Fracture Behaviour of Binary Styrene/Butadiene Block Copolymer Blends

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Abstract

Morphology and fracture behavior of binary block copolymer blends (triblock and star block copolymers being made up of styrene and butadiene) have been studied via transmission electron microscopy (TEM) and instrumented Charpy impact testing. The toughness of the ductile blends has been characterized by dynamic crack resistance curves (R-curves). The lamellar star block copolymer shows nearly elastic behavior of small scale yielding and unstable crack growth. Addition of 20 wt % of a triblock copolymer comprising polystyrene domains dispersed in rubbery matrix leads to a strong increase in toughness. The mechanism of toughness modification, based on the nanophase-separated structures, represents a specific morphology-toughness correlation which differs fundamentally from toughening mechanisms observed in conventional polymer blends.

Introduction

Block copolymers represent a class of self-assembled heterogeneous materials where scale of phase separation lies in the range of gyration radius of the macromolecules. The nanoscale self-assembly in these materials results from intra-molecular phase separation allowing a considerable control over their morphology and mechanical properties via interfacial and architectural modification.[1]

A rich variety of nanostructures (such as body centred cubic (bcc) spheres, hexagonal (hex) cylinders, gyroid phase, lamellae (lam) etc.) develops in block copolymer systems upon microphase separation (MS). The process of MS is a result of two competing effects: a) dissimilar blocks prefer to segregate due to their inherent chemical incompatibility; b) the spatial extent of phase separation is, however, limited by the connectivity of the blocks imposed. As a compromise of both the effects, periodic nanostructures evolve. Therefore, the geometry of the microphase separated structure is

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very sensitive to the chemical nature and molecular structure of the copolymer as well as its total composition. Unlike microphase separated block copolymers, the domain diameter in phase separated polymer blends are typically several hundred nanometers and the morphology is independent of detailed features of the molecules.[1,2]

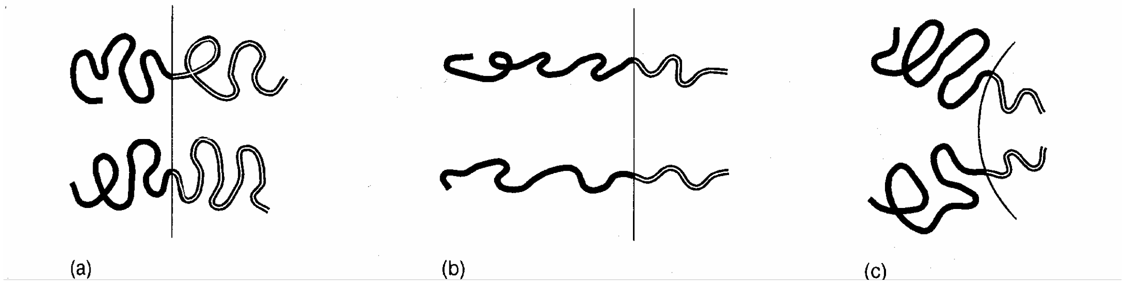


Figure 1: Scheme of chain conformation at the microphase-separated state; a) stable flat interface from a compositionally symmetric AB block copolymer r when the volume fraction of each component is same (i.e. $\Phi_A = \Phi_B$), b) an unstable flat interface in the case $\Phi_A >> \Phi_B$ and c) a stable curved interface in the case of $\Phi_A >> \Phi_B$ [3]

Other factors remaining unchanged, composition of the constituent chains has been reported as one of the most important factors for determining the phase morphology in block copolymers.[3] It is easily understood that the shape of the polymer/polymer interface varies with the relative chain length (or volume fraction Φ) of the component polymer. A compositionally symmetric **AB** diblock copolymer (i.e. when volume fraction of both the components is same) forms a flat interface as shown in Fig. 1(a). When the copolymer becomes compositionally asymmetric, it is more likely that a curved interface is formed as shown in Fig. 1(b) because, the **A** chains must stretch sufficiently to allow the formation of a planer interface. In this case, the conformational entropy loss of the major component (here **A**) is too high. Therefore, the A chains tend to expand along the direction parallel to the interface to gain the conformational entropy under the condition that segment density of both of the block chains have to be kept constant and must be the same as that of the bulk density of the homopolymers. Consequently, the interface becomes convex towards the minor component as shown in Fig. 1(c). This effect of interface curvature becomes more and more pronounced when the composition of the block copolymer becomes further asymmetric. For example, the morphological variations with composition has been reported in a two-component block copolymer are shown in Fig. 2.[4]

