6. STRUCTURE-PROPERTY-CORRELATIONS IN BINARY BLOCK COPOLYMER BLENDS

6.1 Motivation – Why Binary Block Copolymer Blends?
An ideal polymer blend is one which combines the useful properties of constituent blend partners. It is desirable to have mixtures or compounds or copolymers whose properties are even superior than that of either components. Interesting examples in this respect are PS/PnBMA diblock copolymers, in which the tensile strength is found to exceed that of both the components in a certain composition window [111].

For practical applications, polymer mixtures are required which allow a balance of important mechanical properties like stiffness, strength and ductility [1]. In practice, however, polymer pairs seldom show linear dependence of mechanical properties with composition. At a given composition, the properties of one of the components often dominate. For example, a sudden change in elongation at break was observed at a hPS content of 20 wt % in star block copolymer/hPS mixtures (chapter 5). Decreased ductility (compared to pure block copolymer) is, indeed, disadvantage of these blends.

Binary block copolymer blends, both blend partners being microphase separated, may offer the possibility of tailoring mechanical properties by reorganising the macromolecular segments. For this reason, morphology-toughness correlation in binary star block copolymer/triblock copolymer blends has been investigated.

![Figure 6.1: Architecture and morphology (schematic) of the copolymers used to prepare binary blends.](image)

To recall the mechanical behaviour of pure block copolymers having different morphologies, lamellar samples showed ductile behaviour under quasi-static loading condition (section 4.2.1). Under impact conditions, most copolymers showed brittle behaviour irrespective of molecular architecture and the type of microphase morphology. From the practical view point, materials which show tough behaviour both under slow as well as impact loading conditions are preferred.

The following study demonstrates that investigated binary block copolymer mixtures offer the
possibility to achieve these goals. It is the first systematic study of fracture toughness characterisation of binary blends consisting of asymmetric star block and triblock copolymers using crack resistance concept.

6.2 Phase Behaviour and Morphology

6.2.1 Phase Behaviour and Equilibrium Morphologies

The styrene/butadiene block copolymers used in this section are ST2-S74 and LN4-S65 (fig 6.1): one having thermoplastic properties and another one having thermoplastic elastomeric properties (section 4.2.1). The blends consist of 5, 10, 20, 40, 60 and 80 % by weight of LN4-S65.

![DMA spectra of ST2-S74/LN4-S65 blends](image)

Figure 6.2: DMA spectra of ST2-S74/LN4-S65 blends: note that the $T_{g-PB}$ shows a gradual increase with increasing LN4 content (see also table 6.1), measured at a frequency of 1 Hz.

DMA spectra of the blends given in fig 6.2 make it obvious that glass transition temperature of butadiene phase ($T_{g-PB}$) increases almost linearly (table 6.1) with increasing LN4 content which is an indication of incorporation of bulky styrene segments in the flexible butadiene phase.

The intensity of loss peaks (tanδ) and the area thereunder as well as the inclination of plateau region in the $G'$ vs. $T$ curves have been discussed in the literature as indicator for phase miscibility [15,157]. With increasing LN4 content, the intensity of the loss peak for soft phase and the area thereunder increases suggesting that the volume of materials taking part in the interaction at this region has increased with LN4 content, i.e., intensification of mixed phase. A continuous inclination of plateau region in $G'$ vs. $T$ curves further implies the gradual increase in mixed phase which is softer and leads to a decrease in storage modulus. Since LN4 contains already a large part of mixed styrene/butadiene random phase, the increase in mixed phase with increasing LN4 content is quite understandable.
Table 6.1: Glass transition temperature of soft ($T_{g-PB}$) and hard phases ($T_{g-PS}$) in ST2/LN2 blends determined by DMA

