Influence of Phase Separation Behaviour on Toughness of Compression Moulded SBS Star Block Copolymer/Polystyrene Blends

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Summary: The influence of homopolymer molecular weight and compression moulding on morphology formation and deformation behaviour of binary blends of polystyrene-polybutadiene based star block copolymer and polystyrene (PS) homopolymer was investigated. The samples used were a polystyrene-(polystyrene-co-polybutadiene)-polystyrene (S-S/B-S) star block copolymer and anionically prepared polystyrene (aPS). The techniques used were transmission electron microscopy (TEM) and uniaxial tensile testing. A wide range of segregation behaviour was observed depending on the ratio of the length of aPS chains relative to that of corresponding outer blocks of the block copolymer. For the first time, the formation of macrophase-separated 'droplet-like' morphology has been reported, which endows the block copolymer/polystyrene blends with higher toughness. The mechanical properties of blends are discussed in the light of micromechanical processes of deformation. The micromechanical mechanisms and their dependence with inter domain distance are similar to the mechanisms found in rubber network toughened systems.

Keywords: mechanical properties; phase behaviour; polymer blends; polystyrene-polybutadiene star block copolymer; toughness

Introduction

Polymeric materials usually possess only a limited specific properties. However, polymeric products having a broader spectrum of properties are desired by industrial manufacturers. In order to meet these requirements, either new polymers and copolymers are synthesised or the existing polymers are blended so as to achieve a desired combination of material properties. As the synthesis of copolymers (especially that of block copolymers) via classical routes is quite expensive, the blends of different homopolymers or homopolymers and copolymers offer a more attractive alternative towards the development of polymers having advanced property profile. The mechanical properties of the blends are usually determined by their phase morphology as well as various molecular and processing parameters. The molecular weight, molecular weight distribution as well as the configuration and constitution of the blend components are among the important molecular factors.

In the past, the influence of the degree of polymerisation or molecular weight of the homopolymer (M_{homo}) relative to the corresponding block of the block copolymer (M_{block}) on the phase behaviour of their blends has been intensively investigated. In such blends, three regimes of segregation behaviour can be observed depending on the molecular weight ratio α (where $\alpha = M_{homo}/M_{block}$):[1,2]

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1. $\alpha < 1$ (wet brush regime): Homopolymer chains are molecularly mixed with the chains of the corresponding copolymer block.
2. $\alpha \sim 1$ (dry brush regime): Homopolymer chains are dissolved into the corresponding phase, but are not uniformly mixed, i.e. the homopolymer chains are segregated towards the middle of the block domains.
3. $\alpha \gg 1$: Macrophase separation: Homopolymer chains are expelled out of the block domains so that the blend partners form separated phases.

Owing to different possible conformation of the added homopolymer chains in respective domains, entirely different phase behaviour may be expected in the blends in wet brush and dry brush regimes even at identical blend composition. Hasegawa and Hashimoto.[2] observed, for a given homopolymer content (ϕ_{homo}), that an increase in α induces a reduction in the distance between the chemical junctions and thereby the widening of inter-domain spacing and degree of lateral swelling, respectively. In the wet brush regime, the addition of homopolymer increases the concave curvature towards the minority phase facilitating the morphological transition. If $\alpha \sim 1$, the thickness of minority phase of the blend remains constant with increasing ϕ_{homo}. On the other hand, the domain spacing and its distribution increase.

The phase behaviour can be significantly altered during the processing of polymer blends whereby the shear rate as well as the temperature act as important parameters. It is to be noted that the effect of temperature on the segregation behaviour is opposite to that of the shear rate. Higher temperature or lower shear rate favours miscibility while at lower temperature or higher shear rate, the opposite effect may be expected. Also, macrophase separation between the block copolymer and homopolymer can be observed at extreme processing conditions, which may lead to a decrease in toughness.[3] The influence of processing on the (micro-) mechanical behaviour of block copolymer/homopolymer blends depends on the phase separation behaviour. The latter is determined particularly by the molecular properties of the blend components such as molecular weight ratio (α) as well as the processing conditions. Hence, the aim of this work is to investigate the correlation between morphology formation and deformation behaviour of polystyrene-polybutadiene block copolymer/polystyrene blends by altering both α and processing history of the blends.

Experimental Part

Materials Studied

An asymmetric polystyrene-(polystyrene-co-polybutadiene)-polystyrene (S-S/B-S) star block copolymer (named as ST3) and anionic polystyrene homopolymer (aPS) were used in this work. The aPS samples have polydispersity index close to unity and different number average molecular weights (M_n: 51 kg/mol, 100 kg/mol and 323 kg/mol). The subscripts in the nomenclature of each polystyrene sample (aPS_{51}, aPS_{100}, aPS_{323}) reflect the values of M_n in kg/mol.

