FRACTURE BEHAVIOUR OF BLENDS CONSISTING OF ASYMMETRIC STYRENE/BUTADIENE BLOCK COPOLYMERS

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ABSTRACT

Fracture behavior of binary blends consisting of styrene/butadiene block copolymers having star and tri-block architectures are studied via instrumented Charpy impact testing. The toughness of the ductile blends is characterized by dynamic crack resistance curves (R-curves). While the lamellar star block copolymer shows nearly an elastic behavior (small scale yielding and unstable crack growth), adding of 20 wt % of a triblock copolymer with dispersed styrene domains leads to a strong increase in fracture toughness. At this concentration, a transition from mechanism of micro-void coalescence to shear deformation takes place. 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.

KEYWORDS

Block copolymer blends, toughness modification, Charpy impact testing, R-Curves

INTRODUCTION

A large variety of mechanical properties and micromechanical deformation mechanisms are observed in block copolymers attributed to the existence of different highly ordered microphase separated morphologies whose periodicity lies in the range of the radius of gyration, R_g of the copolymer molecules [1-3].
In spite of rapid development of block copolymers with a variety of viscoelastic behavior, only limited investigations have been carried out concerning the influence of morphology on mechanical properties. Only few studies have been reported on the effect of microphase morphology on strength and stiffness of block copolymers [2,4] and blends containing block copolymers [5]. While the application of crack resistance concepts on nanophase-separated block copolymers has not yet been reported, experimental results on crack propagation behavior of other heterogeneous polymers systems under impact loading conditions are well known [6,7]. It should be, however, mentioned that the morphology-toughness correlation observed in the investigated systems are fundamentally different from that found in conventional impact modified or reinforced polymeric systems (matrix-particle morphology). The aim of this paper is to study new toughening mechanisms in binary block copolymer blends using crack resistance concept.

EXPERIMENTAL

Binary blends of a star block copolymer (ST2-S74) and a triblock copolymer (LN4-S65), both based on styrene and butadiene, are used in this study. The characteristics of the block copolymers are given in table 1. After mixing the materials in extruder, the single-edge notched bend (SENB) specimens were prepared by injection molding (mass temperature 250°C and mold temperature 45°C). The blends contain 5, 10, 20, 40, 60 and 80 wt % of LN4-S65.

Table1: Characteristics of the blend components; styrene as hard outer block in LN4 is 32 vol. % while the middle statistical block contains about 50 vol. % styrene.

blend component	M_n (g/mol)	M_w/M_n	$\Phi_{styrene}$	Morphology (TEM)
ST2-S74	109,200	1.69	0.74	lamellar
LN4-S65	116,000	1.20	0.65	PS domains in S/B copolymer matrix

In order to quantify the toughness behavior of investigated block copolymer blends, an instrumented Charpy impact tester IKBV-4J with 4J total work capacity was used. The SENB specimens have following dimension: length L = 80 mm, width W = 10 mm and thickness B = 4 mm. The specimens were notched with a razor blade (notch tip radius = about 0.13 μm). For the measurement of fracture mechanics parameters as resistance against unstable and stable crack growth, the initial crack lengths of 2 mm and 4.5 mm were cut [8]. To minimize the vibration of specimen, the span length was set to 40 mm, and the pendulum hammer speed was 1m/s. The determination of Young's modulus and yield strength as well as the fracture mechanics parameters as resistance against unstable crack initiation is carried out by using the procedures described in ref. [8]. Because blends with LN4 content ≥ 20 wt % reveal stable crack propagation behavior, an equivalent toughness characterization of these blends was only possible by crack resistance (R-) concept of elastic-plastic fracture mechanics. Crack resistance curves (R-Curves) represent the functional dependence of loading parameters (J-integral or δ) 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 is found to be most effective for polymeric materials. Further details on determination and evaluation of R-curves under impact loading conditions are discussed in [8].
A small piece of each sample was cut from the bulk specimen and immersed in an aqueous osmium tetroxide (OsO$_4$) solution for several hours at room temperature to selectively stain the butadiene phase. Ultra-thin sections were cut using an ultramicrotome (Reichert Ultracut E) equipped with a diamond knife (Diatome). Microphase morphology of the samples was examined using a 200 kV transmission electron microscope (TEM, JEOL 2010).
In order to correlate the microstructure and fracture behavior with micromechanical deformation behavior, fracture surfaces of the specimens were qualitatively as well as quantitatively analyzed by scanning electron microscope (SEM, Jeol JSM-6300). Special attention was paid to quantification of some selected areas on the fracture surfaces like crack-tip blunting zone (stretch zone). For this purpose, the fracture surface of the SENB specimens were mounted on 45° sloped specimen target and sputtered with gold prior to the SEM imaging.

