

# FRACTURE BEHAVIOR OF BINARY BLOCK COPOLYMERS BLENDS

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## ABSTRACT

Fracture behavior of binary blends consisting of styrene/butadiene block copolymers having star and triblock architectures are studied by 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 results in a specific structure-toughness correlation which differs fundamentally from toughening mechanisms in polymer blends.

The influence of morphology on fracture behaviour of miscible block copolymer blends has been studied using two S-SB-S triblock copolymers (LN3, LN4). The two copolymer blends have distinct thermoplastic (LN3) and elastomeric (LN4) property profiles. While solution cast films, representing equilibrium morphologies, exhibited wormlike, cylindrical, hexagonal, bicontinuous (gyroid) and lamellae structures, bicontinuous morphology could not be observed for materials processed by rolling, obviously arising from shear forces in the melt. Tensile properties depend strongly on morphology, where a maximum in Young's modulus has been observed for bicontinuous morphology. The fracture behavior was evaluated using essential work of fracture method based on concepts of the "Post Yield" Fracture Mechanics. The elastomeric behavior of the blends was dominant up to a LN3 content of 40 wt%, resulting in a significant increase in stress at 300 % strain. A continuous increase in resistance against crack propagation was observed beyond 50 wt% of LN3 content due to the transition from hexagonal cylindrical morphology to lamellae morphology.

## 1 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 in the nm-range [1-3]. Binary blends of diblock copolymers have been intensively studied during recent years [4]. Comprehensive studies have been published by Hashimoto and co-workers [5-7] who have initially started studying blends of lamellae forming diblock copolymer blends but extended their investigations to other morphologies later. Only few studies have reported on the effect of microphase morphology on strength and stiffness of block copolymers [2,8] and blends containing block copolymers [9]. 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 polymers systems under impact conditions are well known [10,11]. The aim of this paper is to study new toughening mechanisms in binary block copolymer blends using dynamic crack resistance concept and essential work of fracture method (EWF).

## 2 EXPERIMENTAL

Binary blends of a star block copolymer (ST2-S74) and a triblock copolymer (LN4-S65), both based on styrene (S) and butadiene (B), and binary blends of two triblock copolymers (LN3 and LN4) are used in this study. The characteristics of the block copolymers are given in fig. 1 and table 1. After mixing ST2-S74 and LN4-S65 in an extruder, the single-edge notched bend (SENB)

specimens were prepared by injection molding. Binary blends of LN3 and LN4 have been mixed by rolling and plates have been subsequently prepared by compression moulding. Furthermore, equilibrium morphologies (solution cast films) have been studied.

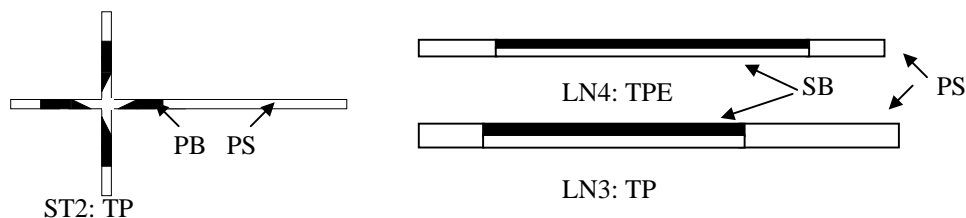


Figure 1: Architectures of the block copolymers (PS – polystyrene, PB – polybutadiene; TP – thermoplastics, TPE – thermoplastic elastomer).

Table 1: Characteristics of the blend components; fraction of styrene as glassy outer blocks in LN4 is 32 vol% while SB-block contains about 50 vol% styrene. Content of PS-blocks in LN3 is about 50 % ( $M_n$  and  $M_w$  – number- and weight-averaged molecular weight,  $\Phi_{\text{styrene}}$  – total fraction of PS).