The molecules of the 4 arm star block copolymer (ST3) having an M_n of 97.4 kg/mol and quite large polydispersity index of 2.1 are both compositionally (PS volume fraction of 0.74) and architecturally (with the arms having different lengths) asymmetric. The arms are coupled with the PS core having a M_n of 4.5 kg/mol. The total polystyrene phase present in the random polystyrene-co-polybutadiene block was estimated to be about 0.35[4] As a result, the amount of polystyrene as glassy or hard phase is approximately 60%. The molecular asymmetry is especially marked by different molecular weights of the outer polystyrene blocks leading finally to different arm length of the star molecules. The longest and the shorter outer polystyrene blocks have an average M_n of about 61 kg/mol and 11 kg/mol, respectively.

Sample preparation

The samples – both pure block copolymer and the blends containing 40%-wt. aPS -

were prepared by solution casting and compression moulding. The solution cast films of each sample having a thickness of about 0.5 mm were cast from its 3% (w/v) toluene solution in a petri dish. Subsequently, the solvent was slowly evaporated over a period of several weeks followed by annealing under reduced pressure for 48 h at 120 °C. The compression moulded plates of the blends (about 1 mm in thickness) were prepared at 200 °C and 200 bar following the mixing of the appropriate amount of blend components in an internal mixer. During mixing, nitrogen gas was used as protection against thermooxidative degradation.

Tensile Testing

The mechanical properties of the samples were characterised using uniaxial tensile testing using a universal tensile machine (Zwick 1425) at 23 °C. The tensile specimens cut from the plates have a total length and width of 50 mm and 4 mm, respectively. The cross-head speed of the tensile machine was 50 mm/min. At least six specimens of each sample were tested.

Electron Microscopy

From a small block of each specimen (neat and deformed), ultrathin sections (thickness less than 100 nm) were prepared using a Leica cryo-ultramicrotome for the examination of sample morphology by means of transmission electron microscopy (TEM: JEM 2010, 200kV, JEOL). The sections were treated with osmium tetroxide (OsO_4) vapour to stain selectively the polybutadiene (PB)-rich phase of the polymer. As a result, the PB and the polystyrene (PS) phases appear dark and bright, respectively in the TEM images.

For the electron microscopic characterisation of micromechanical mechanisms, semi-thin sections (thickness 100–500 nm) were prepared, which were strained in a special tensile device followed by staining with OsO_4 vapour. These sections were studied by means of a transmission electron microscope working at higher acceleration voltage (400 kV, JEM 4010, JEOL).

Results and Discussion

Morphology and Mechanical Behaviour of ST3

TEM image of the star block copolymer studied is presented in Fig. 2a. With respect to the glassy/rubbery volume ratio of 60/40 (see experimental section), one would expect a lamellar morphology in a diblock or a symmetric triblock copolymer. However, 'gyroid-like' morphology characterised by a co-continuous network of polystyrene domains dispersed in the rubbery S/B matrix was observed. The thickness of PS domains measured in the TEM micrograph is approximately 18 nm and the long period is 32 nm. These values remain constant independent of sample preparation methods.

The specific phase behaviour of the ST3 is a consequence of the asymmetric molecular architecture and the random S/B middle block present as soft phase, which leads to a new effective phase volume ratio. Earlier experimental [1] and theoretical [5–7] works on the influence of block copolymer architecture proposed that even a part of short outer **A** blocks can be pulled into the middle **B** block in a highly asymmetric **ABA** triblock copolymer[5] In the line of those findings, owing to the pronounced architectural asymmetry of ST3, we anticipate that a part of short PS segments can be partly incorporated into the rubbery S/B phase of the block copolymer. Additionally, short PS chains situated at the core of the star can be mixed to the rubbery phase with an effect that the overall soft phase volume fraction is further increased. At the same time the stiffness of the rubber phase is also increased. Due to the narrow composition window for the co-continuous morphologies in the block copolymer phase diagram, the phase behaviour of the block copolymers with this particular morphology is very sensitive towards the addition of homopolymers.[4]

Tensile stress-strain curve of ST3 is presented in Fig. 2b. It can be noticed that the block copolymer behaves in a tough manner; and the initial stage of stress-strain

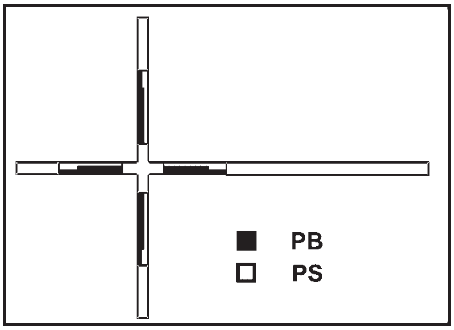

Figure 1.
Scheme of the molecular architecture of S-S/B-S star block copolymer (ST3).