The most asymmetric block copolymer possesses spherical morphology comprising body centered cubic (bcc) spheres of the minor component dispersed in the matrix of the major component. Cylindrical morphology (hexagonal packed cylinders (hex) of minor component in the matrix of major component) evolves when the volume fraction of the minor component increases.

Figure 2: TEM images showing classical morphology of the block copolymers exemplified by that observed in an AB-diblock copolymer (A = polystyrene PS and B = polyisoprene PI, the TEM images are from).[4]

Symmetric block copolymer exhibits a lamellar morphology consisting of alternating layers of the components. It has been reported that, the morphology appears in reversed order (i.e. hexagonal **B** cylinders in **A** matrix and **B** spheres in **A** matrix) With increasing volume fraction of the component **A**.[3,5] In the strong segregation limit, the following sequence of phases has been observed for polystyrene-*block*-polyisoprene or (PS-b-PI) diblocks: $\Phi_{PS}<0.17$, bcc; $0.17< \Phi_{PS} <0.28$, hex; $0.28< \Phi_{PS} <0.34$, gyroid; $0.34< \Phi_{PS} <0.62$, lam; $0.62< \Phi_{PS} <0.66$, gyroid; $0.66< \Phi_{PS} <0.77$, hex; and $0.77< \Phi_{PS}$, bcc (where Φ_{PS} stands for volume fraction of polystyrene).[5]

An important way of influencing the morphology (and thereby their mechanical behaviour) of the block copolymers is provided by blending with homopolymers and other block copolymers. Phase behaviour and morphology formation in block copolymer blends were investigated by different authors in the past. It has been demonstrated that there is interplay between microphase and macrophase separation depending on molecular weight ratio of the blend partners. Nevertheless, only limited works of have been carried out concerning the influence of morphology on mechanical properties.[1,16-18]. Furthermore,

the experimental results on crack propagation behaviour of other heterogeneous polymer systems under impact loading conditions have been reported.[6,7] However, the application of crack resistance concepts on microphase-separated block copolymers has been seldom studied. Therefore, the main aim of this work is to apply the crack resistance concept in the characterization of fracture behaviour of binary blends of styrene/butadiene based block copolymers.

Experimental Methods

The styrene/butadiene based binary blends of a star block copolymer (ST2-S74) and a linear triblock copolymer (LN4-S65) were used in this study. The characteristics of the block copolymers are given in Table 1. After mixing the materials in an extruder, the single-edge notched bend (SENB) specimens were prepared by injection moulding (mass temperature at 250°C and mould temperature at 45°C). The blends contained 5, 10, 20, 40, 60 and 80 wt % of LN4-S65.

Microphase-separated structures were investigated by transmission electron microscopy (200 kV TEM, JOEL). Ultrathin sections of each sample (ca. 50 nm) were prepared from a bulk specimen using an ultramicrotome. The butadiene phase of the samples was electively stained with osmium tetroxide. Thus, butadiene phase appeared dark in the TEM micrographs.

***Table 1**: Characteristics of the blend components; ST and LN stand for star and linear architectures, respectively.*

blend partners	[1]M_n (g/mol)	[1]$M_\mathrm{n}/M_\mathrm{w}$	[2]Φ_styrene
ST2-S74	109,200	1.69	0.74
LN4-S65	116,000	1.20	0.65

[1] *number average (M_n) and weight average (M_w) molecular weights determined by gel permeation chromatography (GPC) using PS calibration*

[2] *total volume fraction of styrene monomer determined by Wijs double bond titration*

Figure 3: Schematic representation of molecular structure and morphology of the block copolymers used in this study.