RESULTS AND DISCUSSION

Samples ST2 and LN4 have equilibrium morphologies comprising of alternating lamellae and randomly distributed cylinders [9] respectively. Morphology of the block copolymers and their blends is strongly influenced by shear stress of injection molding. As shown in fig. 1, lamellar structures of sample ST2 are aligned parallel to the injection direction by the shear stress.
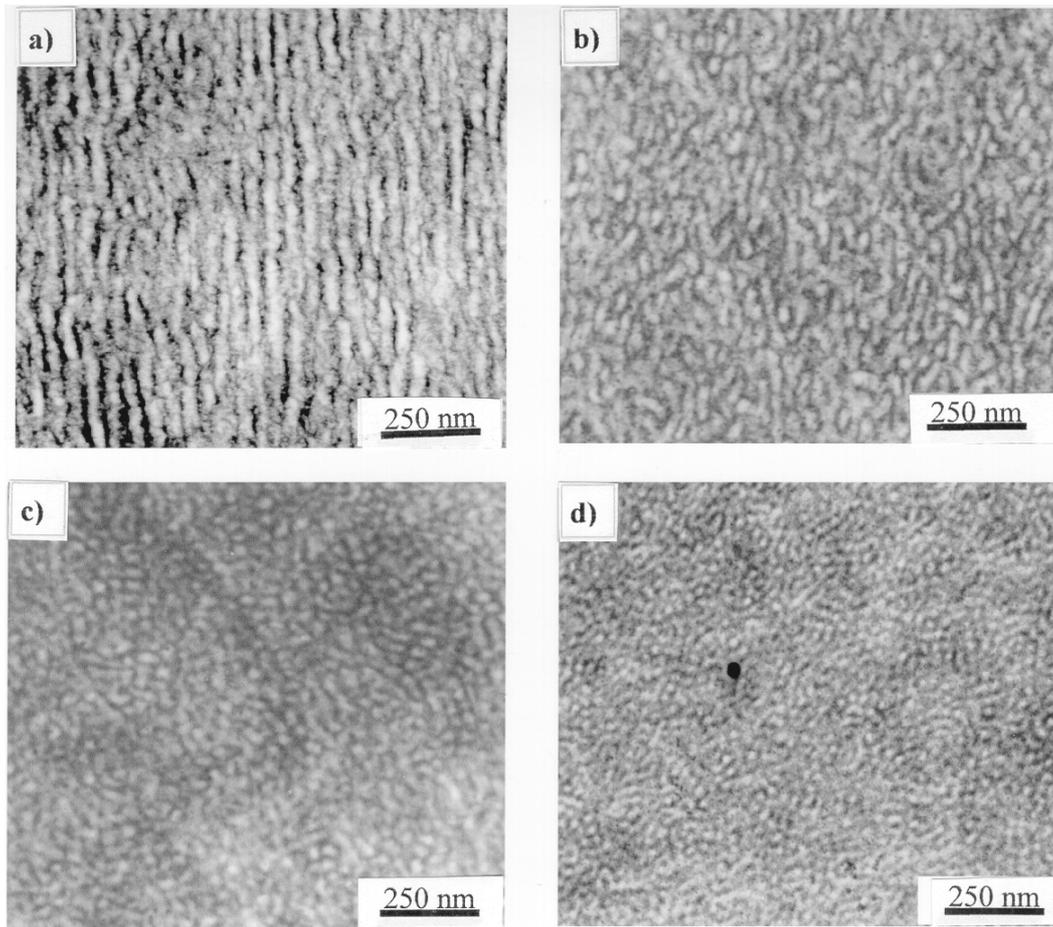
Figure 1: TEM images showing morphology of ST2/LN4 blends: a) pure ST2, b) 20% LN4, c) 80% LN4 and d) pure LN4; injection direction vertical.