curve is characterised by the existence of double yielding phenomenon.[8] This specific yielding behaviour of ST3 and its blends with low molecular weight homopolystyrene is observed in solution cast specimens (equilibrium state) as well as in extruded and compression moulded samples. Similar to the 'double yielding' observed previously in semicrystalline polymers,[9–11] the presence of two yield points in ST3 may be correlated with two different thermal processes caused presumably by the architecture or resulting morphology of ST3.[8]

Equilibrium Morphology of ST3/aPS Blends

The block copolymer used in this study has a special asymmetric architecture having bidisperse polystyrene outer blocks see Fig. 1). Therefore, ST3/aPS blends possess very unlike states of segregation between the aPS chains and the corresponding PS blocks of ST3. Taking into account the different molecular weights of the PS blocks of the copolymer and that of the polystyrene homopolymer added to it, the lower ($\alpha_l = M_{aPS}/M_l$) and the upper ($\alpha_s = M_{aPS}/M_s$) limit of the molecular weight ratio (α) can be estimated (see Table 1), where M_l and M_s stand for molecular weights the long and short outer PS blocks of ST3, respectively.

TEM images presented in Fig. 3 show the equilibrium morphology of ST3/aPS$_{51}$ blend. For this blend, the value of α_1 is close to unity (favouring the mixing in dry-brush regime) while that for α_2 is quite high (favouring macrophase separation). However, formation of macrophase-separated structures were not observed. Instead, the addition of aPS$_{51}$ leads to a transformation of 'gyroid-like' structures of ST3 to a microphase-separated lamellar morphology. It is very interesting to note that the lamellae having different average PS lamella thickness and long periods (compare locations I, II and III in Fig. 3) can be distinguished. The dissimilar lamellae pass from one 'grain' to another, which are not separated by well-defined boundaries.

The formation of lamellar morphology is generally a result of the miscibility of homopolymer chains with the corresponding block of the block copolymer, which increases the relative volume fraction of polystyrene and facilitates the formation of morphology corresponding to higher overall PS content. However, formation of the

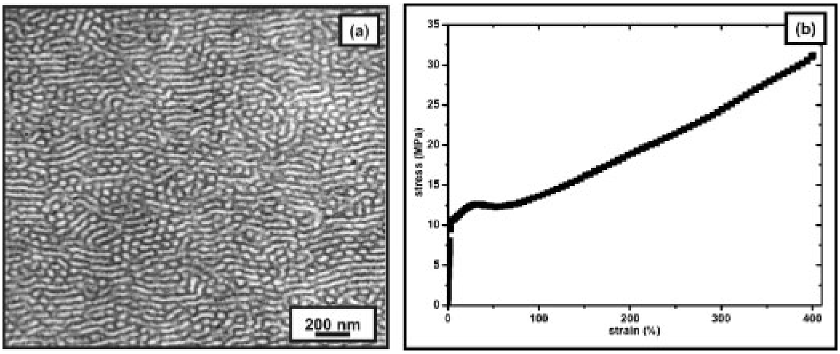

Figure 2.
Morphology (a) and stress-strain curve (b) of compression moulded S-S/B-S star block copolymer (ST3).

Table 1.
The estimated lower (α_l) and upper limit (α_s) of the molecular weight ratio for ST3/aPS blends depending on the molecular weight of aPS

[1] mol. wt. of aPS (M_{aPS})	[2] lower limit of mol. wt. ratio ($\alpha_l = M_{aPS}/M_l$)	[3] upper limit of mol. wt. ratio ($\alpha_s = M_{aPS}/M_s$)
51 kg/mol	0.8	4.6
100 kg/mol	1.6	9.0
323 kg/mol	5.2	29.0

[1] Molecular weight of polystyrene homopolymer used to prepare the blends.
[2] Ratio of molecular weight of aPS to that of the long PS block of ST3.
[3] Ratio of molecular weight of aPS to that of the short PS block of ST3.

lamellar morphology in ST3/aPS$_{51}$ blend cannot be satisfactorily explained by the miscibility criterion alone. This can be better explained by taking into account the remarkably different lengths of the outer PS blocks of ST3.

The lamellar morphology having larger PS lamella thickness (33 nm) and corresponding long period (50 nm) can be envisioned as being formed mainly by the stars having one or more long polystyrene blocks. The swelling of the polystyrene domains leading to the formation of 'thick' lamellae evidences the segregation of aPS chains towards the middle of the absorbing phase (dry brush regime). This notion is further supported by the formation of well-defined vesicles structures in ST3/aPS$_{51}$ blends especially at higher aPS content.[12] The formation of vesicle structures is similar to the blends of polystyrene-polyisoprene diblock copolymer and polystyrene homopolymer ($\alpha = 1.2$.[13]).