In order to quantify the toughness behaviour of the blends, an instrumented Charpy impact tester with 4 J maximum work capacity was used. The SENB specimens had following dimensions: length (L) = 80 mm, width (W) = 10 mm and thickness (B) = 4 mm. After pre-notching by a milling cutter the specimens were notched with a razor blade. The initial notch about 4.5 mm deep was cut for the measurement of fracture mechanics parameters. To minimize the specimen vibration, the span length was set to 40 mm, and the pendulum hammer speed was 1m/s. The determination of dynamic Young's modulus and dynamic yield strength was carried out by using the procedures described elsewhere.[8] An equivalent toughness characterisation of these blends was only possible by crack resistance (R-) concept of elastic-plastic fracture mechanics, because blends with LN4 content ≥ 20 wt % reveal stable crack propagation behaviour.

R-curves represent the dependence of loading parameters (J-integral or crack-tip opening displacement δ_{dk}) with the stable crack growth Δa. These curves allow the determination of fracture mechanics parameters as resistance against stable crack initiation and propagation. The multi-specimen-method in the stop-block-technique has been reported to be most effective for polymeric materials.[9] So called technical crack initiation values were used to quantify the stable initiation process, such as $J_{0.1}$ and $\delta_{0.1}$ at $\Delta a = 0.1$ mm. The tearing moduli, T_J and T_δ, calculated by the slope of the R-curves at $\Delta a = 0.1$ mm are taken as resistance against stable crack propagation. The determination and evaluation of R-curves under impact loading conditions have been discussed elsewhere.[8]

Results and Discussion

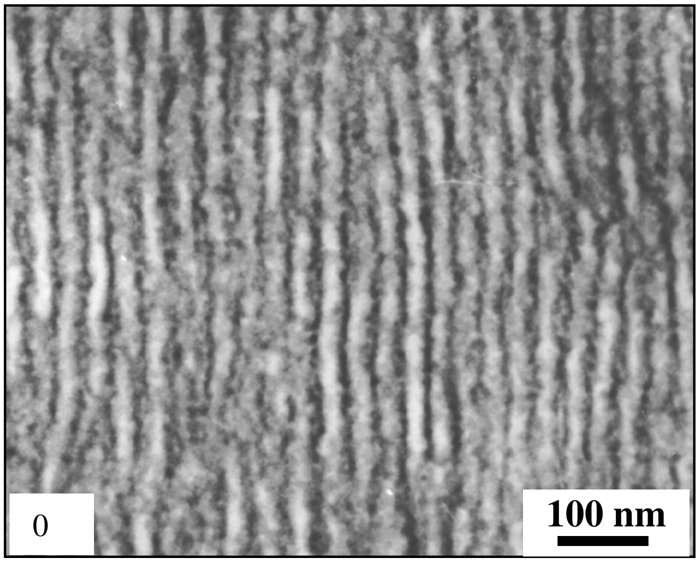
Morphology of the block copolymer blends

The star block copolymer (ST2) used in this study has a typical lamellar consisting of alternating layers of styrene (light areas) and butadiene (dark areas). Each lamellae has a thickness of about 20 nm. The butadiene lamella additionally contains small polystyrene domains about 6 nm in diameter.[19] The linear block copolymer LN4 comprises disordered morphology of short styrene cylinders in rubbery styrene-co-butadiene matrix. Molecular structure and morphology of the block copolymers used in this study are schematically represented in Fig. 3.

The electron microscopic investigations show that the binary blends reveal both mixing and demixing of the copolymer molecules under equilibrium conditions. The phase-segregation (i.e., the demixing of different block copolymer chains) in the microscopic level is, however, strongly suppressed by the shear stress in the melt during the process of injection moulding. In injection moulded samples, two kinds of morphologies are observed: lamellae like morphology at lower LN4 content and disordered PS domains dispersed in rubbery matrix at higher LN4 content as shown in Fig. 4. The morphological change with increasing LN4 content has a strong influence on the achieved toughness as will be discussed later in this paper.