<table>
<thead>
<tr>
<th>LN4 wt %</th>
<th>$T_{g-PB}$ (°C)</th>
<th>$T_{g-PS}$ (°C)</th>
<th>remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-74</td>
<td>~100</td>
<td>-</td>
</tr>
<tr>
<td>20</td>
<td>-68</td>
<td>~100</td>
<td>-</td>
</tr>
<tr>
<td>40</td>
<td>-53</td>
<td>~100</td>
<td>-</td>
</tr>
<tr>
<td>60</td>
<td>-31</td>
<td>~100</td>
<td>-</td>
</tr>
<tr>
<td>80</td>
<td>-25</td>
<td>-</td>
<td>Detection of $T_{g-PS}$ difficult due to softening of the sample, DSC indicated a $T_{g-PS}$ of about 87°C for LN4</td>
</tr>
<tr>
<td>100</td>
<td>-15</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Meanwhile, the glass transition temperature of styrene phase ($T_{g-PS}$) remains more or less unchanged suggesting the presence of pure polystyrene phase. In every sample except pure LN4-S65, the shoulder located in damping curve at about 75°C persists which would indicate the relaxation of short PS chains of the star block copolymers as already discussed in section 4.1. At higher LN4 content, it was difficult to detect a $T_{g-PS}$. This suggests the absence of pure polystyrene phase in the samples although it is microscopically evident as will be discussed later.

Equilibrium morphology of binary ST2/LN4 blends is given in fig 6.3 and 6.4. An addition of 20 wt % LN4 leads to a transition from an ordered lamellar structure to a worm-like morphology with highly reduced long range order (fig 6.3). With the destruction of lamellae structure, the small PS domains originally embedded in PB lamellae of ST2 becomes less pronounced. With increasing LN4 content, the disordered domain structure persists, but the bright stripes of lamellae, with periodicity smaller than the pure ST2, are always phase separated. The size of PS domains in the blends have nearly same thickness distribution as the pure star block copolymer (~20 nm) which at higher LN4 content (80 wt %) drops to a level of pure LN4 (~15 nm).

In binary blends of block copolymers with well defined morphologies, the phase behaviour may be predicted by ‘single phase approximation’ [92], i.e., the morphology of the blends nearly corresponds to the total phase volume ratio of the components. Since the phase volume ratio and morphologies of both the block copolymers ST2 and LN4 are not well defined, it is impossible to assign the binary block copolymer blends a particular classical morphology. The blend morphologies are fully unconventional and difficult to interpret based on the results obtained so far. However, two points are quite obvious:

a. The blends show a considerable compatibility which is supported by DMA results as well.

b. Lamellae forming molecules are segregated from the rest of the others.

The quantification of microphase separated structures show that the polystyrene domains in the blends approach the size of polystyrene lamellae of the star block copolymer (Appendix 6.1).
Figure 6.3: TEM images showing Morphology of solution cast ST2/LN4 blends; the figures at the bottom left of each micrograph stands for LN4 wt %. 

-113-
In TEM images of the blends (fig 6.3), two kinds of domains are apparent: ‘white’ domains almost sharply separated from the ‘dark’ rubbery phase and ‘grey’ domains having diffuse boundary with the rubbery phase. The former domains resemble qualitatively the PS lamellae of pure ST2 while the latter PS domains of pure LN4. Majority of the hard domains in pure LN4 are ‘poorly segregated’ and disordered. The domains with diffuse boundary are especially pronounced at higher LN4 content (>60 wt %) and dominate the corresponding morphology.

![Figure 6.4: SFM phase images showing morphology of solution cast ST2/LN4 blends; note the existence of three distinguishable ‘phases’ at higher LN4 content (LN4 phase, ST2 phase and a mixed phase); at lower LN4 content these phases become indistinguishable; the figures at the bottom left of each micrograph stands for LN4 wt %.