In addition to the regions with thicker lamellae as discussed above, there are regions with much thinner lamellae leading to lower periodicity. For instance, the locations II and III in Fig. 3 have PS lamellae with thicknesses of about 20 nm and 15 nm, respectively. In location III, the average long period of 23 nm is even smaller than of pure ST3. Therefore, the formation of a lamellar morphology having different suggests that the ST3 molecules might have been fractionated already in the neat sample. Consequently, a part of ST3 chains show different phase behaviour with added aPS molecules than the others. Larger stars accommodate more aPS resulting in areas with larger periodicity (such as location I in Fig. 3) and the smaller stars yield thinner lamellae with lower amount of aPS accommodated. In the mixture with aPS$_{51}$, the segregation of the smaller ST3 stars from the larger ones is facilitated by the fact that the smaller stars are far less compatible with added aPS owing to much lower molecular weight of the outer PS blocks.

The observed phase behaviour can be termed as the '*miscibility induced segregation*', which is similar to the macrophase

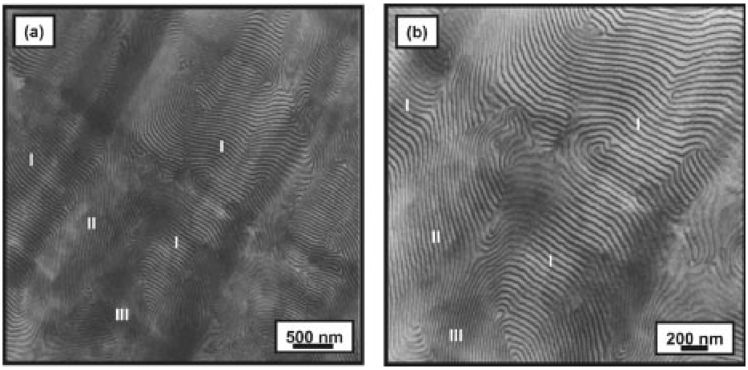

Figure 3.
TEM micrographs showing equilibrium morphology of ST3/aPS$_{51}$; lower (a) and higher (b) magnifications; the locations I-III lamellae having different average long periods; PB-rich phase appears dark.

separation induced by the microphase separation discussed by Hashimoto et. al in binary polystyrene-polyisoprene diblock copolymer blends having a large difference in molecular weights.[14] The lamellar diblock copolymers were segregated in grains separated by a clear macroscopic interface. In our case, the macrophase separation (leading to the macroscopic grain boundaries) is suppressed by the large molecular weight distribution of ST3.

Diverse morphologies (both microphase-separated and microphase-separated) are observed in the ST3/aPS$_{100}$ blend having a lower (α_l) and an upper limit (α_s) of the molecular weight ratio (α) of 1.6 and 9, respectively. Figure 4 shows macrophase-separated polystyrene particle, microphase-separated lamellar structures (location I, II and III in Fig. 4) and glassy spherical/worm-like PS domains embedded in a rubbery phase (location IV in Fig. 4). The lamellar structures are formed in macrophase-separated grains surrounded by the grains of spherical/worm-like structures. The average thickness and average long period of the spherical/worm-like domains are about 28 nm and 45 nm, respectively. Similar to the ST3/aPS$_{51}$ blend (see Fig. 3), the lamellae of the ST3/aPS$_{100}$ blend have variable average lamellae thickness (location I: 14 nm; location II: 28 nm; Location III: 56 nm) and average long periods (location I: 27 nm; location II: 44 nm; Location III: 71 nm).

The formation of grains with various nanostructures having different periodicity can be explained by similar mechanism as for the ST3/aPS$_{51}$ blend case. The observed non-uniform swelling of the PS lamellae is consistent with the fractionation of the star molecules discussed earlier. However, due to the larger molecular weight of aPS$_{100}$ mixed with a small number of outer PS blocks of ST3, the amount of the microphase-separated glassy structures (PS phase) becomes less than in ST3/aPS$_{51}$ blend. Consequently, a part of aPS, which cannot be accommodated by the ST3 molecules, form a separate phase (i.e., the macrophase-separated PS domains, see Fig. 4). It should be pointed out that the average thickness of the worm-like domains is significantly larger than the PS domains of neat ST3. It suggests that a part of ST3 domains have swelled by the aPS$_{100}$ molecules still keeping the nature of block copolymer morphology unaltered. These structures might have been formed by the stars having larger number of longer PS arms, which can accommodate the largest amount of homopolymer in dry brush regime without undergoing any morphological transition.