Macrophase separation in the blends is strongly suppressed by the shear stress in the melt. Basically, two types of morphologies have been found. At lower LN4 content (0-20 wt % LN4), a lamellar morphology prevails which resemble qualitatively the morphology of pure ST2. At higher LN4 content (40-80 wt % LN4), the morphology of the blends is qualitatively comparable to that of pure LN4. The structural reorganization ("disorder") which occurs with increasing LN4-content has, as will be shown below, a strong influence on the achieved toughness level and underlying crack propagation mechanisms.

Physical crack initiation values (J_i and δ_i) were determined based on the considerations of crack propagation kinetics, i.e. analysis of different phases of crack growth (like crack-tip blunting, stable crack initiation and propagation or the unstable crack propagation) as a function of time. Parameters determined at physical crack initiation points are more structurally motivated than those at technical ones (e.g. $J_{0.1}$ and $\delta_{0.1}$ which are determined for stable crack growth of 0.1 mm, i.e. $\Delta a = 0.1$ mm). The slope of the R-curves at $\Delta a = 0.1$ mm (i.e. measured as $dJ/d(\Delta a)|_{0.1}$ 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 $T_\delta = d\delta/d(\Delta a)|_{0.1} \times E_d/\sigma_{yd}$ are determined as resistance against stable crack propagation.

As shown in fig. 2a, R-curves with J or δ as loading parameters exhibit identical behavior. The slope of the R-curves at $\Delta a = 0.1$ mm and the tearing modulus increase with LN4 concentration until 80 wt% (fig. 2b). This indicates that the increasing ductility of the unnotched samples with increasing LN4 content, connected with decreasing elasticity modulus E_d and yield strength σ_{yd}, is also causing an increasing resistance against stable crack propagation. It should be, however, mentioned that this correlation does not have a general validity as shown by our recent results [9]. The physical crack initiation values (J_i and δ_i, fig. 2c) are insensitive to morphology which is in accordance with the previous results obtained for heterophase polymeric systems [7]. 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_δ, fig. 2b).
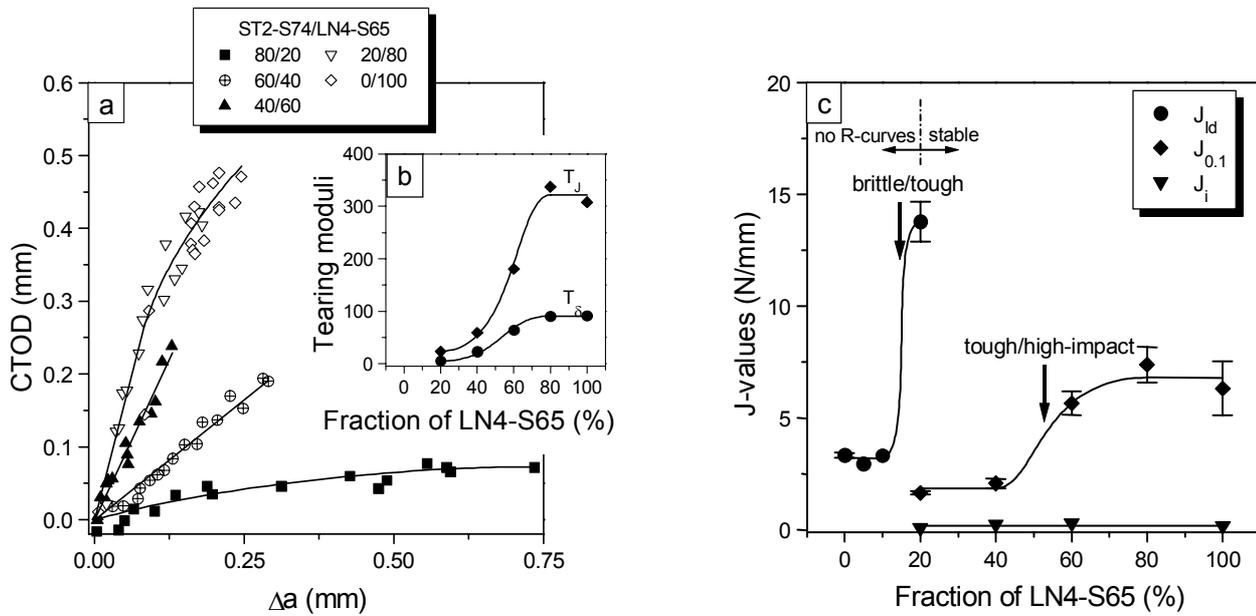
Figure 2: Crack resistance curve (a) and fracture mechanics parameters as resistance against stable crack propagation, tearing modulus (b) as well as resistance against unstable crack initiation J_{Id}; $J_{0.1}$ und J_i (c) as a function of blend composition