Dark regions in the TEM image are results of preferential staining of double bond containing butadiene phase which also contains a considerable amount of styrene segments especially in the blends. Presence of styrene segments in the butadiene phase is also suggested by an increasing glass transition temperature of the soft phase. These styrene segments which cannot be stained by OsO$_4$ may reduce the local density of stained material whereby ‘grey’ domains results. The phase behaviour of ST2/LN4 blends is, indeed, very complex compared to conventional polymer blends and even binary block copolymer blends mentioned in the literature [88-91] due to their complex architecture and morphology.
Since the phase signals in SFM are sensitive to materials heterogeneity [158-161], the contrast in the phase images may be used to extract more qualitative information on the phase behaviour of the binary blends. The separation of lamellae forming molecules into separate domains is further supported by SFM phase images presented in fig 6.4 where the regions of alternating layers are more pronounced. Additionally, three phases become apparent especially at higher LN4 content: bright PS domains in dark rubbery matrix characteristic of LN4 (indicated by D), alternating layer structures (indicated by letter L) and worm-like domains packed close to each other forming an interpenetrating network-like structures (indicated by letter M). The latter might have originated by union of butadiene rich stars and LN4 molecules and may represent the mixed phase. Star molecules having higher amount of styrene may phase separate and form lamellar structures (as indicated by L in fig 6.4). The evolution of these domains are schematically illustrated in fig 6.5.

![Figure 6.5: Schematic showing chain reorganisation in ST2/LN4 blends forming LN4 domains (D), ST2 lamellae (L) and mixed phase (M).](image)

Since a fraction of stars is butadiene rich and contains nearly as much polystyrene hard block as LN4 molecules (in the range of 18000 g/mole), these stars are compatible with the LN4 molecules and may form common domain structure. This compatibilisation is further favoured by the presence of random copolymer middle block of rather high molecular weight in LN4. Nonetheless, molecules of the block copolymers ST2 and LN4 are clearly phase separated forming domains of different size and geometry.

Macrophase separation of block copolymer molecules resulting in the coexistence of different microphase separated structures was reported by several authors in different systems [86,87,91]. While Hashimoto et al. [91] found the coexistence of lamellae with different periodicity in a blend of copolymers having a large molecular weight difference, Jiang [87] reported the strange structures evolving from the incompatibility between the copolymer molecules of different molecular weights.
The observed incompatibility of the copolymer molecules in spite of identical chemical constitution can be discussed by the consideration of total entropy of the system. If the constituents (styrene blocks and butadiene blocks in the present case) of two different kinds of molecules (having very different molecular weights) have to reside in the like domains, the middle block of the ‘smaller’ molecules have to stretch which results in decrease in entropy. Since the chemical junctions must be located at the interface the outer block of the these small molecules cannot reach the domain centre which produces a density heterogeneity [87]. Hence, this process is not favourable, and the system tends to gain entropy by phase separation.

6.2.2 Morphology of Injection Moulded Samples

The investigation of block copolymers at thermodynamic equilibrium is the foundation of physical characterisation of these materials, e.g., through phase diagram. In the technical applications of block copolymers, this thermodynamic equilibrium is, however, never attained due especially to the technological constraints like limited processing time and associated economical considerations. Therefore, analysis of correlation between the non-equilibrium structures (i.e. the influence of processing conditions) and mechanical properties should find a more intensive consideration. Hence, morphology of the binary blends is analysed using injection moulded blends (fig 6.6). Injection moulded blends are further used in order to correlate the mechanical behaviour (tensile testing and fracture mechanics) with their micromechanical deformation behaviour.

Figure 6.6: TEM images showing morphology of injection moulded ST2/LN4 blends, injection direction vertical; the figures at the bottom left of each micrograph stands for LN4 wt %. 

-116-
It has been mentioned that the blends show partial miscibility in molecular level. In injection moulded samples, macrophase separation of the component block copolymers is further suppressed by the shear stress. The phase separated lamellar domains observed clearly in the solution cast samples are not distinct. Furthermore, the morphology is qualitatively similar to those observed in solution cast films (predominantly worm-like morphology in both the cases). Hence, it seems reasonable to use bulk injection moulded samples to study the morphology-toughness correlation in these binary block copolymer blends.