If the difference between the molecular weights of polystyrene homopolymer and the outer polystyrene blocks of ST3 is too

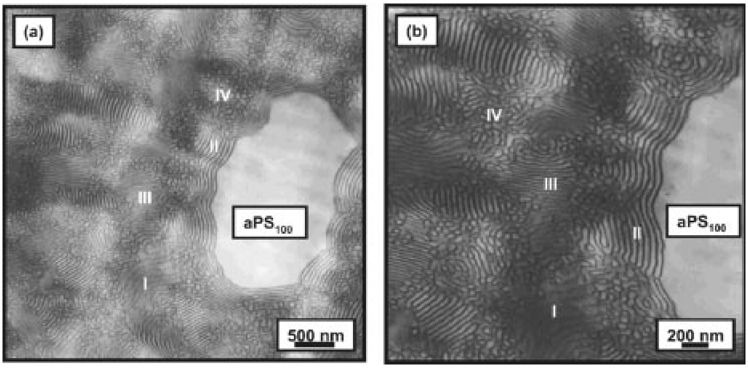

Figure 4.
TEM micrographs showing the equilibrium morphology of ST3/aPS$_{100}$ blend; lower (a) and higher (b) magnifications; PB-rich phase appears dark.

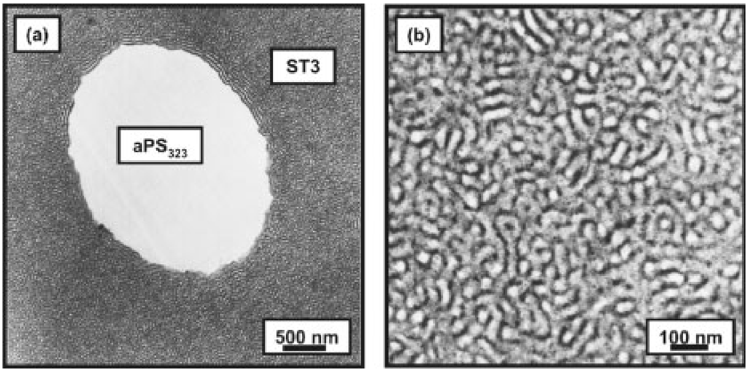

Figure 5.
TEM micrographs showing the equilibrium morphology of ST3/aPS_{323} blend; lower (a) and higher (b) magnifications; PB-rich phase appears dark.

large (i.e., the case of very high value of α), the homopolystyrene molecules cannot be solubilised by the PS blocks of the copolymer. Thus the macrophase separations dominates. In this case, the added aPS forms separate phase in the form of PS particles (see Fig. 5) and the morphology of pure ST3 is restored in the matrix.

Morphology of Compression Moulded ST3/aPS Blends

The non-uniform lamellar morphology of ST3/aPS_{51} blend that was formed at equilibrium condition was not observed on compression moulding of the samples. The mechanical mixing of the components at a temperature of about 200 °C led to the formation of uniform lamellar morphology, a result of enhanced miscibility of the blend (see Fig. 6, top, left). The transformation to the uniform lamellae is indicative of the homogeneous distribution of the homopolymer chains in polystyrene phase as in the works of Kimishima and Hashimoto.[15] The average thickness of PS lamellae and the average long period are about 19 nm and 26 nm, respectively. Interestingly, the thickness of the rubbery layers in this blend is rather small (smaller than in the pure ST3).

The processing induced miscibility enhancement is particularly visible for the blends, in which the macrophase-separation occurred at equilibrium (such as ST3/aPS_{100}, and ST3/aPS_{323} blends; see Figs. 4 and 5). After compression moulding, a discontinuous morphology with glassy inclusions surrounded by a rubbery phase evolved instead of macrophase-separated structures (see Fig. 6, top, right), which can be termed as ‘droplet-like’ morphology. For the first time, we have observed such a new processing induced morphology in the block copolymer systems.

As the molecular weight of the added polystyrene approaches that of the longest PS block of the block copolymer, the blend shows a typical morphology comprising droplets of glassy domains surrounded by rubbery phase and the co-continuous texture of lamellae-like nanostructures. In compression moulded ST3/aPS_{100} blend, the ‘worm-like’ glassy inclusions have average thickness of about 47 nm. The average thickness of the rubbery phase is about 10 nm. Actually, the so called ‘droplet-like’ morphology begins to form in ST3/aPS_{100} blend, which becomes fully developed at higher aPS molecular weight of the (see below).

At higher aPS molecular weight, the co-continuous ‘worm-like’ glassy inclusions dominating the morphology of ST3/aPS_{100} blend disappear and more spherical ‘droplets’ evolve in the compression moulded ST3/aPS_{323} blend (see Fig. 6, bottom). The

