Importance of Molecular Coupling for Mechanical Performance of Block Copolymer Compounds

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Summary: Mixtures of polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS) triblock copolymer and various styrenic block copolymers (having diblock and triblock architectures) as well as polystyrene homopolymer (PS) were prepared via solution blending to determine the influence of molecular coupling on the large strain mechanical performance of the block copolymers. The techniques used were transmission electron microscopy (TEM) as well as scanning electron microscopy (SEM) for the morphological characterization and uniaxial tensile testing for the determination of mechanical properties. In the block copolymer blends, it was possible to tailor the mechanical properties as long as the molecular coupling was present among the outer polystyrene blocks. The mechanical performance of the triblock copolymer was found to deteriorate by the presence of dangling chains in the microphase-separated domains. In the blends comprising an SIS triblock copolymer and polystyrene homopolymers, the macrophase-separated compounds containing PS having molar mass exceeding the entanglement molar mass showed the optimum mechanical properties. The observed mechanical behaviour has been correlated with the fracture surface morphology of the corresponding blends.

Keywords: electron microscopy; fracture behaviour; mechanical properties; styrenic block copolymers

Introduction

Block copolymers belong to the family of heterogeneous soft matters, in which the molecules self-assemble into a large variety of periodic nanostructures via intramolecular phase separation.[1–3] The periodicity of these structures lies in the same range as the gyration radius of macromolecules. The type and the size-scale of these structures are controlled by various parameters such as molecular weight, composition, molecular architectures etc.[1–6] A precise control of these structures enables to tailor their mechanical properties over a wide range.[7,8] Further, many of their physical properties are generally controlled by the nature, dimension and orientation of morphologies, and the latter can be significantly altered by processing histories.[9–12]

Polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) and Polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS) triblock copolymers are used as thermoplastic elastomers.[2] Their significance from the practical point of view lies in the fact that the transparent polymers having a wide range of mechanical properties can be achieved by simply changing the composition and hence the nature of phase morphology.[1,2]

In a series of studies on styrenic block copolymer systems (reviewed in,[13] we demonstrated that the modification of block copolymer architectures may open up new avenues of controlling self-assembly

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processes in these nanostructured materials. As a result, a wide spectrum of microphase-separated morphology could be obtained without changing the net chemical composition.

Different authors have performed comprehensive studies on block copolymer blends and described their solubility limits (discussed in detail by Hamley in[3]). In particular, the influence of the molecular weight ratio (**r**) of the corresponding blocks and relative composition of the copolymers have been addressed.[14–18] It was shown that macrophase separation occurs, if the value of **'r'** is higher than 10, forming regions of lamellar domains with different periods. In contrast, if the value of $\mathbf{r} \leq 5$, the blend components were found to be mixed in molecular level. Hashimoto et al., by studying the phase behaviour of binary diblock copolymer blends in the range $5 \geq \mathbf{r} \leq 10$, demonstrated that a partial demixing of the blend components may occur at certain composition range. The investigations were extended to non-lamellar morphologies too.

For the practical applications, SBS or SIS triblock copolymers are of great interest. In those block copolymers, the outer polystyrene blocks form a sort of physical cross-links resulting in their strength at room temperature and their thermoplastic processability at elevated temperature. One concern frequently raised from the point of view of application of these polymers is the effect of presence of diblock chains on their properties.[19–21] Based on systematic thermomechanical studies of different diblock/triblock blends, it was concluded that the mechanical properties of the triblock copolymer are deteriorated by the presence of diblock chains. Some of the manufacturers even claim that their copolymers are absolutely pure and contain no diblock chains.[21]

The aim of this work is to study the consequence of the presence of other polymer chains in the tensile mechanical properties of a styrenic block copolymer (SIS triblock copolymer) with special emphasis on the role of chain coupling. The techniques used are uniaxial tensile testing and electron microscopy.

Experimantal Part

Materials and Sample Preparation

The polymers used in this work are listed in Table 1. The basic polymeric material was a linear polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS) triblock copolymer produced by Kraton polymers (Kraton D1160) containing 18.5 wt.-% polystyrene and contains very small amount of diblock chains. The polymer was supplied by Nordmann & Rassmann GmbH, Hamburg, Germany. To study the effect of molecular coupling on the block copolymer proper-

Table 1.
Characteristics of the samples used in this study.