Crack toughness behaviour

It is found that block copolymer blends with < 20 wt % LN4 show unstable crack propagation behaviour. With increasing LN4 content, transition to stable crack propagation is observed clearly as shown in Fig. 5. Thus, above 20 wt % LN4, R-curves could be constructed, and hence the fracture toughness parameters could be evaluated as shown in Fig. 6. The R-curves represent the dependence of the loading parameters (energy determined parameter J-integral or deformation determined parameter δ_{dK}) as a function of stable crack growth (Δa) and are constructed by analysing so called load – deflection (F-f) diagrams registered during the instrumented Charpy impact testing.



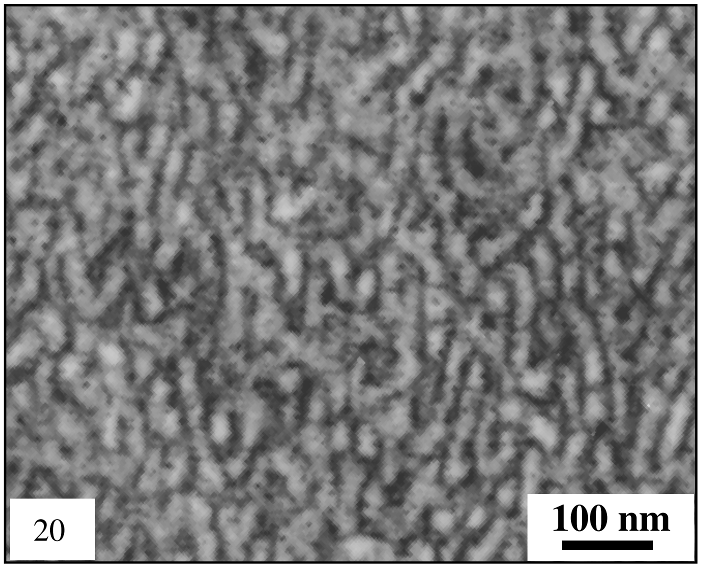
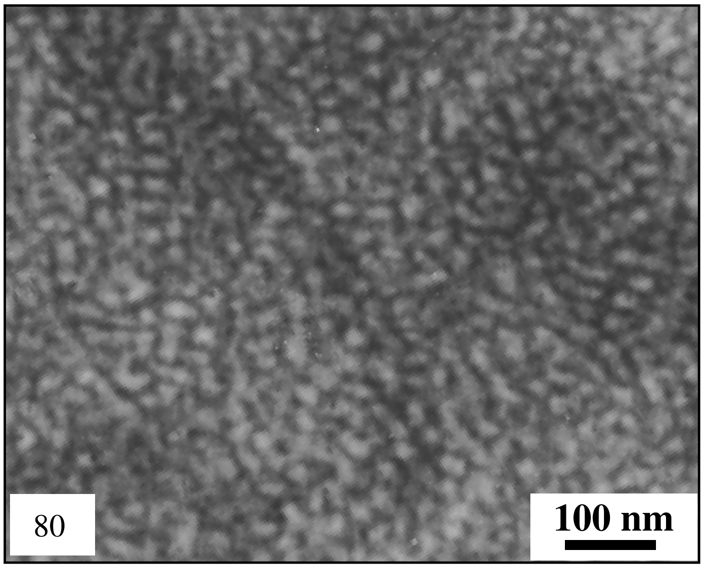


Figure 4: TEM images showing morphology of injection moulded ST2/LN4 blends; the figures at the left corners of each micrograph stand for the LN4 wt % in the blends, OsO_4 staining causes polystyrene appear brighter).



