and how this is related to morphology changes.

Several theories[12-16] have been published concerning the miscibility of homopolymer–copolymer blends. These theories all predict a strong molecular weight dependence for homopolymer solubility. However, there are discrepancies in the predicted amounts of homopolymer that can be incorporated into the copolymer morphology before macrophase separation occurs. Several blending studies have evaluated homopolymer solubility in both diblock and triblock copolymer systems.[4-7,17-23] From these studies it has been concluded that the homopolymer molecular weight must be less than or on the order of the length of the corresponding copolymer block for solubilization to occur. However, as with the theoretical predictions, there is much less agreement on the amount of homopolymer that can be solubilized.

Quan et al.[21] examined the effect of molecular weight on the solubilization of 20 wt % homopolymer into the lamellar morphology of a triblock copolymer. Homopolymers with molecular weights less than or equal to the block length of the copolymer were solubilized. When the homopolymer molecular weight was twice the block length, virtually all the homopolymer was excluded from the microdomains as has been predicted.[13]

Cheng et al.[22] studied homopolymer solubilization into the spherical microdomains of a diblock copolymer. Macrophase separation began to occur at a much lower homopolymer concentration than has been observed for blend systems where the copolymer has a lamellar morphology. This result qualitatively agrees with the predictions of Xie et al.[16] However, experimental evidence suggested that the result may have been due to sample preparation and therefore may not reflect the equilibrium state for the blends. Roe and Zin,[20] also using a copolymer exhibiting a spherical morphology, found a much higher homopolymer solubility than that determined by Cheng et al. Other investigators have demonstrated that homopolymer blending into a copolymer can lead to transitions from lamellar to double diamond, cylindrical and spherical morphologies.[19,23] The solubility limits for systems in which a microstructural transition occurs due to blending have not yet been considered theoretically.

Only a few of the studies concerned with determining the bulk properties of SBS–polystyrene blends have also examined the microstructure of the blends.[4-7] In addition, the majority of these studies did not critically consider the effects of homopolymer concentration and molecular weight. High loadings (>20 wt %) of high molecular

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weight, polydisperse polystyrene were often used. In contrast, studies blending low loadings (<10 wt %)[8] of polystyrene into copolymers exhibiting both spherical and cylindrical morphologies have noted that the mechanical properties are affected by the molecular weight and the amount of the homopolymer added, even at small concentrations of homopolymer. This suggests that the blend morphologies are also dependent on the molecular weight and concentration of the homopolymer added.

There has been very little published on the effects of additives, other than homopolymers, on the properties or morphology of copolymers. Investigations of the mechanical[24] and rheological behavior[25] of copolymer–mineral oil blends have indicated that mineral oil is preferentially solubilized into the butadiene phase of SBS copolymers and that the copolymer domain structure is selectively affected. It was suggested[24] that a morphological transition occurs with increasing oil content. Recently, Polizzi et al.[26] presented small-angle X-ray scattering results, which agree with the earlier conclusions. Starting with a 32 vol % styrene content copolymer, addition of oil to a volume fraction of 33% results in the long period decreasing strongly. This is interpreted as arising due to a transition from polystyrene cylindrical domains to spherical domains.

Homopolystyrene has also recently been blended into SBS–mineral oil systems.[27] The total polystyrene content was an important factor in determining the mechanical properties of the blends, and the ratio of the homopolystyrene molecular weight to styrene block length was also a critical variable.

In this work we have continued our examination of the effects of polystyrene molecular weight and concentration on the mechanical properties and morphology of SBS copolymer–polystyrene–mineral oil blends. We have observed that the morphology of the SBS–polystyrene–mineral oil blends appears to depend mainly on the total styrene content of the material, as for pure copolymers. We have observed that changing the polystyrene content by blending leads to morphological transitions and that these changes in morphology are accompanied by corresponding changes in the tensile properties.

Experimental Section

The copolymer used for blending was Kraton D2104 produced by Shell Chemical Co. This material is a blend of a SBS copolymer (31 wt % styrene content) with ~35 wt % mineral oil; thus the total styrene content is 21 wt %. For this block copolymer, it has been reported that M_n = 74 100 and M_w = 100 000.[27] Blends of the D2104 material and monodisperse polystyrene (Pressure Chemical Co.) were prepared in toluene, a nonpreferential solvent, precipitated in excess methanol, and dried thoroughly.[27] Since mineral oil can be lost in the precipitation step, UV absorbance spectroscopy was used to determine the actual styrene content for each blend. Blends are referred to as follows: 9000 molecular weight polystyrene blended with Kraton D2104 to a total styrene content of 28 wt % is designated 9PS/D2104-28. The first number refers to the molecular weight of the homopolymer (in kilodaltons) and the last number refers to the total styrene content. For the mechanical property analysis the blends were compression molded into films. Mechanical tests were performed on an Instron 1125. The test conditions were the same as reported earlier.[27] The results for each material are an average of five or more samples. The typical error associated with the measured stresses for the materials is 10%.