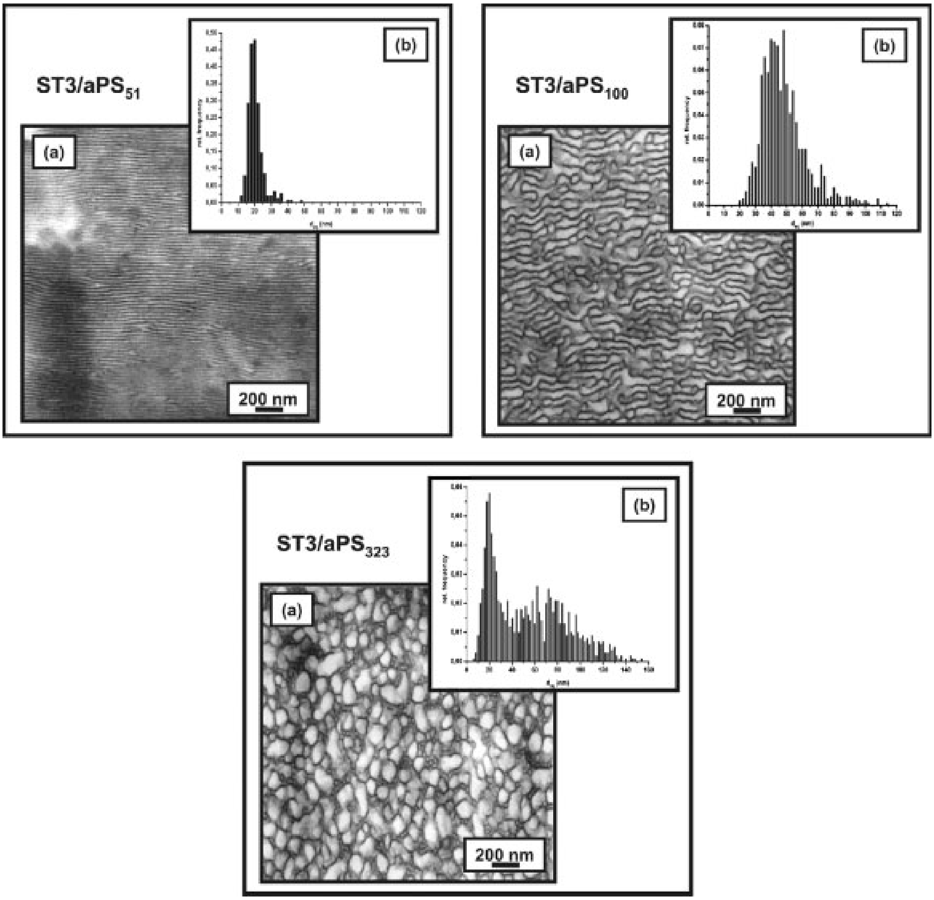

Figure 6.
(a) TEM micrographs showing the morphology of compression moulded ST3/aPS$_{51}$, ST3/aPS$_{100}$, and ST3/aPS$_{323}$ blends with 40 %-wt aPS and (b) corresponding distribution of thickness of PS lamellae; PB-rich phase appears dark in TEM images.

inclusions possess a bimodal distribution of thickness with average values of about 18 nm and 72 nm.

The formation of nearly bimodal spherical PS inclusions results from a large difference in the length of outer PS segments of the star block copolymer. Despite the effect of increasing miscibility induced by present processing conditions, the smallest outer polystyrene segments do not mix with anionic polystyrene. The smallest outer PS blocks might preferably form the small glassy domains together with the chain segments of the random polystyrene-polybutadiene middle block having a large content of polystyrene. Likewise, the longer PS blocks accommodating the aPS chains form the larger glassy domains.

(Micro-) Mechanical Behaviour of Compression Moulded Blends

The pure star block copolymer shows a tough behaviour (see Fig. 2b) independent of the processing conditions.[8] Fig. 7 presents the stress-strain curves of compression moulded ST3/aPS blends investigated. In general, the toughness decreases on blending the star block copolymer with polystyrene, the decrease being most significant for the ST3/aPS$_{51}$ blend, which possesses morphology comprising a two dimensionally continuous PS lamellae (see

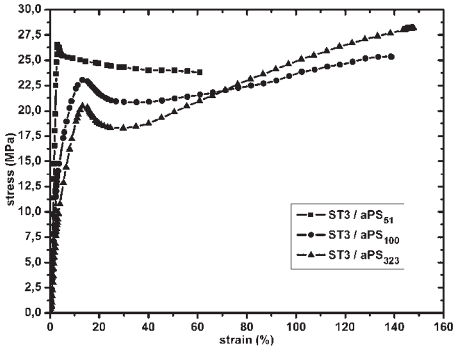

Figure 7.

Tensile stress-strain curves of the compression moulded ST3/aPS$_{51}$, ST3/aPS$_{100}$, and ST3/aPS$_{323}$ blends containing 40 %-wt. aPS.

Fig. 6, top, left). The strain at break of this blend is only about 40%.

It is clear that the yield stress (σ_y) of the blends is higher than that of ST3 (about 10 MPa). As expected, the value of σ_y is highest (27 MPa) for the ST3/aPS$_{51}$ blend (lamellar morphology). It goes on decreasing as the continuity of the glassy phase decreases. Therefore, the lowest value of σ_y is observed for ST3/aPS$_{323}$ blend, in which the matrix is formed by rubbery phase. The double yielding behaviour characteristic of the star block copolymer is not observed in the blends as the morphology departs significantly from that of pure ST3. In ST3/aPS$_{51}$ blend the stress beyond the yield point is at a high level which decreases slowly until the break.