Blend component	$M_n$ (g/mol)	$M_n/M_w$	$\Phi_{\text{styrene}}$	Morphology (TEM)
ST2-S74	109,200	1.69	0.74	Lamellae
LN3	111,000	1.15	0.72	Lamellae
LN4-S65	119,000	1.20	0.65	PS domains in S/B copolymer matrix

### 2.1 Dynamic Crack Resistance Concept

In order to quantify the toughness behavior of investigated block copolymer blends, an instrumented Charpy impact tester with 4 J 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. 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 [12]. To minimize the vibration of specimen, the span length was set to 40 mm, and the pendulum hammer speed was 1 m/s. Because blends with LN4 content  $\geq 20$  wt % reveal stable crack propagation behavior, an equivalent toughness characterization of these blends was only possible by crack resistance concept of elastic-plastic fracture mechanics. Crack resistance curves (R curves) represent the dependence of loading parameters (J integral or CTOD) with the stable crack growth  $\Delta a$ . 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 [12].

The PB-block of the samples was stained by osmium tetroxide ( $\text{OsO}_4$ ) and ultra-thin sections were cut using an ultra microtome equipped with a diamond knife (Diatome). Microphase morphology of the samples was examined using a 200 kV transmission electron microscope. The fracture surfaces of the specimens were analyzed by scanning electron microscopy.

### 2.2 EWF Method

To study the fracture behaviour of LN3/LN4 block copolymer blends essential work of fracture concept (EWF) was applied. Therefore 1 mm thick double edge-notched tension (DENT) specimens with dimensions of 80 mm length, 20 mm width were used. They were cut from plates

and notched by using a special milling device. Final sharpening of these pre-notches was done using a razor blade. For each composition, 10 to 15 specimens were tested having different ligament lengths between ca. 2 mm and ca. 10 mm. The experiment was carried out with a universal testing machine ZWICK Z010 with a clamps distance of 40 mm and with a strain rate of 1 mm/min. The EWF-method is mainly used for highly ductile materials, films and thin plates. More details about the application and conditions of the concept are discussed in [13-15]. By calculating the specific work of fracture of the compositions the essential work of fracture  $w_e$  with the meaning of a “crack moving force”, and the non-essential work of fracture  $\beta w_p$  as a measure of the resistance against stable crack propagation are analyzed.

### 3 RESULTS AND DISCUSSION

#### 3.1 Fracture Behavior of ST2/LN4 Blends

Samples ST2 and LN4 have equilibrium morphologies comprising of alternating lamellae and randomly distributed cylinders [16] respectively. Morphology of the block copolymers and their blends is strongly influenced by shear stress of injection molding. 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 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.

As shown in fig. 2a, R-curves with  $J$  or  $\delta$  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). The physical crack initiation values ( $J_i$  and  $\delta_i$ , fig. 2c) are insensitive to morphology which is in accordance with the previous results obtained for heterophase polymeric systems [11]. 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. 2b).

Two different brittle/ductile transitions (BDT) were observed in other heterophase polymers [17,18]: 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 propagation. While a pronounced BDT1 can be observed at about 20 wt% of LN4, the quite wide BDT2 is observed at about 60 wt% of LN4 (fig. 2c). As demonstrated in recent studies [10,11], a BDT1 occurs if the crack growth mechanism shifts from unstable towards stable one.

Examination of fracture surfaces also allows an analysis of crack propagation phenomenon. 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, visible as structures formed by coalescence of micro-voids. In the composition range 40-80 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. The crack propagation kinetics found for low amount of TPE is similar to that observed for semi crystalline polymers like HDPE [19]. With increasing TPE contents it changes to that typical for many amorphous polymers like polycarbonate [20].