Transmission electron microscopy (TEM) was used to examine the morphology of the blends. Ultrathin films were cast onto a distilled water surface from dilute solutions in toluene. The film thickness is approximated to be between 90 and 200 nm, based on the gold to purple interference color of light reflecting from the film surface. Small sections of the films were floated onto 300-mesh copper grids, dried, and stained by exposure to osmium tetraoxide vapors. Examination of the films was made in a JEOL JEM100B electron microscope operating at 100 kV in the bright-field mode. A 20-μm-diameter objective aperture was used to improve image contrast and the magnification was determined with a calibration grating (21 600 lines/cm). Some compression-molded films were stained with osmium tetraoxide to harden the rubber domains sectioned by cryoultramicrotomy and stained again in osmium tetraoxide for examination in the electron microscope.

Table I
Effect of Removing Mineral Oil on the Tensile Properties of Kraton D2104 and Comparison with the Properties of Oil-Free Copolymers

	stress level, MPa				ultimate strain	tensile strength, MPa
	$\epsilon = 1$	$\epsilon = 4$	$\epsilon = 8$	$\epsilon = 12$		
Kraton D2104						
as received	0.4	0.7	1.2	2.9	17.3	10.3
25 wt %[a]	0.8	1.3	2.4	5.7	15.2	13.0
30 wt %[a]	1.2	2.0	4.5	13.3	12.4	16.1
31 wt %[a]	1.6	2.9	6.8		11.1	15.3
Kraton D1102[b]	1.3	2.2	5.1	15.9	13.0	20.0
Kraton D1101[c]	1.5	2.2	5.7		12.0	18.6

[a] Total styrene contents were measured by UV absorption. [b] Kraton D1102 has a styrene content of 28 wt % and molecular weight of 71 000.[28,29] [c] Kraton D1101 has a styrene content of 31 wt % and molecular weight of 102 000.[10,27]

Results and Discussion

Tensile Properties. The effects of removing mineral oil on the tensile properties for the Kraton D2104 copolymer are presented in Table I. The mineral oil was removed by repeatedly dissolving and precipitating the material until no further change in the measured styrene content or mechanical properties was observed.

As the styrene content increases due to the removal of mineral oil in D2104, the stress at a given strain increases and the ultimate elongation decreases. These observations agree with the results presented by others[24,25] for SBS copolymers extended with mineral oil. These authors concluded, without verification, that the changes in the mechanical properties were due to a morphological transition that occurred as the polystyrene volume fraction was reduced.

The "clean" copolymer (mineral oil free D2104) exhibits tensile properties that are very similar to Kraton D1101 and Kraton D1102, SBS copolymers that have no mineral oil blended into them. This agreement between the properties of the three "clean" copolymers is not surprising considering the similar molecular weights and styrene contents for the three materials.

The molecular weights of polystyrene blended into the as-received Kraton D2104 ranged from 2000 to 51 000. The effects of increasing the homopolymer content on the tensile properties for some of the Kraton D2104-polystyrene blends are given in Table II. The tensile properties for the series of 9000 MW PS-Kraton D2104 blends are also shown in Figure 1. The tensile properties for all the blends can be separated into three catagories based on the total styrene content. The blends with styrene contents up to 31 wt % exhibit low moduli, low tensile strengths, and high extensibilities similar to the Kraton D2104 material. The results for these lower polystyrene content blends were presented and compared earlier.[27] For these blends, stress increased with total styrene content and increasing homopolymer molecular weight, up to a molecular weight of 9000, while elongation remained the same. For higher molecular weight homopolymer blends, the strength showed no further improvement and the elongation was reduced.

Table II
Effect of Homopolymer Molecular Weight and Total Polystyrene Content on the Tensile Properties of Kraton D2104–Polystyrene Blends

total styrene content, wt %	initial modulus, MPa	yield stress, MPa	ultimate strain	tensile strength, MPa
	2000 MW PS–Kraton D2104			
24	0.7		17	12.1
28	0.8		17	12.1
32	4.4	1.2	12	10.5
35	6.6	1.7	13	16.6
41	5.9	1.5	14	14.3
	4000 MW PS–Kraton D2104			
24	0.8		17	12.4
28	1.1		17	13.9
36	6.4	1.7	14	16.2
37	6.8	1.8	13	14.4
44	18.3	2.4	11	15.1
	9000 MW PS–Kraton D2104			
27	0.9		17	12.4
31	1.2		17	15.2
33	6.9	1.8	12	18.1
40	18.1	2.4	11	13.5
		Kraton D1102		
(28)	3.1		13	20.0
		Kraton D1101		
(31)	5.3	1.5	12	18.6

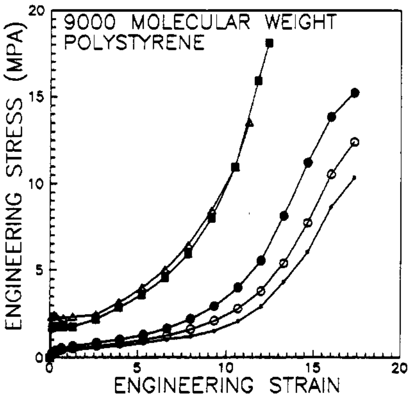

Figure 1. Effect of increasing total styrene content on the tensile properties of 9000 MW polystyrene–D2104 blends. Key: (*) Kraton D2104, (○) 27 wt %, (●) 31 wt %, (■) 33 wt %, (△) 40 wt %.