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 as resistance against temporal change of fracture mechanics parameters e.g. CTOD-velocity $d\delta/dt$. In fig 3., the stages of crack propagation are represented by the slopes of $d\delta/dt$ values. Stage I 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 II, the blunted crack propagates stable but non-stationary, i.e. the $d\delta/dt$ values increase with Δa. In stage III, the non-stationary stable crack propagation finally reaches a stationary stable crack growth, 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).
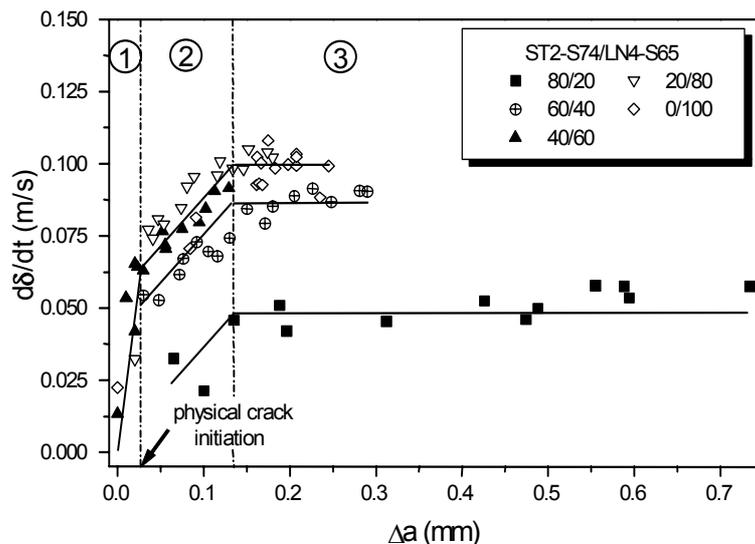

Figure 3: Crack-tip-opening-displacement-velocity $d\delta/dt$ as a function of stable crack growth and blend composition

Two different brittle/ductile transitions (BDT) were observed in other heterophase polymers [10,11]: the conventional BDT1 ("brittle/tough" transition) as a measure for the safety against unstable crack initiation

and BDT2 ("tough/high-impact" transition) as a measure for the protection against stable crack initiation. While a pronounced BDT1 can be observed at 10-20% wt of LN4, the quite wide BDT2 is observed between 50 and 60% of LN4 (fig. 2c). As demonstrated in recent studies [10,11], a shift from BDT1 to BDT2 occurs if the crack growth mechanism shifts from stable towards unstable one. As discussed in [10], differences in deformation mechanisms leading to BDT1 and BDT2 may be explained by Wu's percolation theory [12] and Margolina's theory [13] respectively. This classification is, however, impossible in the investigated system where the structural heterogeneity lies on the nanometer scale in contrast to a particle-matrix structure of polymer blends where particles sizes are usually in the µm scale.