Samples	PS content[1]	M_w (kDa)[2]	PDI[3]	Morphology[4]	Remarks
SIS	0.19	ca. 170		cylindrical	SIS triblock copolymer, Kraton D1160
SI	0.54	46.5	1.03	lamellar	SI diblock copolymer supplied by Dr. Marc Langela
SB	0.50	49	1.10	lamellar	SB diblock copolymer supplied by Dr. R. C. Bening
SBS	0.50	48	1.10	lamellar	SBS triblock copolymer supplied by Dr. R. C. Bening
PS010	100	12	1.60	–	PS homopolymer
P 018	100	18	1.40	–	PS homopolymer
PS035	100	35	1.30	–	PS homopolymer

[1] Total polystyrene weight fraction; the figures are as provided by the supplier.
[2] Weight average molar mass determined by GPS using PS standard.
[3] Polydispersity index determined by GPC.
[4] Morphology of the samples as determined by TEM.

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ties, SIS was blended with different diblock and triblock copolymers as well as polystyrene homopolymer having different molar masses.

The sample films approximately 0.5 mm thick were solution cast using toluene as solvent. The latter was allowed to evaporate slowly over a period of a week. The resulting films were dried for several days at 23 °C and annealed at 120 °C for 48 hours in a vacuum oven in order to allow the formation of well ordered structures. Tensile specimens were punched out of the cast films.

Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM)

The microphase-separated morphology of the samples was investigated by means of a transmission electron microscope (TEM, 120 kV, Leo 912, Germany). Ultrathin sections of the samples were microtomed from a bulk specimen. Prior to the TEM inspection, butadiene and isoprene phases of the respective samples were selectively stained by osmium tetroxide. As a result, the butadiene-rich or isoprene-rich (soft) and styrene-ich (hard) phases appear dark and bright respectively in the TEM micrographs.

The fracture surfaces of the samples broken in tensile tests was inspected under a scanning electron microscope (SEM; JSM 6300, JEOL, Japan). For the SEM imaging, the fracture surfaces were sputter-coated with about 5 nm thick gold film.

Tensile Testing

Uniaxial tensile tests were carried out at 25 °C using universal tensile machine (Zwick 1425, Ulm, Germany) at cross-head speed of 50 mm/min. The total length and the thickness of tensile specimens were 50 mm and 0.5 mm respectively. The distance between the cross-heads of the tensile machine was 30 mm. At least 6 specimens of each sample were tested.

Results and Discussion

Molecular Characteristics of the Investigated Polymers

Figure 1 presents the schemes of the molecular structures of the block copolymers which have been investigated in this work. In the triblock copolymers (Figure 1a), the outer blocks (i.e., the polystyrene chains) of the molecule can reside either in the same domain or in different domains giving rise to so called loop and bridge conformations, respectively.[3]

The bridge conformation is of particular interest for the practical applications of the block copolymer thermoplastic elastomers as the former endows the rubbery middle block (isoprene chain in present case) with mechanical stability and strength. It has been demonstrated that the bridge/loop conformation ratio is critical for the

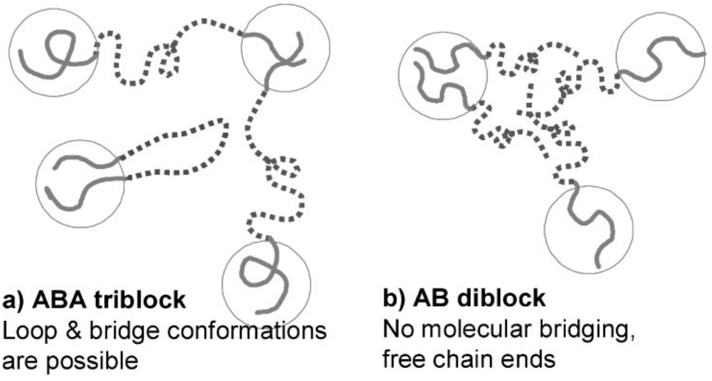

Figure 1.
Scheme of chain conformations in ABA tri- and AB diblock copolymers; note that the molecular bridging of the B chains is possible only in triblock copolymers.

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mechanical properties of the block copolymer systems.[22–25]

The molecular bridging of the polyisoprene (PI) chains leading to excellent thermoplastic elasomeric properties of polystyrene-*block*-polyisoprene-*block*-polyisoprene (SIS) triblock copolymer is not found in the corresponding polystyrene-*block*-polyisoprene (SI) diblock copolymers (see Figure 1). In the latter case, the polyisoprene blocks are physically cross-linked only on one side of the molecule while half of the chain ends remain uncoupled. As a result, the polyisoprene chains, whose glass transition temperature is far below room temperature, remain simply dangling in the rubbery phase of the block copolymer.[19,20] Obviously, if the diblock chains are present in the triblock copolymer, the number of molecular bridging does decrease. Higher the amount of the diblock content in the triblock copolymer, lower will be the total molecular bridging. The effect of the presence of of diblock chains in the mechanical properties of the triblock copolymer thermoplastic elastomers have been the object of some recent studies.[22–24] The objective of the discussion outlined in this paper is to further explore the effect of diblock as well as homopolymer chains on the morphology and deformation behaviour of the triblock copolymers.