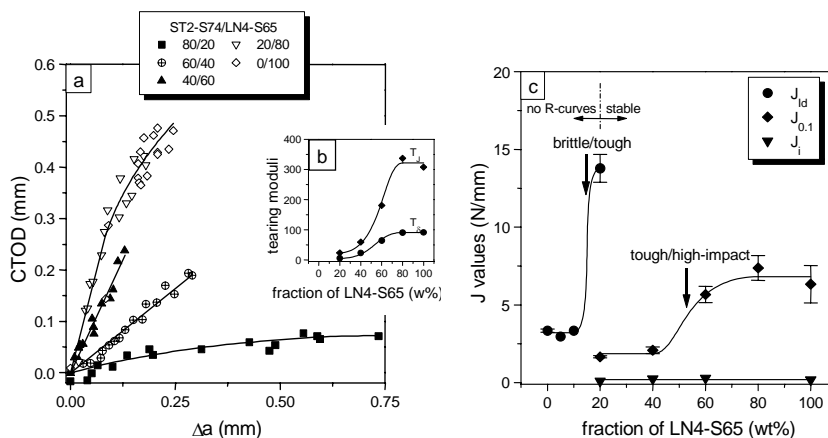


Figure 2: Crack resistance curve (a) and fracture mechanics parameters as resistance against stable crack propagation, tearing modulus (b), as well as resistance against unstable ( $J_{Id}$ ) and stable crack initiation ( $J_{0.1}$  and  $J_i$ , measured at engineering and physical initiation point respectively) (c) as a function of blend composition [16].

### 3.2 Morphology and Fracture Behavior of LN3/LN4 Blends

The morphology of triblock copolymer blends was found to be process dependent. The films prepared from solution (thickness about 0.5 mm) exhibit wormlike (0-20 wt% LN3) – cylindrical (30-40 wt% LN3) – hexagonal (50-60 wt% LN3) – bicontinuous (gyroid) (70-80 wt% LN3) – lamellar (90-100 wt% LN3) morphological sequence (fig. 3 a-f), whereas in the compression moulded plates the bicontinuous morphology could not be observed, obviously arising from shear forces in the melt (fig. 3 g, h).

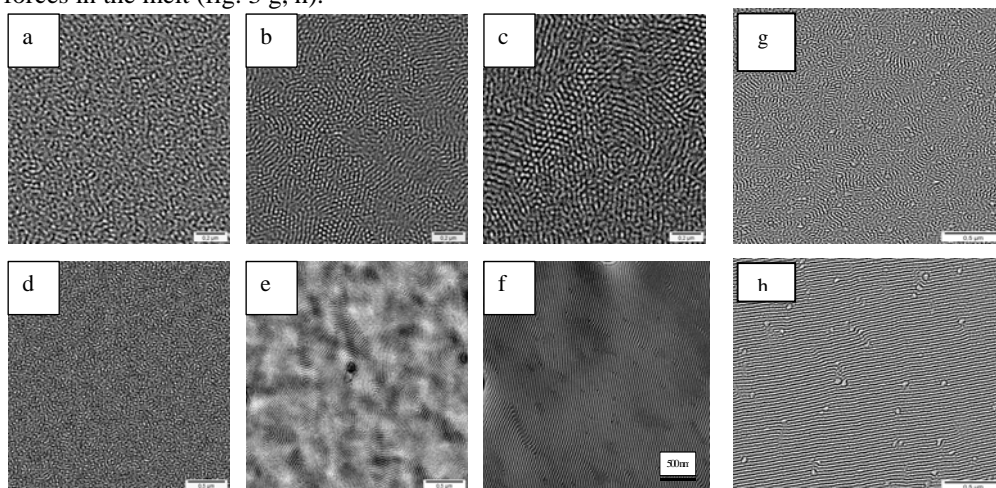


Figure 3: Equilibrium morphologies of LN3/LN4 blends: (a) – worms (LN4), (b) – cylindrical (30 wt% LN3), (c) – hexagonal (60 wt% LN3), d – gyroid (70 wt% LN3), e – lamellae (90 wt% LN3), f – lamellae (LN3) and oriented morphologies after processing (rolling): g – PS-rich cylinder (60 wt% LN3), and h – lamellae (80 wt% LN3)

Tensile strength and Young's modulus of blends with about 30 wt% LN4 are even larger than that of the pure thermoplastic triblock copolymer (fig. 4) resulting in non-linear morphology-property correlation for binary block copolymer blends in contrast to macrophase separated ST2/LN4 blends [21]. The Young's modulus of the blends can be calculated from a phenomenological percolation model incorporating different morphologies. The fracture toughness was evaluated at LN3/LN4 plates using essential work of fracture method. The elastomeric behaviour of the blends was dominant up to a LN3 content of 40 wt%, resulting in a significant increase in stress at 300 %