The most interesting observation for the blends is the change that occurs in the tensile properties when the total styrene content is increased. When the total styrene content is 32–37 wt %, the initial modulus is significantly increased, a yield stress and a necking region are observed, and the extensibility of the material is reduced. These observations are characteristic of a transition from a state in which the polystyrene domains behave as predominantly discontinuous filler particles to one in which the polystyrene domains exhibit a large degree of continuity. When the total styrene content is 40 wt % or above, the tensile properties can no longer be explained simply in terms of increasing styrene content.

For the Kraton D2104-2000 molecular weight polystyrene blends the modulus, yield stress, and tensile strength tend to increase when the total styrene content is increased, up to a styrene content of 35 wt %. The blend 2PS/D2104-41 shows somewhat reduced modulus and strength. For the Kraton D2104-4000 molecular weight polystyrene blends the modulus and yield stress are observed to increase with increasing styrene content for the blends evaluated. When 9000 molecular weight polystyrene is blended into Kraton D2104, the 33 wt % total styrene content blend exhibits the highest tensile strength. The stress–strain curves for 4PS/D2104-36, 4PS/D2104-37, and 2PS/D2104-35 are very similar. All these blends have yield stresses comparable to that for 9PS/D2104-33 and ultimate tensile strengths that are only 10–15% lower than the tensile stress for the 9000 MW blend.

The tensile properties for the blends all appear to change from a cross-linked rubberlike behavior to a more plasticlike behavior at a total styrene content of ~32 wt %. Assuming densities of 1.05, 0.91, and 0.87 g/cm^3 for polystyrene, polybutadiene, and mineral oil, respectively, the styrene volume fraction at which this transition occurs is 31%. This value is slightly lower than the predicted transition for cylindrical to lamellar domains occurring at 33[31,33] to 35 vol %.[32] Although the morphologies of these blends are not expected to be exactly in equilibrium, the blends were prepared in a nonselective solvent, and we believe that the morphologies of these blends will be cylindrical. This is also supported by the close comparison of the blend properties with the tensile properties of pure copolymers Kraton D1101 and Kraton D1102, which are known to exhibit cylindrical morphologies when compression molded.[34] It should be pointed out that the styrene contents for these blends are slightly higher than for the pure copolymers. The blends studied here exhibited lower stresses than pure copolymers having the same overall styrene content.

The blends with lower styrene contents (24–31 wt %) are also expected to exhibit cylindrical morphologies based on total styrene content. However, as discussed previously, the mechanical properties suggest a material having little or no degree of continuity in the glassy domains. This supports the observation of Diamont et al.[35] that a cylindrical morphology may need to exhibit a minimum degree of continuity before the material will begin to exhibit plasticlike behavior. In the study of Diamont et al., two SBS copolymers having styrene contents of 26 and 29 wt % were cast from a selective solvent for polybutadiene. Neither copolymer exhibited yielding, and the tensile curves were very similar. When a selective solvent system for polystyrene was used for casting, the 29 wt % SBS copolymer exhibited yielding and necking, characteristic of long rods or alternating lamellar, while the tensile behavior for the 26 wt % SBS copolymer was altered only slightly and showed no yielding or necking behavior. It was concluded that although the morphology of the 26 wt % copolymer was cylindrical when cast from the second solvent system, the degree of polystyrene continuity was not enough to cause a plastic to rubber transition in the mechanical behavior as is observed for the 29 wt % copolymer.

Small-angle X-ray scattering (SAXS) has also been utilized in determining the deformation behavior of triblock copolymers exhibiting cylindrical[29,36,37] and spherical[36] morphologies. Upon extension of long, oriented, cylindrical domains a four-point scattering pattern is observed.[29,36] This pattern is characteristic of a domain orientation inclined to the stretching direction. Extension of samples with spherical domains gives rise to a scattering pattern made up of layer lines perpendicular to the stretching direction and a spherical intensity distribution.[36] The scattering pattern due to deformation of a copolymer with a morphology consisting of short, unoriented cylinders showed an intermediate behavior between that for long cylinders and spherical domains.[37]

When the total polystyrene content of the blends is 40 wt % and above, there is no longer a simple dependence of the tensile properties on styrene content. Other considerations, such as molecular weight, are becoming more important in determining the behavior of the blends. For the 2000 MW blends, increasing the styrene content from 35 to 41 wt % results in a decrease in yield and tensile stresses and an increase in elongation. As continuous polystyrene domains develop, the ability of the added homopolymer in supporting tensile stress as compared to the styrene blocks of the copolymer becomes more important. The 2000 MW homopolymer, which accounts for more than half of the polystyrene phase at this point, has a lower molecular weight than the styrene blocks of the copolymer and is also not "tied" to the rubbery domains. Therefore, the homopolymer will more easily exhibit plastic flow and be less effective at supporting stress. Blends with higher molecular weight homopolymers appear to be more effective.