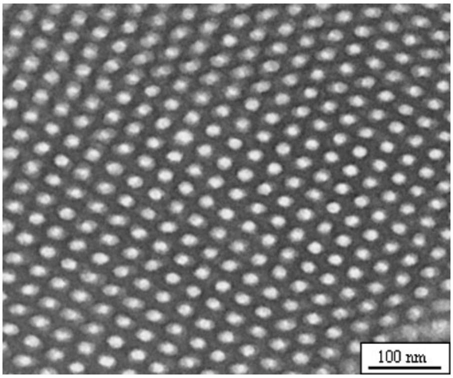

Figure 2.
Representative TEM micrograph of the SIS triblock copolymer.

Morphological Characterization by TEM

Figure 2 presents the representative TEM micrograph of the SIS triblock copolymer SIS. As expected from the polystyrene/polyisoprene weight ratio (PS content ~ 19 wt.-%), the block copolymer possesses highly ordered cylindrical morphology comprising polystyrene cylinders (bright domains in the TEM image) dispersed in the matrix of polyisoprene (dark areas in the TEM image).

The polyisoprene (PI) matrix can be envisaged as being formed both by the bridged and looped SIS molecules (see Figure 1a).The average thickness of the polystyrene domains (PS cylinders) and long period of the domains measured in the TEM micrograph of the SIS triblock copolymer are approximately 16 nm and 32 nm, respectively.

Let us analyze now how the morphology of the block copolymer changes when added with polystyrene-*block*-polyisoprene (SI) diblock copolymer containing 54 wt.-% of polystyrene (PS). The diblock copolymer was prepared by sequential anionic polymerisation.[26] It should be noted that molar mass of both polystyrene and polyisoprene chains in SI diblock is approximately 23 kDa. Thus the PS molar mass of the diblock copolymer (ca. 16 kDa) is approximately 1.8 times that of the corresponding block of the SIS. On the other hand, the molar mass of polyisoprene (PI) blocks of the diblock copolymer (approximately 23 kDa) is about six times that of the corresponding block of the triblock copolymer (approximately 140 kDa).

According to the solubility criteria discussed for the block copolymer blends,[16–18] the PS block of the diblock is partially compatible with the corresponding block of the diblock while the PI block of the diblock is completely soluble in the corresponding blocks of the triblock copolymer. In overall, the binary block copolymer blends studied represents a partially miscible one. The representative TEM images of the SIS/SI blends of varying compositions are presented in Figures 3–6. In all the micrographs presented, the diene

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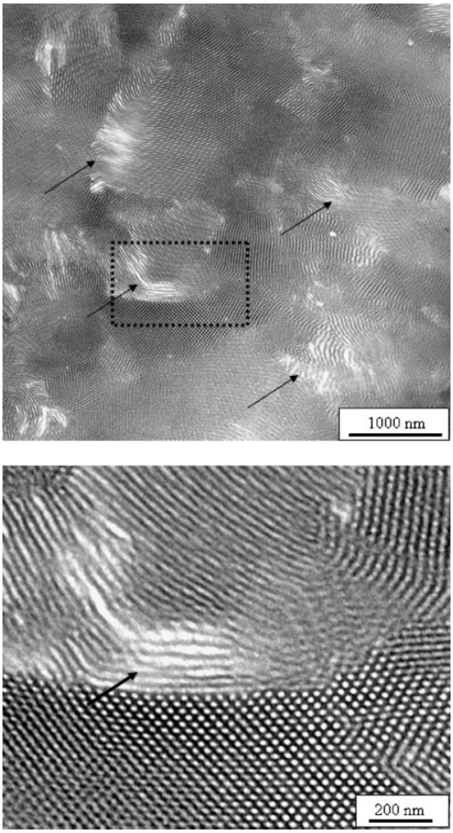

Figure 3.
Higher (top) and lower (bottom) magnifications of the TEM micrographs of the sample SIS/SI (80/20).

component appears dark due to staining by osmium tetroxide. The compositions of the blends are expressed in weight fractions.