Basically, two types of morphologies are apparent: at lower LN4 content (0-20 wt %), lamellar morphology prevails which qualitatively resembles the structure of pure ST2. At higher LN4 content (40-80 wt %), the structures are qualitatively comparable to that of pure LN4. The structural reorganisation ("disorder") appearing with increasing LN4 content has, as will be shown in section 6.3.2, a strong influence on the achieved toughness level and underlying crack propagation mechanisms.

Opposed to the conventional polymer blends, where an amorphous soft phase (e.g., rubber) is dispersed in the matrix of hard phase, no percolation of soft phase (i.e., no phase inversion) may be observed in the blends of ST2 and LN4. This results from the absence of macrophase separation of corresponding block copolymer microdomains. This is partly due to high shear stress of injection moulding and partly to the partial miscibility of the similar block domains of the constituent block copolymers.

6.3 Mechanical Properties and Micromechanical Behaviour

6.3.1 Tensile Properties

Stress-strain curves of binary block copolymer blends given in fig 6.7 provide an excellent example of synergistic blends in which the mechanical properties show almost a linear dependence with composition. These diagrams elucidate how the balance of elastic to plastic deformation shifts with composition. The mechanical behaviour shifts gradually from a thermoplastic to an elastomer with increasing LN4 content.

Gradual disappearance of alternating layer structure (characteristic of the sample ST2) associated with appearance of sphere-like domains dispersed in rubbery matrix (characteristic of LN4) with increasing LN4 content is the reason for the observed continuous shift in mechanical behaviour. In solution cast samples, where the domains are randomly oriented, the yield stress is lower than that of injection moulded blends. The yield point which is already diffuse in ST2, becomes less pronounced with increasing LN4 concentration. The yield point in the injection moulded samples is visible until an LN4 content of 60 wt %. Appearance of the more pronounced yield point in
injection moulded sample is connected with domain orientation and thicker size of the tensile bars.

A linear dependence of Young’s modulus and elongation at break with composition as demonstrated in fig 6.8 manifests the possibility of fine tuning stiffness and ductility of the investigated binary block copolymer blends.

![Stress-strain behaviour of the binary ST2/LN4 blends at room temperature; a) solution cast samples and b) injection moulded samples, cross head speed 50mm/min.](image)

![Young’s modulus and Elongation at break plotted as a function of blend composition in ST2/LN4 blends (injection moulded samples, 50 mm/min at room temperature).](image)

The elongation at break increases with LN4 concentration while the stress at break remains more or less constant. Higher maximum stress level is achieved in solution cast samples than in injection moulds which is attributable to better phase separation in the former.

With increasing LN4 content, the amount of elastic deformation in the blends progressively increases making it more difficult to analyse the strain induced structural changes. However, important inferences on micromechanical processes of deformation may be obtained by analysing the fracture surfaces of the tensile specimens broken in tensile tests. Representative fracture surface morphology of some binary blends is presented in fig 6.9.
Fracture surface of pure star block copolymer shows ductile fracture of the specimen accompanied with large plastic stretching and fibrillation. The fracture process begins somewhere at the middle and expands towards periphery of the tensile bar (fig 5.16). A transition in deformation behaviour is observed at an LN4 content of 20 wt %, when the fracture surface shows the structures typical of shear deformation. The typical shear lips (fracture parables), which represent cracks propagating along different planes, are clearly visible (fig 46.9a).

Figure 6.9: Lower (left) and higher (right) magnification of SEM micrographs showing fracture surface morphology of binary ST2/LN4 blends, fracture surfaces from injection moulded bars broken in tensile test a) 20 wt % LN4 and b) 60 wt % LN4

With increasing LN4 content, the fracture surface becomes increasingly smoother suggesting increasing tendency of elastic deformation. The extent of plastic deformation decreases, and the fracture surface shows isolated regions of plastically drawn materials (fig 6.9b).