Blend 4PS/D2104-44 exhibits an increase in yield stress as compared to the lower styrene content blends, but the tensile stress remains essentially unchanged and the extensibility is reduced. For the 9000 molecular weight blends, increasing the polystyrene content from 33 to 40 wt % results in an increase in the yield stress. However, at the end of the necking region, the stress–strain curve for the 40 wt % blend lies very close to that for the 33 wt % blend until failure occurs at a lower tensile stress and ultimate elongation. In addition, the properties for both the 4000 and the 9000 MW high styrene content blends are very similar. For the 9PS/D2104-40 blend, at high strains the stresses appear to be no longer increasing with styrene content. This effect has been attributed to homopolymer segregation[8] and will be discussed further in the next section.

Morphology. Because of the high rubber content of these materials and the inclusion of mineral oil into the matrix, a direct casting technique proved to be much easier than cryoultramicrotomy in preparing the thin sections needed for electron microscopy. Direct casting of ultrathin films has been shown to be a very useful technique in examining the morphology of diblock and triblock copolymers.[28,38-43] Although surface effects become important in determining the packing arrangement of domains in ultrathin films, the morphological structure, whether spherical, cylindrical, or lamellar, has generally been the same as observed for the bulk morphology of cast films from a given solvent. The cast films were not annealed; therefore, the morphologies are not expected to be in equilibrium, and highly ordered structures were generally not observed except in some of the lower styrene content blends.

Toluene, a nonpreferential solvent for polystyrene and polybutadiene, was chosen so that the morphology of the cast films examined by TEM would be similar to the morphology of the compression-molded films used for determination of the mechanical properties. This has been confirmed for 9PS/D2104-31 in which the resulting morphology from both the solution casting and the compression-molding techniques was determined to be one of polystyrene cylinders in a butadiene–oil matrix. Figure 2 shows the morphology for 9PS/D2104-31 thin sections, prepared from compression-molded films by cryoultramicrotomy. The butadiene domains, which are stained by osmium tetraoxide, appear dark while the polystyrene domains appear light. The cylindrical domains, both end-on and parallel orientations to the section surface, can be seen in the micrograph. The morphology of a cast film, Figure 3, tends to exhibit more continuity and more order in the polystyrene domains than the molded film, as expected,[34,39] and there were few domains oriented end-on in the film.

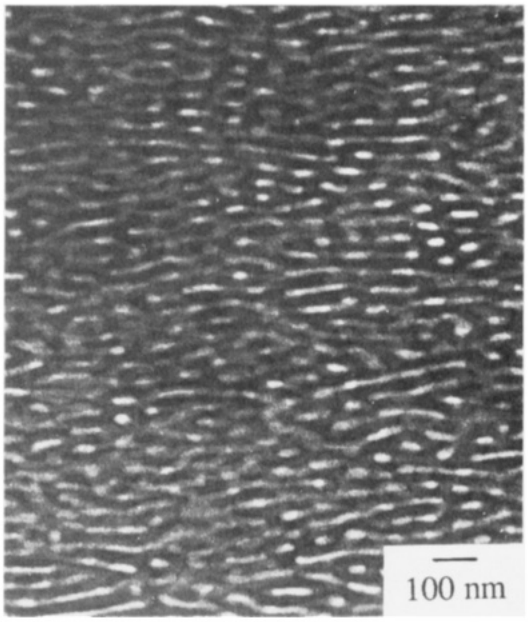

Figure 2. Electron micrograph of compression-molded 9PS/D2014-31.