Figure 3 shows the TEM micrographs of the sample SIS/SI (80/20). The blends comprises clearly two components: one appearing as brighter irregular islands scattered in the relatively darker matrix. The former (i.e., the dispersed phase) is richer in polystyrene (PS) and is made up of lamellar arrangement of the PS and PI while the latter (i.e., the matrix phase) is richer in polyisoprene and comprises cylindrical microphase-separated PS domains embedded in the polyisoprene (PI) matrix. The demixed lamellar block copolymer (obviously the diblock fraction) components are indicated by the arrows in Figure 3. A part of Figure 3a with an SIS/SI interface has been magnified in Figure 3b. That a clearly defined sharp interface is absent between the lamellar and hexagonal phases attests the partial miscibility of the systems studied.

A closer look in Figure 3b reveals that the area with lamellar microdomains consists of the layers of different thicknesses which might have been formed by the unequal mixing of the corresponding chains of the block copolymers.

By increasing further the SI diblock copolymer content in the mixture, the segregation of the lamellae and cylinder forming polymers persists, see Figure 4. The co-existence of lamellar and hexagonal microdomains is the evidence of the partial demixing of the block copolymers. The

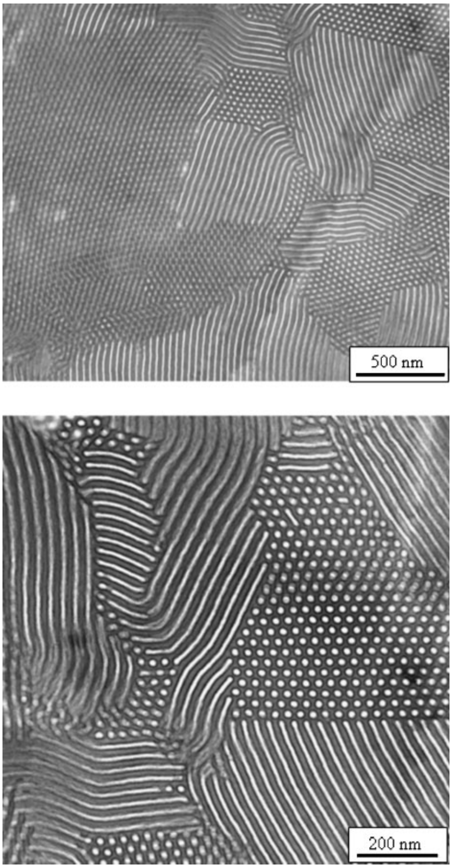

Figure 4.
Higher (top) and lower (bottom) magnifications of the TEM micrographs of the sample SIS/SI (60/40).

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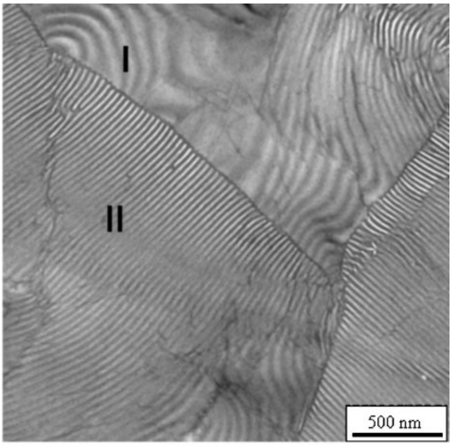
periodicity of lamellae as well as hexagonal phase both in this blend is approximately 55 nm. The periodicity of the cylindrical microdomains is significantly higher than that of pure triblock copolymer (i.e., 32 nm). This observation implies that a part of the diblock chains has been added to the triblock domains which increases the total polystyrene content and thereby the spacing between the adjacent domains.

The situation changes dramatically when the lamellar diblock copolymer forms the majority component of the mixture. Figure 5 shows the representative TEM micrographs of the blend SIS/SI (40/60). In this composition, the hexagonal morphology completely disappears. The micrographs of different magnifications of this sample depict the lamellar morphology with different periodicities. It should be noted that at higher amount of the SI diblock, the amount of larger polystyrene chain (i.e., with a molar mass of approximately 23 kDa) increases compared to the corresponding block of the SIS triblock copolymer (i.e. approximately 16 kDa). This fact suggests that the PS blocks of the diblock copolymer can accommodate more of the shorter polystyrene blocks coming from the triblock copolymer into the lamellar framework. Under these circumstances, the periodicity of the lamellar domains increases (region I in Figure 5).



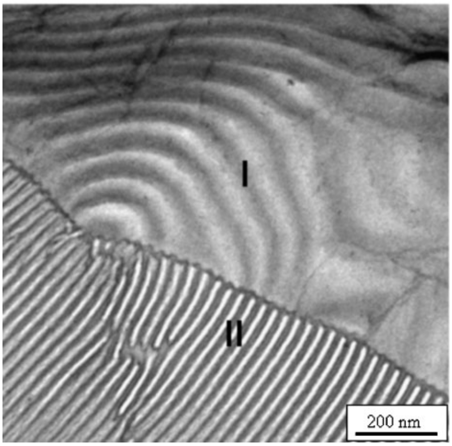


Figure 5.
Higher (top) and lower (bottom) magnifications of the TEM micrographs of the sample SIS/SI (40/60).