TEM micrographs of ST3/aPS$_{51}$ blend deformed in tensile test are presented in Fig. 8. Thin sections for the TEM study were prepared from the locations close to the fracture surface. The micrographs reveal that the PS lamellae (white areas in Fig. 8) have alternating thicker and thinner regions suggesting the micro-necking of these lamellae. As the necking was not accompanied by the subsequent drawing of the lamellae, the ductility of the macroscopic sample was highly reduced.

In spite of similar dimension of PS lamella thickness as in a lamellar star block copolymer reported in an earlier work[16] (which deformed through the homogeneous plastic flow of the lamellae) the ST3/aPS$_{51}$ blend shows a brittle behaviour. One reason would be the reduced thickness of the rubbery layer, which hinders the 'slippage' of polystyrene lamellae thereby reducing the maximum achievable macroscopic strain at break. Furthermore, the absence of strain hardening in this blend, which indicates the premature failure of the sample, might have also been caused by segregation of aPS chains towards the centre of the PS lamellae.

The formation of the 'droplet-like' morphology in the ST3/aPS blends caused by the increasing molecular weight of anionic polystyrene is associated with an improvement of toughness (see Fig. 7, compare the area under corresponding stress-strain curves of ST3/aPS blends).

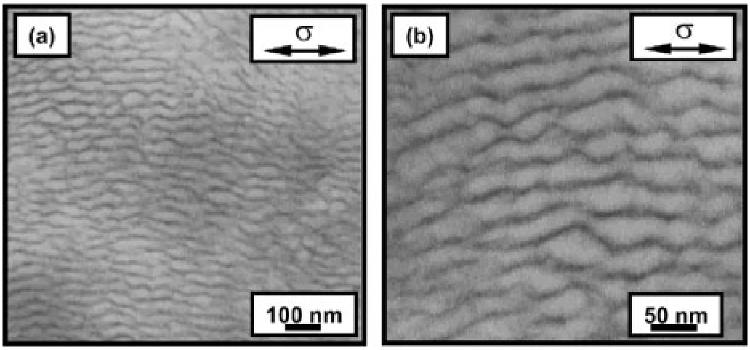

Figure 8.

TEM micrographs showing the structural changes after deformation of compression moulded ST3/aPS$_{51}$ blend with 40 %-wt. aPS$_{51}$ (a) lower magnification and (b) higher magnification, PB-rich phase appears dark.

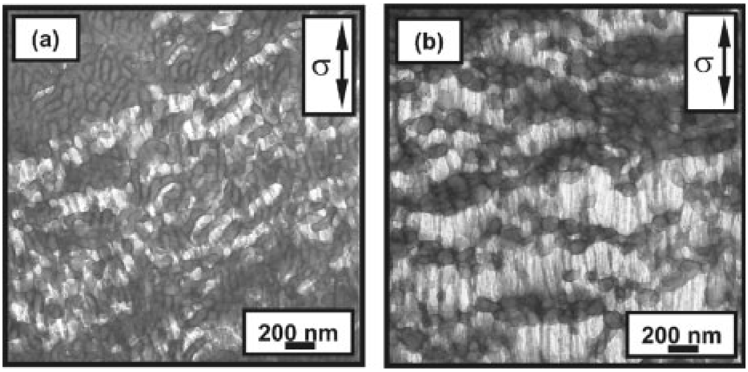

Figure 9.
TEM micrographs showing the deformation structures of compression moulded blends; (a) ST3/aPS$_{100}$ and (b) ST3/aPS$_{323}$; 40 %-wt aPS, PB-rich phase appears dark.

The toughness enhancement is independent of the appearance and dimension of the polystyrene inclusions, i.e., the mechanical behaviour of the blends is predominately determined by the continuous rubbery matrix. For the blends with aPS$_{100}$ and aPS$_{323}$ having 'droplet-like' morphology, the stress level drops after the clearly defined yield point followed by the region of strain hardening.

The strain hardening effect in ST3/aPS$_{323}$ blend is stronger than in ST3/aPS$_{100}$ pair, which is correlated with the least degree of plastic deformation at the initial stage of deformation as demanded by its morphology (rubber-like matrix with reinforcing 'PS droplets'). The examination of deformed phase-separated structures provide evidences to the proposed correlation between stress-strain behaviour and plastic deformation of the blend having 'droplet-like' morphology. A closer view of the TEM images presented in Fig. 8 reveals that the 'droplet-like' structures are inhomogeneously deformed in both the blend systems.