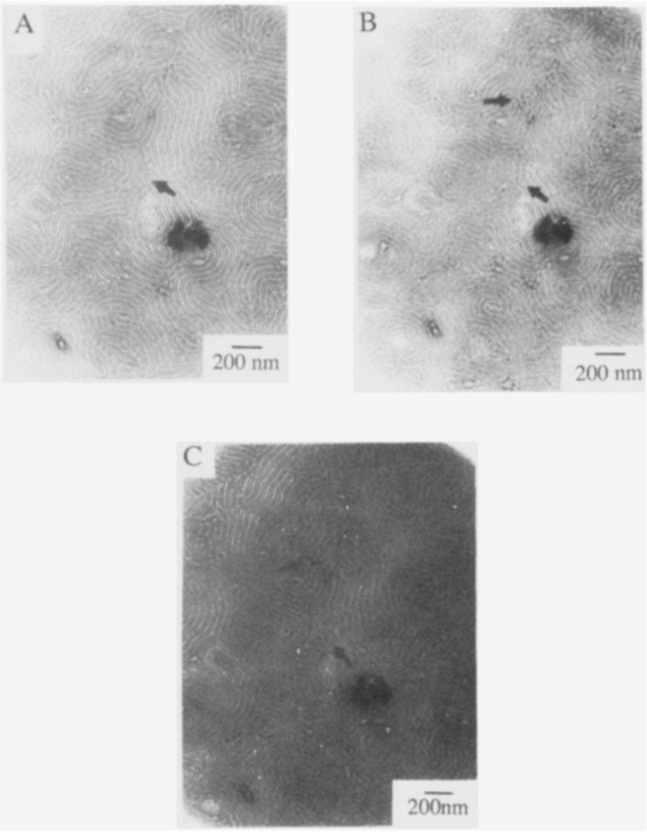

Figure 3. Electron micrograph of toluene-cast 9PS/D2104-31. (A) 0° tilt. (B) 20° tilt around x axis. (C) 30° tilt around y axis.

Because domain orientation and ordering is critical in distinguishing morphology, particularly cylindrical versus lamellar structures, the determination of the morphological structure of the cast film was more difficult. Hoffman et al.[38] and Henkee et al.[42] have both observed that cylindrical domains orient in the plane of the ultrathin film surface. An end-on orientation was never observed when the film

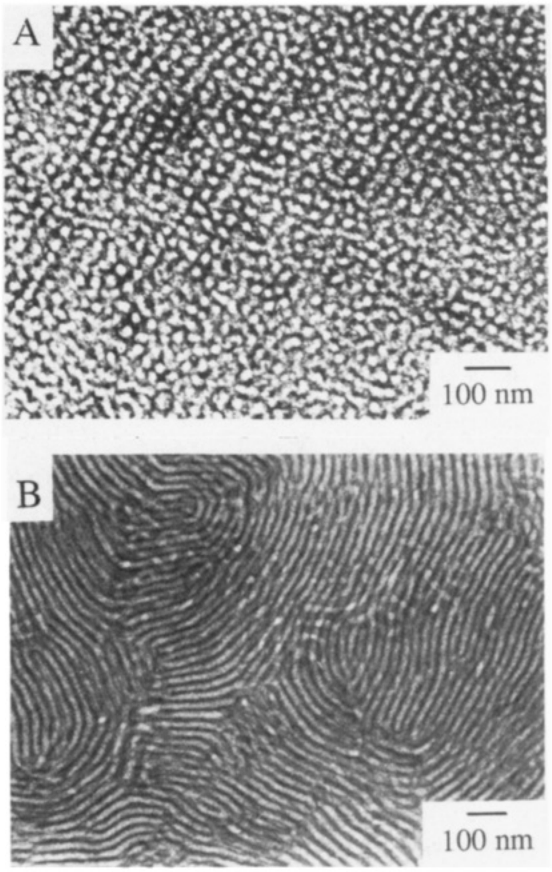

Figure 4. Electron micrographs showing change in morphology of toluene-cast Kraton D2104 as mineral oil is removed. Total styrene contents: (A) 21 wt % (as received), (B) 30 wt %.

thickness was less that 150 nm.[42] In contrast, lamellar domains for a higher molecular weight copolymer were observed to lay both parallel and perpendicular with respect to the film surface. Because most of the film thicknesses used in this work ranged from 90 to 150 nm, a cylindrical structure oriented parallel to the film surface resembles a lamellar structure oriented perpendicular to the surface. For the solvent-cast 9PS/D2104-31, a tilting experiment suggests a cylindrical morphology instead of lamellae. The morphology appears to show only one layer of domains in some areas, while other areas show a criss-crossed pattern resulting from stacked layers of domains oriented parallel to the film surface but whose principal axes are different. Arrows are used to point out examples of this criss-crossed pattern in the micrographs. As the sample is tilted, the contrast in some apparently single layer regions is reduced. This is an indication that rather than a single layer of domains there are actually two layers of domains, which are initially projected directly atop one another. As the sample is tilted, the polybutadiene phase of one layer is lined up with the polystyrene phase of the second layer, thus reducing the contrast. The sample was tilted around both the x and y axes, and these regions of poor contrast changed with the tilting axes. At all angles of tilt the areas exhibiting the criss-crossed pattern were visible. These observations are consistent with a morphology of cylindrical domains oriented parallel to the film surface.

Figure 4A shows an electron micrograph of the morphological structure for the as-received Kraton D2104. As expected, based on its mechanical properties,[27] D2104 has a morphology of polystyrene spheres embedded in a rubbery butadiene–oil matrix. This result agrees with thermodynamic theories for pure copolymers[31,32] which predict that the transition from spherical to cylindrical microdomains occurs at a polystyrene volume fraction around 0.20. D2104 has a polystyrene volume fraction of 0.18. Figure 4B shows the change in morphology that occurs with increasing polystyrene content as the mineral oil is removed from the D2104. When the polystyrene content is 30 wt %, the polystyrene domains are continuous cylinders, thus explaining the observed changes in the tensile properties.