The rest of the diblock copolymer chains microphase separate forming, as usual, the lamellar structure with lower periodicity (see region II in Figure 5). The notion of the formation of lamellar microdomains of different periodicities is also supported by the presence of clearly defined boundary between the grains of lamellar structures which is represented by a thin layer of polyisoprene (see a dark line separating the grains in Figure 5).

For the sake of comparison, we prepared a blend of the SIS triblock copolymer with a polystyrene-*block*-polybutadiene (SB) diblock copolymer having similar PS content and total molar mass as the SI diblock copolymer used so far. The TEM images of a SIS/SB (60/40) are presented in Figure 6. We will compare later the results on mechanical properties of SIS/SI systems with that of SIS/SB systems.

SIS/SB blends represents a semi-compatible system because polystyrene blocks of both the polymers have tendency to mix each other at least in part while the elastomeric blocks (i.e. PI and PB blocks) are incompatible. The behaviour expected in SIS/SB blends under considerations is reflected in the TEM micrographs presented in Figure 6. In the SIS/SB (60/40) blends, the matrix is obviously formed by the SIS triblock copolymer (hexagonal morphology; periodicity measured = 32 nm) whereas the dispersed phase is formed by the fragments of lamellar

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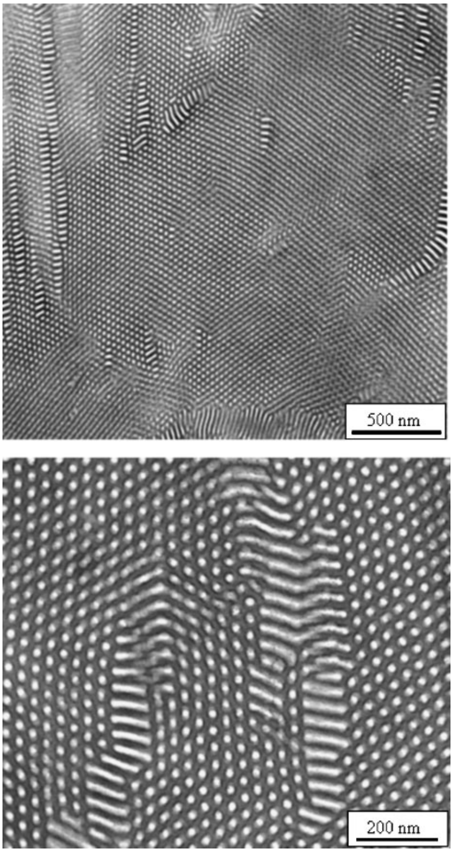

Figure 6.
Higher (top) and lower (bottom) magnifications of the TEM micrographs of the sample SIS/SB (60/40).

microdomains (periodicity measured = 40 nm). The periodicities of the parent block copolymers are maintained in the respective microdomains in the blend.

Tensile Mechanical Properties of Block Copolymer Blends

The goal of this paper is focused at the analysis of the influence of diblock chains on the deformation behaviour of triblock copolymers. In addition, we will attempt to correlate the mechanical properties of the investigated blends with their respective microphase separated morphologies and fracture surface morphologies of the respective samples.

The tensile stress-strain curves of some of the SIS/SI blends are presented in Figure 7. Each sample, except SIS/SI (40/60), shows elastomeric behaviour typical of styrenic thermoplastic elastomer. The pure block copolymer and the blends containing up to 20 wt.-% SI undergo elongation up to 1,500% and reach a maximum stress level of 12–15 MPa. The curves are similar, and the difference among them lies within experimental error.

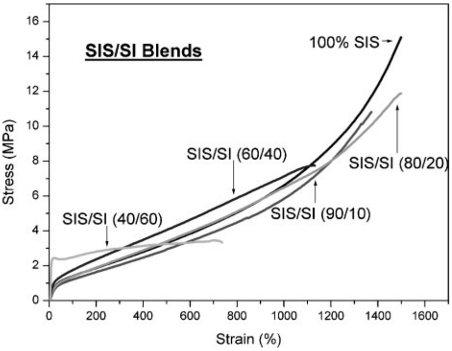

Figure 7.
Tensile stress-strain curves of SIS/SI blend samples prepared by solution casting.