Micromechanical behaviour of the pure block copolymers ST2 and LN4 has been discussed in section 4.3.1. It has been mentioned that ST1 shows a large homogeneous plastic deformation of PS lamellae while LN4 exhibits principally an elastic behaviour. The deformation mechanisms is coupled with the orientation of microstructures as well.
The morphology of the blends become more complex with increasing LN4 content as the elastic deformation becomes more and more dominating. These factors introduce difficulty in the determination (especially in the quantification) of strain induced structural changes in the samples. Therefore, deformation structures in solution cast blend containing 60 wt % LN4 have been investigated by TEM. The representative TEM micrographs are given in fig 6.10.

In the first glance, it may be noticed that lamellar grains are turned into chevron-like patterns as observed in cylindrical and lamellar block copolymers under tensile deformation [126,143]. Almost all the kink boundaries in these ‘inverse chevrons’ are, however, perpendicular to the strain direction in contrast to the deformation structures in lamellar block copolymer (e.g., compare with fig 4.12b). Low magnification of TEM image reveals that the ellipsoidal worm-like PS domains in the ‘matrix’ are aligned in the strain direction. This is an indication of plastic deformation of the matrix-domains. Furthermore, the thickness of PS lamellae has been reduced from about 22 nm to about 15 nm due to deformation (Appendix 6.2).

Since the kink boundaries produced by deformation are almost always perpendicular to the strain axis, the dispersed lamellar grains must have rotated. Obviously, the chevrons are formed by the relaxation of the plastically deformed lamellae when the elastic energy absorbed by the matrix

\* Because the kink boundaries are almost perpendicular to the strain axis in contrast to chevron formation in lamellar block copolymers, the chevron in the present case may be referred to as ‘inverse chevron morphology’. 

-120-
phase has been released. This is the same mechanism as proposed for injection moulded ST2/PS190 blends at higher PS content (compare with fig 5.15 and 5.18). Hence the deformation of this sample is mainly controlled by the predominantly elastic stretching of matrix consisting of dispersed PS domains which allows a large plastic deformation of lamellar grains and at the same time also contributes to delay fracture by elastically absorbing a large part of supplied energy.

6.3.2 **Toughness Characterisation by Fracture Mechanics Approach**

In this section, results from fracture mechanics experiments using an instrumented Charpy impact tester are discussed. Among others, a main objective of fracture mechanics methodology is to determine fracture mechanics parameter which quantify the materials resistance against unstable and stable crack growth. Three-point bending specimens (single edge notched bend, SENB) having a sharp notch made by razor blade allow the determination of the load-deflection (F-f) curves from which the parameters like stress intensity factor (K), J-integral values (J) and critical crack-tip opening displacement CTOD (δ) can be calculated [149].

**a. Load deflection (F-f) curves**

![Load-deflection (F-f) curves for some binary star block copolymer/triblock copolymer blends](image)

Figure 6.11: Load-deflection (F-f) curves for some binary star block copolymer/triblock copolymer blends; all the samples except ST2-S74 were not broken.

Representative load-deflection (F-f) curves of some of the notched samples are given in fig 6.11. These diagrams give an insight into materials behaviour under impact loading conditions. While pure star block copolymer shows nearly linear elastic behaviour, the blend with ≥ 20 wt % LN4 shows elastic-plastic behaviour combined with crack propagation energy after the load maximum. F-f diagrams recorded with unnotched samples allow the determination of Young’s modulus E_d and yield stress σ_yd under impact loading conditions (fig 6.12). A continuous
decrease of these parameters with ascending LN4 concentration qualitatively suggests the increasing trend of toughness modification.

Fig 6.12: Dependence of a) Young’s modulus $E_d$ and b) yield stress $\sigma_{yd}$ as a function of blend composition in ST2/LN4 blends determined by evaluating F-f diagrams of unnotched specimens.

b. Characterisation of Crack Resistance Behaviour

As already mentioned, the pure star block copolymer shows nearly linear elastic behaviour while the blend containing 20 wt % LN4 shows an elastic-plastic behaviour. Meanwhile, this change in F-f behaviour is connected with a transition from predominantly unstable crack growth to stable crack growth leading to a rapid increase in fracture toughness.