In addition to in-situ investigation, examination of fracture surfaces also allows an analysis of crack propagation phenomenon. As shown in fig. 4, the transition BDT1 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 micro-voids (fig. 4a,b). Such a crack propagation mechanism is typical for semicrystalline polymers like HDPE [14], 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 stable crack propagation via coalescence of micro-voids to the crack propagation via shear-flow occurs (fig. 4c). The individual crack growth areas (fracture parable) are separated by clearly visible shear-lips. Crack growth via shear-flow mechanism is typical for many amorphous polymers like polycarbonate [15]. Here, the crack becomes again sharp after blunting and propagates through the material by translation of the whole crack front [11]. 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.
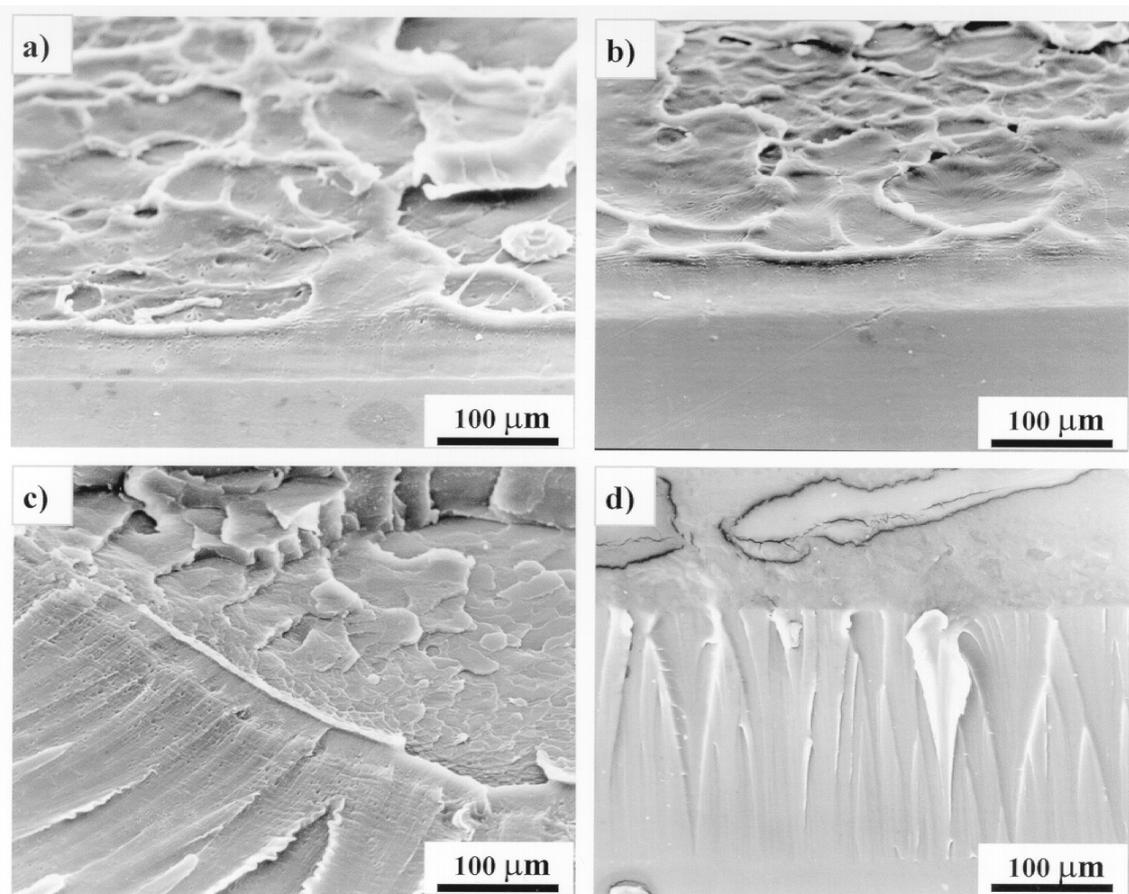

Figure 4: SEM images showing fracture surface morphology as a function of LN4 content: a) pure ST2, b) 5% LN4, c) 20% LN4 and d) pure LN4

The geometry 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. The decrease of SZW in the blends with increasing LN4 content (fig. 4) may

be attributed to the transition from the behavior of a conventional thermoplastic material (ST2) to that of a thermoplastic elastomer (LN4) i.e. a transition from viscoelastic to an entropy-elastic deformation behavior.

CONCLUSION

In contrast to conventional polymer blends where the toughness modification is achieved through 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 structure-toughness correlation which differs fundamentally from toughening mechanism in conventional polymer blends.

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