The addition of SI diblock copolymer up to 20 wt.-%, the tensile properties alter insignificantly. This behaviour is correlated with the presence of morphology comprising the matrix of SIS triblock copolymer whereby the lamellar SI diblock copolymer formed the irregularly shaped islands (see Figure 3). During tensile deformation, the failure of the sample could have been originated by a micro-crack formed at the rubber phase of the diblock polymer which, however, would be arrested when reaching the SIS matrix. Thus the property of SIS triblock copolymer is maintained.

For SI content $\geq$ 40 wt.-%, the shape of the curves changes, the stress at break and elongation of the sample being drastically dropped (Figure 7). At 60 wt.-% of SI diblock content, the sample even shows the well defined yield point. Those curves can be correlated to the morphology of the corresponding sample. For instance, at 40 wt.-% of SI, the morphology of the sample showed the hexagonal and lamellar morphologies existing side by side (see Figure 4). Thus, the applied load could act

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simultaneously both on triblock (hexagonal phase) and diblock (lamellar) domains with the consequence that the enhanced cavitation of the rubbery phase might lead to the premature failure. As a consequence, the elongation at break and maximum stress level attained are reduced.

On increasing the SI diblock content to 60 wt.-%, both elongation at break and stress level were found to reduce drastically. One remarkable feature observed in stress-strain behaviour of this sample is that there is a clearly defined yield point, which is a characteristic of a lamellae forming block copolymer; and, indeed, this sample has a lamellar morphology (see Figure 5). Beyond the yield point the stress level tends to increase slightly and remains constant till the specimen undergoes fracture. The significant deterioration in the mechanical properties of the blend at 60 wt.-% of SI lies in the fact that the copolymer chains with physical cross-links only on one side (i.e., the diblock chains) practically overweighs the triblock copolymer and containing PI block chains physically cross-linked at both the ends by PS blocks.

Even for the SIS/SI (60/40) blend, the mechanical behaviour is quite disappointing as the stress level reached by the sample is pretty low where the hexagonal and lamellar morphologies exist side by side. The stress-strain curve of the sample lies above that of the rest of the samples showing ductile behaviour. However, beyond approximately 900% strain, the stress level begins to increase relatively slowly until the sample shows premature fracture. The concentration of the applied stress at the diblock component (at the region containing dangling PI chains) leading to the cavitation in the lamellar phase could be the reason behind the lower ductility of this blend.

To further analyze the effect of the dangling rubbery chains on the mechanical deformation of the SIS triblock copolymer, we studied the tensile properties of the SIS/SB blends, in which the molecular coupling is worse than in the case of SIS/SI blends as the polybutadiene chains not only dangle in the rubbery polybutadiene domains but also has incompatibility with the corresponding rubbery blocks of the SIS copolymer. The stress-strain curves of some of those blends are presented in Figure 8.

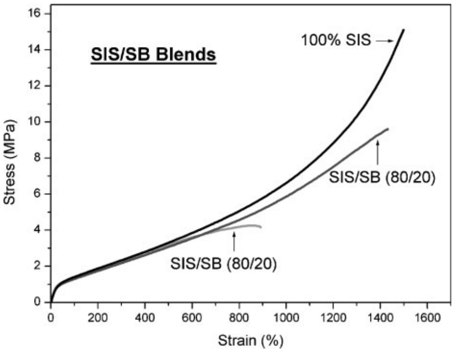

Figure 8.
Tensile stress-strain diagrams of selected SIS/SB blend samples.

Up to 20 wt.-% of diblock, both SIS/SI and SIS/SB blends show similar behaviour with respect to strain and stress at break. At higher diblock content, for instance for SIS/SB (60/40), both stress and strain at break (900% and 4.5 MPa, respectively) are significantly lower than that of the corresponding SIS/SI (60/40) blends (compare with Figure 7).

The situation changes when we prepare blends of the SBS triblock copolymer (having same composition as SB diblock) with the SIS triblock copolymer. It should be noted that for both SIS and SBS block copolymers, the rubbery middle blocks are physically cross-linked with outer polystyrene blocks of their molecules albeit the middle blocks (namely polyisoprene and polybutadiene) are incompatible with each other.

As in the case of SIS/SB blends (see Figure 6), the blend components segregate in SIS and SBS rich areas (the results are not discussed in this paper). With the addition of the SBS triblock copolymer, the mechanical properties of the blends do not worsen, as can be observed in stress-strain curves of SIS/SBS blends presented in

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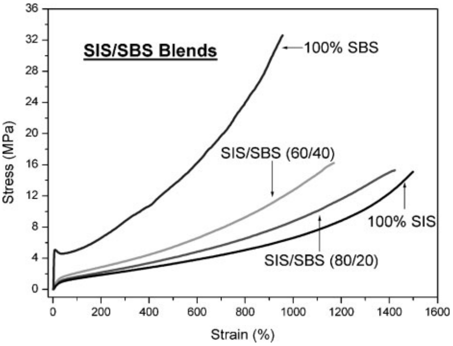

Figure 9.
Tensile stress-strain diagrams of selected SIS/SBS blend samples.