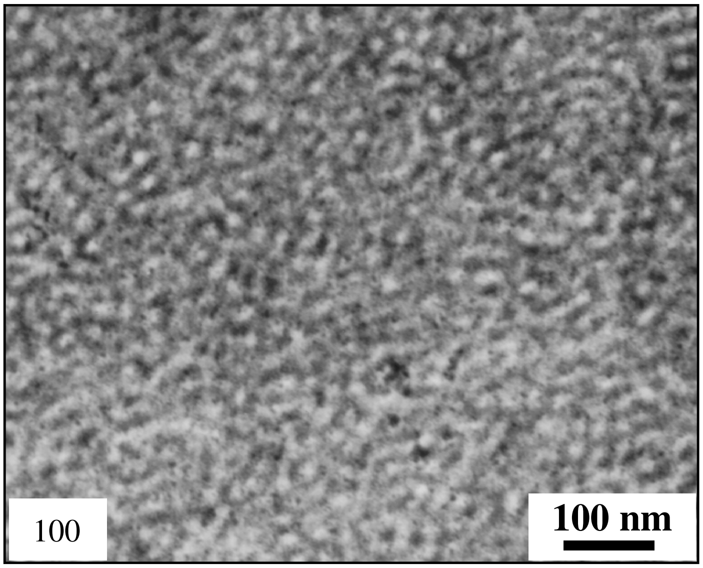


Figure 4 contd.

The increasing toughness of these blends with increasing LN4 content (fig. 6) indicates that the samples with 20-50 wt % LN4 have a sufficient resistance against unstable crack initiation. The R-curves with J-integral or crack tip opening displacement CTOD values (J or δ_{dK}) as loading parameters exhibit nearly identical behavior as shown in Fig. 5.

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In general, the crack initiation and crack propagation values have been used to characterize the toughness of the materials.[7] Higher the magnitude of these parameters, higher will be the crack toughness of the materials. The crack initiation values (such as technical crack initiation value, $J_{0.1}$ and $\delta_{0.1}$) are the measured from J and δ values at a stable crack propagation (Δa) of 0.1 mm. Furthermore, the crack propagation is characterised by the magnitude of tearing moduli T_J and T_δ, which are determined by the slope of corresponding R-curves at the point Δa = 0.1 mm.

The technical crack initiation values ($J_{0.1}$ and $\delta_{0.1}$) and also the tearing moduli, T_J and T_δ, increase until a LN4 content of 80 wt % as shown in Fig. 6. The transition from unstable to stable crack propagation is found at 20 wt% LN4 which corresponds to the usual brittle/tough-transition. At higher LN4 contents, an additional transition can be observed. The change from the low (≤ 40 wt % LN4) to the high (≥ 80 wt % LN4) level of toughness is associated with a strong increase of the toughness between 50 and 60 wt % of LN4 indicating a 'tough/high-impact' transition (THT), which can be regarded as a measure of the resistance against stable crack initiation as shown in Fig. 6.

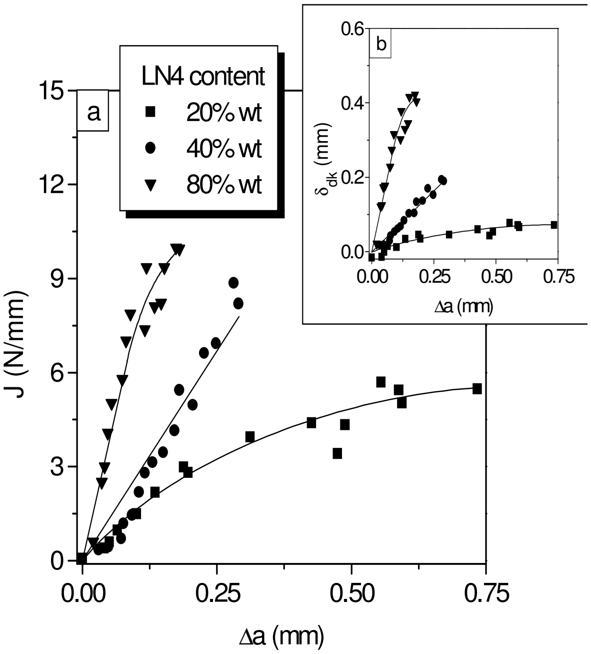

Figure 5: Crack resistance curves (R-curves) with J and δ_{dK} as loading parameters for ST2/LN4 blends