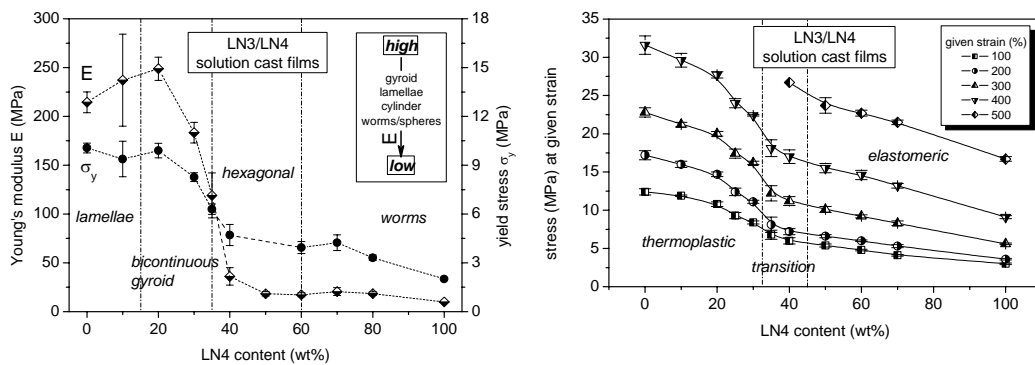


Figure 4: Tensile properties of LN3/LN4 films: (a) dependence of mechanical properties on composition and (b) stress at given strains for different blends [21].

strain. A continuous increase in resistance against crack propagation was observed beyond 50 wt% LN3 (fig. 5). This behaviour is attributed to a transition from hexagonal cylindrical morphology to lamellae morphology. The load/displacement ratio increases continuously till 70 wt% LN3 correlated to an increasing strength and decreasing ductility.

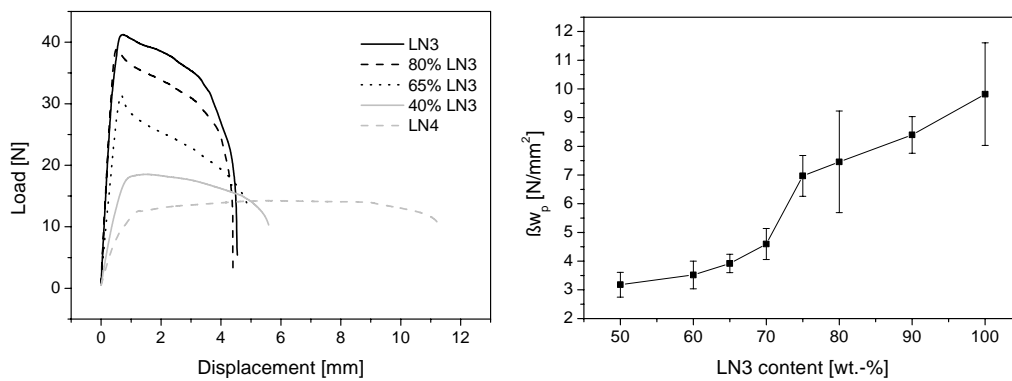


Figure 5: Load-displacement curves for different LN3/LN4 blends (processed by rolling) at a ligament length of 3 mm (left) and resistance against crack propagation in dependence of composition (right).

#### 4 CONCLUSION

In contrast to conventional polymer blends where the toughness modification is achieved through dispersion of a soft phase in a hard matrix, the investigated binary block copolymer blends represent nanometer-structured materials. New mechanism of toughness results in a specific structure-toughness correlation which differs fundamentally from toughening mechanism in conventional polymer blends. EWF method was found to be representative to analyze fracture behavior of thermoplastic elastomeric block copolymer blends. In contrast to star block/triblock copolymer blends, triblock copolymer blends reveal a non-linear dependence of mechanical properties on composition arising from the presence of gyroid morphology not observed in the pure triblocks. This work provides a first inside into correlations between microstructure, fracture behavior and mechanical properties of miscible copolymer blends.

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