For blends containing <20 wt % LN4, very small amount of plastic flow may be ascertained. Since the maximum achievable stable crack growth in this composition range was very small ($\Delta a \leq 70 \ \mu m$, small scale yielding), crack arresting was impossible. Hence, the experimental determination of crack resistance curves (R-curves) was possible only at LN4 concentration $\geq 20$ wt %. The quantitative description of stable crack propagation behaviour resulting therefrom is based on the quantification of fracture mechanics parameters as resistance against stable crack initiation and propagation.

Crack resistance (R-) curves for ST2/LN4 blends are given in fig 6.13, which show the dependence of fracture mechanics parameters (J-integral $J$ as well as crack-tip opening displacement, CTOD) as a function of stable crack growth $\Delta a$. Both $J-\Delta a$ and $\delta-\Delta a$ curves (i.e., R-curves with $J$ or $\delta$ as loading parameter) exhibit the identical behaviour indicating the similar applicability of both the concepts in determining the R-curves of these blends. At 80 wt % LN4, the behaviour is nearly equivalent to that of pure LN4, and hence, these curves may be evaluated simultaneously.
The technical crack initiation values (\(J_{0.1}\) and \(\delta_{0.1}\)) are generally employed in order to characterise the stable crack initiation. At these values the predetermined magnitude of small crack growth (e.g., \(\Delta a = 0.1\) mm) will be reached. On the other hand, based on the considerations of the kinetics of crack propagation processes, i.e., analysis of different phases of crack growth (like crack-tip blunting, stable crack initiation and propagation, and perhaps the unstable crack propagation) as a function of time, physical crack initiation values (i.e., \(J_i\) and \(\delta_i\)) can be determined. The parameters determined at physical crack initiation points are more theoretically motivated than those at technical ones (e.g., at \(J_{0.1}\) and \(\delta_{0.1}\) which are determined for stable crack growth \(\Delta a = 0.1\) mm). Additionally, inferences about the magnitude of physical crack initiation values can be deduced through the quantitative analysis of stretch zone on the fracture surfaces.

Like corresponding R-curves, the crack initiation values based on J-integral and \(\delta\) concepts show similar tendency. Fracture mechanics parameters as resistance against unstable crack propagation (\(J_{id}\)) and stable crack initiation (\(J_{0.1}, J_i\)) are plotted in fig 6.14a as a function of blend composition.

As a resistance against stable crack propagation, the slope of the R-curves at \(\Delta a = 0.1\) mm (i.e. \(dJ/d(\Delta a)_{0.1}\) and \(d\delta/d(\Delta a)_{0.1}\)) and resulting tearing modulus (\(T_{J} = dJ/d(\Delta a)_{0.1} \times E_d/\sigma_{yd}^2\) and \(T_{\delta} = d\delta/d(\Delta a)_{0.1} \times E_d/\sigma_{yd}\)) can be utilised. As shown in fig 6.14b, the slopes of the R-curves at \(\Delta a = 0.1\) mm and the tearing modulus increase up to 80 wt % LN4 after which these values remain constant. This indicates that the increasing ductility of the unnotched samples in the present case with increasing LN4 content associated with decreasing elasticity modulus \(E_d\) and yield strength \(\sigma_{yd}\) (fig 6.12) also manifests the resistance against stable crack propagation. It should be,
however, mentioned that this correlation does not have a general validity as shown by recent results (discussed in part II of ref. [118]). The physical crack initiation values ($J_i$ and $\delta_i$, fig. 6.14a) are insensitive to morphology which is in accordance with the previous results obtained for heterophase polymeric systems [176]. Furthermore, it is found that crack initiation values (e.g., $J_{0.1}$ and $\delta_{0.1}$) are generally not (or less pronounced) sensitive to the structure of the materials in contrast to the crack propagation values (like tearing modulus $T_J$ and $T_\delta$, fig. 6.14b).