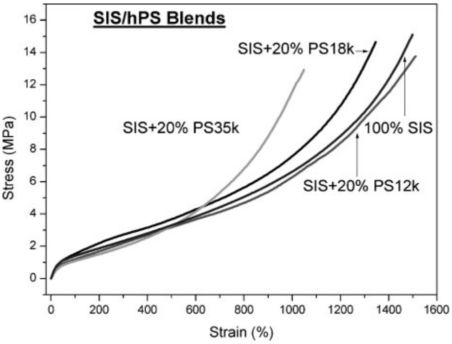

Figure 10.
Tensile stress-strain diagrams of selected SIS/20 wt.-% hPS blends prepared by solution casting; note the variation in hPS molar mass.

Figure 9 (details to follow in a future publication).

Figure 9 makes it clear that the addition of SBS to SIS triblock copolymer rather leads to an improvement in the tensile properties. In the present case, the blend with 40 wt.-% SBS has higher tensile strength (approximately 15 MPa) than the corresponding SIS/SI blend (approximately 8 MPa) while the strain at break is almost identical in both the cases. Also the SIS/SBS blends having other compositions were found to possess better tensile mechanical properties than the corresponding SIS/SI blends.

Tensile Deformation Behaviour of SIS/PS Blends

In previous section, we noticed that the tensile mechanical properties of the styrenic thermoplastic elastomers (for instance, SIS triblock copolymer) are strongly influenced by the presence of the freely hanging rubbery chains irrespective of the origin of the soft phase (i.e., polybutadiene or polyisoprene). We further deduced that the properties of the block copolymers are enhanced by the presence of the triblock copolymers in which the rubber blocks are physically cross-linked on both the ends by glassy PS blocks. It turns out that the presence of soft phase chains, whose terminal points lack physical cross-linking connections with glassy domains, are crucial for the determination of the mechanical properties.

In this section, we study the effect of addition of small amount of (20 wt.-%) polystyrene homopolymer (hPS) to the SIS block copolymer with especial emphasis on the impact of hPS molar mass. Figure 10 plots tensile stress-strain curves of blends of SIS triblock copolymer with polystyrene homopolymer having different molar masses. For all the blends the hPS content is 20 wt.-%. Among the homopolystyrene samples, PS010 ($Mw = 10$ kDa) has the molar mass below the entanglement molar mass of polystyrene ($M_e \sim 18$ kDa[27]); PS018 ($M_w = 18$ kDa) has the molar mass very close to M_e and PS035 ($M_w = 35$ kDa) has the molar mass approximately double the value of M_e. It should be noted that the molar mass of polystyrene blocks of the SIS triblock copolymer is approximately 15 kDa, which is close to M_e.

The comparison of the curves presented in Figure 10 reveals that the blends containing hPS having molar mass $\geq 2M_e$ (as shown by the blend with PS035 in Figure 10) show the properties similar to that of the neat triblock copolymer. In such cases, there is a trend of even improvement in the tensile properties. The properties of the system, with respect to strain and stress at break, shows a nominal worsening if the molar mass is $\approx M_e$ (as shown by the blend with PS018 in Figure 10) while the proper-

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ties degrade if the hPS molar mass of the added hPS $< M_e$ (as shown by the blend with PS010 in Figure 10). Thus the presence of low molar mass homopolymer is critical for the mechanical properties of the thermoplastic elastomer, especially when the hPS molar mass is below the M_e. However, the presence of a small amount of hPS having higher molar mass is advantageous for the tensile properties as the latter might work as reinforcing agent.

If we throw a closer glance at the stress-strain curve of SIS/PS010 blend, it becomes apparent that the elongation at break of this sample is much smaller and the stress at given strain (particularly beyond 600% strain) much higher than that of the pure SIS triblock copolymer (see Figure 10). Since the molar mass of the PS010 is less than the PS block of the SIS block copolymer (ca. 16 kDa), one can expect the solubilization of the added homopolymer into the block copolymer leading to the swelling of the PS domains. The widening of the glassy domains contributes to enhance the strength of the overall polymer, thus leading to large strength. However, the tensile strength of this blend is not higher than that of the neat SIS block copolymer. On the other hand, the bad coupling of the short homopolymer chains to the existing PS domains (due to absence of entanglements with each other in those domains) leads to the breakage of the polystyrene cylinders and hence to the decrease in the strain at break.