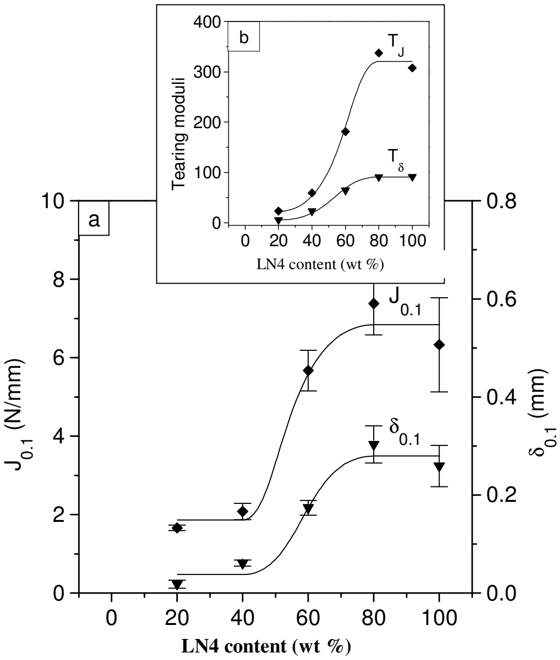

Figure 6: a) $J_{0.1}$ and $\delta_{0.1}$ and b) tearing moduli T_j and T_δ as a function of LN4 content

For the materials investigated in this study and for other heterophase polymers reported elsewhere[10,11], two different brittle/ductile transitions were observed: the THT and the conventional 'brittle/tough' transition (BTT) as a measure for the safety against unstable crack initiation. In contrast to the BTT, the THT can be described as a measure for the safety against stable crack initiation. As demonstrated in recent studies[6,7], a BTT occured if the crack growth mechanism shifts from stable towards unstable one. However, the THT should also be correlated to a change in deformation mechanism. Differences in deformation mechanisms leading to BTT and THT may be explained by Wu's percolation theory[12] and Margolina's theory[13], respectively, as discussed by Grellmann et al.[10] This classification is, however, applicable in the investigated system where the structural heterogeneity lies in nanometer scale in contrast to particle-matrix morphology of polymer blends.

The strong increase in stable crack growth at LN4 content of 20 wt % is associated with a principal transition in crack growth mechanism from predominantly unstable crack propagation via micro-void-coalescence to the stable crack propagation via shear-flow as revealed by fracture surface morphology.[19] While micro-void-coalescence is typical of semicrystalline polymers having lamellar structure in nanometer scale such as HDPE, shear-flow mechanism is characteristic of many amorphous polymers like PC.

Conclusions

Fracture behavior of binary blends consisting of styrene/butadiene block copolymers having star and triblock architectures are studied via instrumented Charpy impact testing. The toughness of the ductile blends is characterized by R-curves. The lamellar star block copolymer shows nearly elastic behavior (small scale yielding and unstable crack growth). The addition of 20 wt % of a triblock copolymer with dispersed polystyrene domains leads to a strong increase in fracture toughness. In the present study, the characterization of the stable crack propagation behavior of these blends is only possible by crack resistance (R-) concept of elastic-plastic fracture mechanics. These curves allow the determination of fracture mechanics parameters as resistance against stable crack initiation and propagation. The strong increase of the toughness values between 50 and 60% of LN4 indicates a 'tough/high-impact' transition as a measure for the protection against stable crack initiation.

New mechanism of toughness modification (where the transition from a lamellar structure with a long range order to a less ordered structure plays the central role) results in a specific morphology-toughness correlation which differs fundamentally from toughening mechanisms in conventional polymer blends.

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