The kinetics of crack growth, especially the demarcation of each stage of crack growth, can be described by the crack propagation velocity. Additionally, it may be described by values like temporal change of fracture mechanics parameters e.g., CTOD-rate $d\delta/dt$ as a function of stable crack growth. In fig 6.15, the stages of crack propagation are represented by the slopes of $d\delta/dt$ values. Stage (1) is correlated with the region of crack tip blunting, where the original razor-sharp crack blunts resulting in a strong increase in $d\delta/dt$ values. In stage (2), the blunted crack propagates stable but non-stationary, i.e., the $d\delta/dt$ values increase with $\Delta a$. In stage (3), the non-stationary stable crack propagation finally reaches a stationary stable crack growth (equilibrium state), and the value of $d\delta/dt$ remains constant. The meaning of the constancy of $d\delta/dt$ values is equivalent to that of crack tip opening angles (CTOA). The maximum value of $d\delta/dt$ attained increase with LN4 content in the blends: 0.05 m/s and 0.09 m/s for 20 and 40 wt % of LN4 respectively and 0.10 m/s for 60 wt % and onwards.

![Figure 6.14: Fracture mechanics parameters as a function of blend composition: a) crack initiation and b) crack propagation values.](image-url)
Two different brittle/ductile transitions (BDT) were observed in other heterophase polymers [176,177]: the conventional BDT1 (“brittle/tough” transition) as a measure for the safety against unstable crack propagation and THT (“tough/high-impact” transition) as a measure for the protection against stable crack initiation. In the investigated binary block copolymer blends, a pronounced BDT can be observed at 10-20 wt % LN4 while a quite broad BDT2 is observed between 50 and 60 wt % LN4 (fig 6.14a).

As demonstrated in recent studies [176,177], a shift from THT to BDT occurs if the crack growth mechanism shifts from stable towards unstable one. As discussed in [177], differences in deformation mechanisms leading to BDT and THT may be explained by Wu’s percolation theory [178] and Margolina’s theory [179], respectively. Wu’s approach has taken a critical inter-particle distance or a critical matrix-ligament thickness into consideration, which represents a material constant. Margolina has, however, demonstrated that critical inter-particle distance is strongly dependent on the loading conditions (like speed, loading mode and temperature). Especially, the temperature dependence of the critical inter-particle distance shows nearly a linear behaviour. This classification is, however, irrelevance in the investigated system where the structural heterogeneity lies on nanometer scale in contrast to a particle-matrix morphology of most conventional polymer blends.

Examination of fracture surfaces allows an analysis of crack propagation phenomena. As shown in SEM micrographs of fracture surfaces in fig 6.16, the transition BDT is associated not only with a strong increase in stable crack growth but also with a principal change in crack propagation mechanism. ST2 undergoes a brittle failure after crack-tip blunting via unstable crack propagation. In the blends with 5 and 10 wt % LN4, a small amount of stable crack growth
may be observed before the unstable crack growth begins, which is visible in SEM micrographs as structures formed by coalescence of microvoids (fig 6.16a,b and 6.17a). Such a crack propagation mechanism is typical for semicrystalline polymers like HDPE [173], where the structures are in nanometer scale, as well. In a composition range 10-20 wt % LN4, as a consequence of increasing disordered morphology, a sudden change from unstable crack propagation via coalescence of microvoids to the crack propagation via shear-flow occurs (fig 6.16c and 6.17b). The individual crack growth areas (parabolic marks) are separated by clearly visible shear-lips. Crack growth via shear-flow mechanism is typical for many amorphous polymers like polycarbonate [172].

Figure 6.16: Scanning electron micrographs of fracture surfaces of ST2/LN4 blends (SENB specimens) loaded in impact test; the figures at the lower left bottom corner of each image stands for LN4 wt %.
Here, the crack becomes again sharp after blunting and propagates through the material by translation of the whole crack front [176]. This leads to the stretch zone at the end of whole fracture surface length in contrast to the stretch-zone in blends containing 5 and 10 wt % of LN4 which is formed at the end of razor-notch.