Detailed examination of the deformation structures of ST3/aPS$_{100}$ blends revealed that the 'droplet-like' PS inclusions can deform very strongly (plastic deformation) with a decrease in their thicknesses from 47 nm down up to 23 nm. On the basis of this plastic stretching, the local elongation of the glassy domains of about $\lambda \sim 4$ could be estimated [17], which lies in the same order as the maximum elongation of craze fibrils in polystyrene.[17,18] The deformation mechanism of the ST3/aPS$_{100}$ blend is similar to the mechanism of the rubbery network toughening of blends possessing glassy domains surrounded by a rubbery network (such as polyvinyl-chloride (PVC)/ethylene-vinyl-acetate copolymer (EVAc) blend and polystyrene/polyethylene (PE) blend).[17,19] The continuous rubbery phase is stretched and a three-dimensional (hydrostatic) stress state is built up in the surrounding rubbery network at the beginning of deformation. The glassy 'droplet-like' inclusions, which can be regarded as physical network points, are not deformed plastically at this state of deformation. If the rubbery phase is stretched enough and the stress reaches the yield stress of the polystyrene inclusions, the PS particles start to yield plastically following the stress transfer from the rubber phase to the glassy inclusions. The yielding of the 'droplet-like' inclusions absorbs large part of fracture energy. Consequently, the expense of total energy for deformation is not so high; and only the yielding of 'droplet-like' inclusions takes place. If the local stress is too high for a part of rubbery network, also the microvoids appear in the rubbery phase.

An essential stress transfer leading to the yielding of the polystyrene inclusions was observed earlier in blends with rigid thermoplastic particles and a matrix possessing slightly lower yield stress.[20,21] This deformation mechanism observed in blends having polycarbonate (PC) matrix and poly(styrene-acrylnitrile) copolymer (SAN), is called as 'inclusion yielding' or 'hard particle yielding'.

In contrast to the yielding of the 'droplet-like' inclusions of the ST3/aPS$_{100}$ blend, no intense plastic deformation of large droplets was noticed in ST3/aPS$_{323}$ blend. The TEM- image of deformed semi-thin section (thickness before deformation ~ 500 nm) of the ST3/aPS$_{323}$ blend (see Fig. 8b) reveals that only the rubbery phase deforms, which is characterised by the formation of micro-voids and fibrillation of the network. Embedded in the fibrils are also small polystyrene domains deformed during the stretching of soft phase. The observed micromechanical behaviour is similar to the deformation processes observed in the PVC/EVAc blends having very thick rubbery phase and a larger inter-particle distance. In those blends microvoid formation and strong fibrillation of the soft phase was observed and the PVC particles remained undeformed.[17] It was proposed that this micromechanism is related with the creation of three-dimensional (hydrostatic) stress, which is lower than the yield stress of the stiff particles.

Although the thickness of the soft phase in ST3/aPS$_{323}$ blend is quite small (~10 nm), the effective volume of the soft phase is significantly larger as the small PS particles practically belong to the soft phase. Consequently, the inter-domain distance between the large 'droplet-like' inclusions increases pronouncedly (~50 nm).

Conclusions

The morphology and deformation behaviour of blends comprising a polystyrene-polybutadiene star block copolymer and anionic polystyrene (aPS) were investigated. Depending on the ratio of molecular weight of aPS to that of the polystyrene outer blocks of the block copolymer, the blends exhibited different segregation behaviour (miscible, partially miscible and immiscible). Particularly, owing to the complex molecular structure of the copolymer, fractionation of the microphase-separated structures (presence of lamellar grains with different long periods) was observed for the compatible blends. The extent of macrophase separation of the blends was suppressed significantly on compression moulding of the samples compared to the solution cast films.

For the first time, a new 'droplet-like' morphology was observed in compression moulded blends, which basically formed macrophase-separated structures at equilibrium. The new morphology is characterised by nano-sized glassy polystyrene domains (diameter 10–200 nm) embedded in a rubbery phase. It has been demonstrated that the new morphology leads to a pronounced increase in toughness of the binary block copolymer/polystyrene blends, whose micromechanical mechanisms are found to be similar to that observed earlier in rubber network toughened PVC.

Acknowledgements: The research was supported by the Government of Sachsen – Anhalt and the German Science Foundation (DFG: Project: 'Transferinitiative: Optimierung von Steifigkeit/-Festigkeit/Zähigkeit von Polymerwerkstoffen'). M. Buschnakowski thankfully acknowledges the financial support from the 'Kultusministerium des Landes Sachsen – Anhalt' in the frame of the 'Stipendium zum 500 - jährigen Jubiläum der Martin – Luther Universität Halle – Wittenberg'. The authors would like to thank G. Kittel, D. Schieck and Y. Schwarz for assisting during tensile. Our sincere thanks go to Prof H.-J. Radusch and Dr. L. Fiedler for providing internal mixer.

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