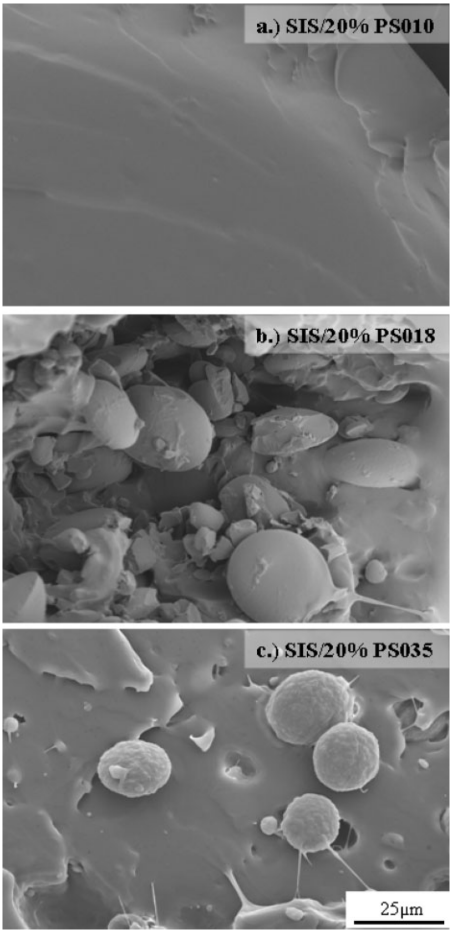

Figure 11.
SEM images of SIS/hPS blends with variable molar mass of polystyrene.

Finally, to support the results discussed so far on the tensile properties of the SIS/hPS blends, we present representative SEM micrographs of the tensile fracture surfaces of those materials, see Figure 11. The blend containing with 20 wt.-% PS010 homopolymer shows the fracture surface morphology that looks very similar to that of neat block copolymer (Figure 11a). The fracture surface is mainly characterized by the flat area formed by the elastic recovery of the highly stretched polymer fibrils. There is no indication of macrophase separation of the added polystyrene (e.g., in the form of islands or droplets which shall be the case in the other blends with PS018 and PS035. It implies that the added polystyrene is solubilized in the PS domains of the SIS triblock copolymer leading to PS domain swelling. It correlates well with the resulting worsening in the tensile mechanical property.

When the molar mass of the added polystyrene (M_{hPS}) approaches the entanglement molar mass of polystyrene (i.e. about 18 kDa[27]), a part of hPS may be solubilized in the corresponding domains in the dry brush regime[3] but a large part of the hPS is excluded from the domains that forms separate dispersed phase embedded in the matrix (see the spherical and oval particles having a diameter of about 20 μm in Figure 11b). If the M_{hPS} is higher than M_e, the former is easily macrophase-separated forming the segregated particles of hPS dispersed in the matrix (see Figure 11c).

In spite of the similar particle-matrix morphology of the SIS/PS018 and SIS/PS035 blends, there are some striking differences in their fracture surface morphologies especially in the surface roughness of the hPS particles. In the former, the hPS particles are smooth like *eggs* while in the later they appear as rough as the *ice-cream balls*. These appearances in the surface morphology provide the clue about the interface between the SIS matrix and hPS particles. The smooth *egg-like* appearance of the particles in the blend with PS018 ($M_{hPS} \approx M_e$) results from the simple detachment of the poorly bounded particles from the matrix whereas the rough *ice-cream balls* originate from the relaxation of strongly adhered PS035 ($M_{hPS} \approx 2M_e$) particles into the matrix. The latter plays a vital role for the reinforcing effect in the elastomeric block copolymers.

Conclusion

In this work, binary mixtures of polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS) triblock copolymer and different other polymers (including SI and SB diblocks, SBS triblock, and PS homopolymers) were prepared via solution blending. The samples were investigated with the aim of determining the influence of molecular coupling on large strain tensile mechanical property of the block copolymers.

In the block copolymer blends, it was possible to tailor the mechanical properties as long as the molecular coupling was present among the outer polystyrene blocks. The mechanical performance of the triblock copolymer was found to significantly deteriorate by the presence of dangling chains in the microphase-separated domains when the diblock content exceeded 40 wt.-%. In the blends comprising an SIS triblock copolymer and polystyrene homopolymers, the macrophase-separated compounds containing hPS (having molar mass $> M_e$) showed the optimum mechanical properties while the presence of low molar mass hPS led to worsening in the tensile behaviour.

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