The transition in deformation mechanisms at LN4 content of 20 wt % (microvoids coalescence to shear-flow) associated with change in crack growth mode is demonstrated clearly by high magnification of SEM micrographs given in fig 6.17.

![Figure 6.17: High magnification of SEM pictures of fracture surfaces of ST2/LN4 blends (SENB specimens) loaded in impact test; the figures at the lower left bottom corner of each image stands for LN4 wt %.

The size of the stretch zone can be used as a measure for plastic deformation during crack-tip blunting, which is indicated by stretch zone width (SZW) and stretch zone height (SZH) along and normal to the direction of crack propagation, respectively. The decrease of SZW in the blends with increasing LN4 content (fig. 6.16) may be attributed to the transition from the behaviour of a conventional thermoplastic material (ST2) to that of a thermoplastic elastomer (LN4) i.e., a transition from viscoelastic to entropy-elastic deformation behaviour.

In contrast to conventional polymer blends where the toughness modification is achieved through the dispersion of a soft phase in a hard matrix (macrophase separation), the investigated binary block copolymer blends represent nanometer structured materials. New mechanism of toughness modification (where the transition from a lamellar structure with a high long range order to a less ordered structure plays the central role) results in a specific morphology-toughness correlation which differs fundamentally from toughening mechanism in conventional polymer blends.

An evidence of a strong correlation between fracture toughness and structural disorder of the microphase separated domains is provided by another set of binary block copolymer blends. TEM image of injection moulded LN2-S74/20 wt % LN4-S65, given in fig 6.18a, exhibits a long range order nearly as pronounced as in the pure triblock copolymer LN2. This highly ordered
morphology results in F-f diagram presented in fig 6.18b under same set of condition as ST2/LN2 blends. In contrast to ST2/20 wt % LN4 blend, LN2/LN4 blends with identical composition shows predominantly unstable crack propagation and nearly linear elastic behaviour (compare with fig 6.11).

6.4 Conclusions

Morphology, mechanical properties and deformation behaviour of binary blends consisting of asymmetric styrene/butadiene block copolymers are investigated. Toughness of the blends is especially characterised by the use of fracture mechanics approach. The mixtures represent a partially compatible system in which both micrphase and macrophase separation of the blend components (which are themselves microphase separated) are observed.

The studied binary blends allow a balance of stiffness/toughness ratio in a wide composition range. Further, these blends provide unique combinations for preparing transparent ultra-high impact thermoplastically processable materials whose toughness appears to be favoured by structurally disordered microphase separated morphology.

The fracture behaviour of binary block copolymer blends investigated in this work is summarised in fig 6.19. A transition from brittle to tough behaviour occurs at ~ 10-20 wt % LN4, when the morphology changes from highly ordered lamellae to worm-like PS domains in a rubbery matrix. Meanwhile, the crack propagation mechanism shifts from microvoid coalescence to shear-flow. A second broad transition (tough/high impact) takes place at ~ 50-60 LN4 content as the morphology closely resembles that of pure LN4, and the rubber-like crack propagation mechanism (tearing) predominates.
voids coalescence shearing tearing
Like crystalline polymer (e.g., PE)
Like amorphous polymers (e.g., PC)
Like rubber (e.g., SBR)

Fracture behaviour
“brittle” tough ultra-tough

Crack growth mechanism
voids coalescence shearing tearing

Fracture surface morphology
brittle fracture
pl. zone stable crack growth
Stretch zone
broken using LN$_2$ after test
st. crack growth

Figure 6.19: Scheme showing correlation between microphase morphology, fracture mechanism and fracture surface morphology of binary block copolymer blends.

To adequately clarify the toughness enhancement in the investigated block copolymer blends from the micromechanical standpoint, in situ microscopic deformation tests should be carried out in future.