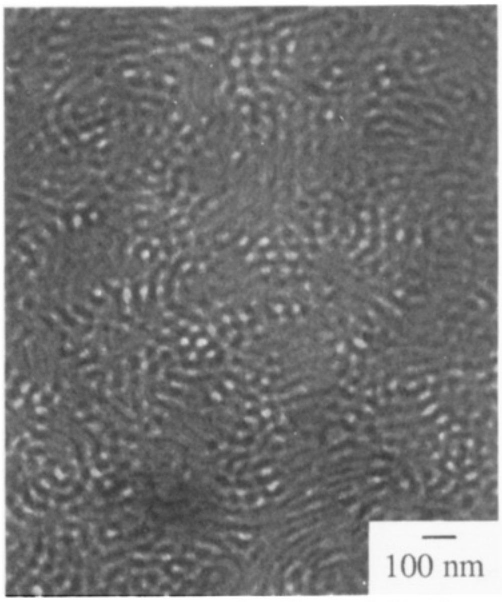

Figure 5. Electron micrograph of the morphology for a toluene-cast 4000 MW polystyrene–D2104 blend, 36 wt % total styrene content.

Generally, the morphology changes from spherical to cylindrical as homopolystyrene is blended into Kraton D2104. Reasonable comparisions between the mechanical properties from compression-molded films and the morphology of cast films can be made by carefully evaluating the actual morphology observed in the electron micrographs and taking into account the differences in the ordering of domain structures due to processing.

When 2000, 4000, or 9000 molecular weight polystyrene is blended into Kraton D2104 to a total styrene content of 24–27 wt %, the morphology of a toluene-cast film consists of a predominantly discontinuous hard phase exhibiting some spherical and short cylindrical polystyrene domains.[44] This is as expected, based on the mechanical properties.

When the total styrene content is increased further, either long cylinders or alternating lamellae are observed. As an example, Figure 5 clearly shows a cylindrical morphology for 4PS/D2104-36. Both parallel and end-on orientations of the domains are observable. Therefore we believe that the predominant morphological type exhibited by the blends in the composition region from 28 to 36 wt % total styrene is cylindrical, even though the mechanical properties of the lower styrene content blends in this range are characteristic of a more discontinuous hard phase. As observed with 9PS/D2104-31, compression-molded films are less ordered and have a lesser degree of continuity. In addition, as mentioned earlier, it may be necessary to have a minimum styrene content or degree of continuity before a material will exhibit plasticlike behavior. At styrene contents of 32–36 wt % even the compression-molded films would have a large degree of continuity in the domains, thus explaining the yielding and plasticlike behavior observed for these materials.

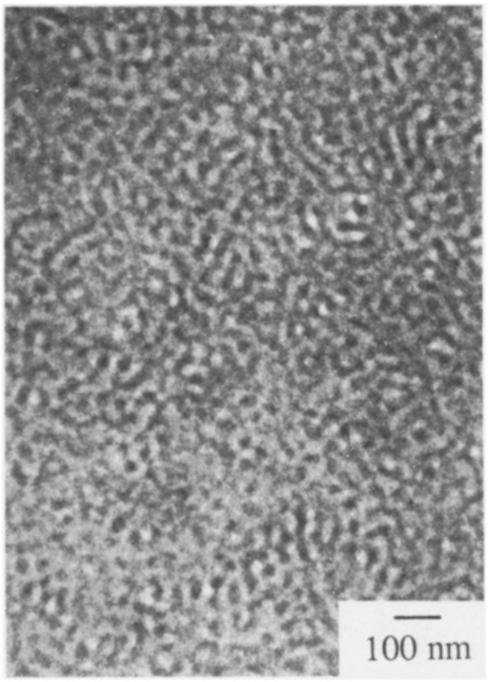

Figure 6. Electron micrograph of the morphology for a toluene-cast 2000 MW polystyrene–D2104 blend, 41 wt % total styrene content.

Blend 2PS/D2104-41, shown in Figure 6, exhibits a polystyrene continuous phase and no sign of macroscopic-phase separation. In contrast, 9PS/D2104-40, Figure 7, appears to exhibit homopolymer-phase separation. The morphology for this blend exhibits both homopolymer- and copolymer-rich regions. Even though the blend exhibits two phases, there appears to be a significant degree of mixing between the homopolymer and the styrene blocks of the copolymer. There is no sharp interface between the homopolymer-rich regions, labeled I, and the copolymer-rich regions, labeled II. Instead there are smooth transitions in which the microphase separated domains of the copolymer-rich region gradually extend into the homopolymer-rich regions.

This behavior is very different from what has recently been reported for an SIS–poly(α-methylstyrene) system.[30] In that work, 30 wt % homopolymers of varying molecular weights were blended into a 14 wt % styrene content SIS copolymer (styrene block length, 10 000). Low molecular weight homopolymer (M_w = 2000) was solubilized into the polystyrene domains of the copolymer while a higher molecular weight homopolymer (M_w = 8000) macrophase separated. The interface between the homopolymer and copolymer regions was sharp and it was unclear from the micrograph whether any homopolymer was incorporated into the microstructure of the copolymer. Since morphological results were not presented for any other homopolymer molecular weights or blend compositions, it is unclear how and at what conditions macroscopic-phase separation occurred for this system. On the basis of our results, it seems unlikely that at these molecular weights macrophase separation would occur before a significant amount of homopolymer is solubilized into the copolymer microstructure.

The mechanical properties observed for the 9PS/D2104-40 blend may be explained by the morphology exhibited. The homopolymer phases are important in determining the yield stress for these blends because of the good interface between the macrophase separated domains. If the transition between phases was sharp, the copolymer matrix would bear most of the load and the yield stress for the material would be lower. At the end of the necking region the homopolymer domains have yielded and the copolymer determines the stress. Since excess polystyrene is included in the homopolymer regions, the stresses measured at the intermediate strains are determined by the microphase separated phase, which is essentially the same as for a lower styrene content blend that has not macrophase separated. This is observed for the 9000 MW polystyrene–D2104 blends, indicating that the solubility limit is probably close to 33 wt %. At high strains the macrophase separated morphology again becomes important, and as a result, the blends exhibit a lower elongation and tensile strength.

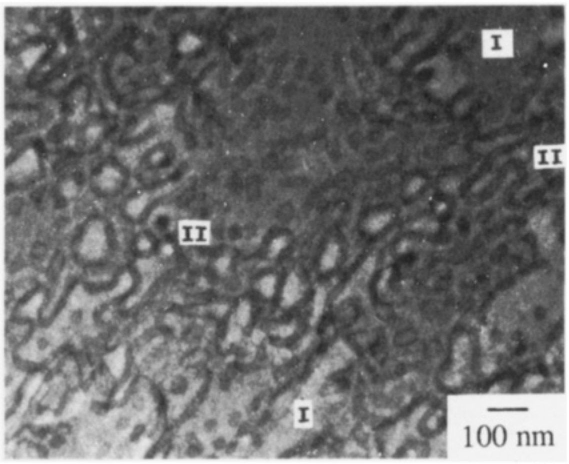

Figure 7. Electron micrograph of the morphology for a toluene-cast 9000 MW polystyrene–D2104 blend, 40 wt % styrene content.

Figure 8 shows the morphology for blends 17.5PS/D2104-24 and 17.5PS/D2104-28. At a total styrene content of 24 wt %, most of the homopolymer is solubilized into the styrene domains of the copolymer. When the total styrene content is increased to 28 wt %, macrophase separation is more predominant. This is indicated by the differences in the morphologies for the two blends. First, both blends show evidence of homopolymer macrophase separation occurring. However, the sizes of the domains for the 17.5PS/D2104-24 blend are smaller than for the 17.5PS/D2104-28. Although it is unclear from these two micrographs, examination of large areas of films of several samples indicates that the frequency of observation of homopolymer macrophases in the lower styrene content blend is much less. A more direct indication of homopolymer solubilization into the microdomains of the copolymer is the appearance of the microphase separated domains, which exhibit a greater degree of continuity than the microstructure of the as-received Kraton D2104. Even though macrophase separation has occurred, some of the homopolymer is incorporated into the block copolymer morphology, as evidenced by the appearance of cylindrical polystyrene domains. In all the blends studied it appeared that as more homopolymer was added to the system the resulting morphology became more and more disordered. Therefore, the differences in the degree of order for the two 17 500 MW polystyrene–D2104 blends appear to be related to total polystyrene content or homopolymer loading. However, since these are not equilibrium structures the possibility of the differences being due simply to sample preparation cannot be ruled out.

Unlike the macrophase separated 9PS/D2104-40 blend, there is a definite interface between the homopolymer regions and the microphase separated copolymer. The appearance of this interface is very similar to what has

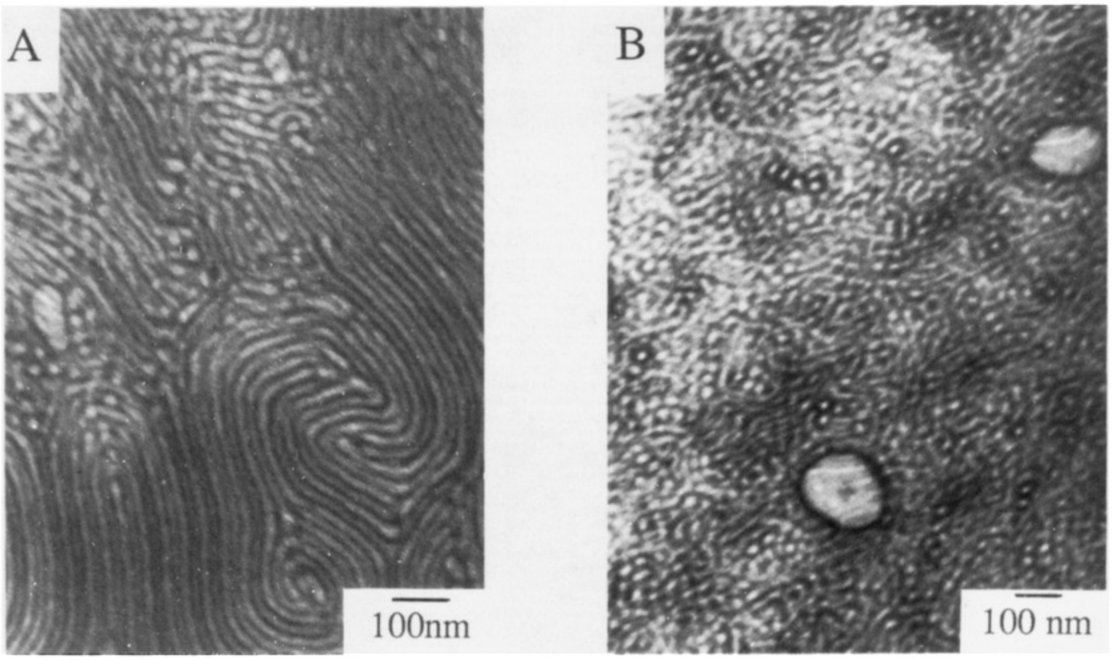

Figure 8. Electron micrographs of morphology changes with increasing polystyrene content for toluene-cast 17 500 MW polystyrene–D2104 blends. (A) 24 wt %, (B) 28 wt %.

been observed be Niinomi et al.,[4] Kotaka et al.,[7] and Inoue et al.[19] when relatively high molecular weight homopolymer is blended with a triblock copolymer. The appearance of domains that are observed inside some of the homopolymer regions may be due to a small amount of copolymer in the domains; however, we believe it more likely that these are microphase separated copolymer domains, which are layered either above or below the homopolymer regions. This conclusion is supported by the appearance of many of the domains that seem to continue into the microphase separated regions outside the homopolymer domains.

When 51 000 MW polystyrene is blended into D2104 homopolymer, phase separation, very similar in appearance[44] to that for 17.5PS/D2014-28, occurs at a total styrene content of 24 wt %. This was the lowest blend composition examined. The mechanical properties for the higher molecular weight polystyrene–D2104 blends were reported earlier.[27] The higher MW polystyrene–D2104 blends exhibited no improvement in strength over the 9000 MW polystyrene–D2104 blends of the same total styrene content; in addition, the extensibility was reduced.

Other studies have shown that the tensile properties of SBS–polystyrene blends increase and then decrease with homopolymer molecular weight or total styrene content,[3,7–9] but the studies were not as detailed and therefore the dependencies observed were not as sensitive as those presented here. As mentioned earlier, polydisperse homopolymer was often used in these studies, and in most studies, only two or three homopolymer molecular weights were used or the molecular weight range was too large.

The blend compositions at which microphase separation begins to occur in these systems agree reasonably well with the results reported by Roe and Zin.[20] They determined solubility limits of homopolymer into a styrene–butadiene diblock copolymer using cloud point measurements. They did not however present any electron microscopy evidence to confirm their results. Even though mineral oil is a significant component in the blends studied here, the agreement between these results and the results and predictions for oil-free copolymers and blends indicate that the total styrene content and the ratio of homopolymer molecular weight to styrene block length are the important factors in determining mechanical properties for these systems.

Conclusions

In this work we have shown conclusively that blending mineral oil into an SBS copolymer can alter the morphology and that the resulting microstructure is dictated by the total styrene content of the system. When a 31 wt % styrene content SBS copolymer is extended with mineral oil to a total styrene content of 21 wt %, the morphology changes from polystyrene cylinders to polystyrene spheres in a rubbery matrix. This is accompanied by reduced yield and tensile stresses as well as increased elongations as the hard-phase continuity is diminished. When homopolystyrene is blended into the SBS–mineral oil system, the mechanical properties are clearly dependent on homopolymer molecular weight and total styrene content. The dependence on molecular weight is much more sensitive than has previously been reported. This is believed to be due to the use of monodisperse homopolymers of several molecular weights in a relatively narrow range. The changes in tensile properties have also been explained as relating to observed changes in the morphology.

A definite transition from the spherical morphology of the SBS–mineral oil system to a morphology of polystyrene cylinders in a rubbery matrix is observed when the total polystyrene content is increased by blending with homopolymer. This transition depends on the overall styrene content of the system as for pure SBS copolymers. Finally, the SBS–mineral oil–polystyrene blends appear to follow the same behavior as SBS–polystyrene blends, namely, that homopolymer solubility is dependent on molecular weight and that the solubility limit is significantly reduced when the homopolymer molecular weight is larger than the styrene block length of the copolymer. As a result, mineral oil extension of block copolymers and block copolymer–homopolymer blends may be useful in determining and evaluating the relationships between composition, morphology, and material properties for these systems.

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