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Morphology and crack resistance behavior of binary block copolymer blends

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Abstract

Fracture behavior of binary blends comprising of styrene–butadiene block copolymers having star and triblock architectures was studied via instrumented Charpy impact test. The toughness of the ductile blends was characterized by dynamic crack resistance curves (*R*-curves).

This study represents a systematic investigation of crack resistance behavior of nanometer structured binary block copolymer blends and the development of a new material with a combination of high toughness and transparency, usually not observed in incompatible polymer blends. While the lamellar star block copolymer shows an elastic behavior (small-scale yielding and unstable crack growth), adding of 20 wt% of the triblock copolymer leads to a stable crack growth and at 60 wt% of the triblock copolymer the strong increase of toughness values indicate a tough/high-impact transition, demonstrating the existence of novel toughening concepts for polymers based on nanometer structured materials.

Keywords: Block copolymer blends; Charpy impact testing; *R*-curves

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1. Introduction

Block copolymers represent a special class of self-assembled nanostructured materials, where the structure and size of their morphology can be controlled via molecular architecture. Self-assembled materials provide a versatile tool to create desired nanostructures in bulk materials or at interfaces, which have potential applications in biomaterials, optics, and microelectronics [1,2]. However, until recently, very little quantitative information was available on blends of block copolymers. Hashimoto and coworkers [3–5] have performed comprehensive studies on blends of block copolymers, starting with blends of lamellae forming block copolymers. It was shown that a macrophase separation occurs if the ratio of molecular weight is higher than 10, forming macrophase-separated lamellar domains with different periods. The investigations were extended to non-lamellar morphologies. Different authors [6] have described solubility limits of block copolymer blends.

Despite of recent advances in knowledge of phase behavior and morphology of block copolymer blends, only limited investigations have been carried out concerning the influence of morphology on mechanical properties. Only a few studies have been reported on the effect of microphase morphology on strength and stiffness of block copolymers [7–9] and blends containing block copolymers [10]. While the application of crack resistance concepts onto microphase-separated block copolymers has not been reported yet, experimental results on crack propagation behavior of other heterogeneous polymer systems under impact loading conditions are well known [11,12]. This study represents a systematic investigation of crack resistance behavior of nanometer-structured binary block copolymer blends to create a new material with a high toughness without any loss of transparency.

2. Experimental

Binary blends of a star block copolymer (ST2) and a triblock copolymer (LN4), both based on styrene and butadiene, 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 molding (mass temperature 250 °C and mold temperature 45 °C). The blends contain 5, 10, 20, 40, 60, and 80 wt% of LN4.

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Table 1
Characteristics of the blend components

Blend component	M_n (g/mol)	M_w/M_n	Φ_{styrene}	Morphology (TEM)
ST2	109,200	1.69	0.74	Lamellar
LN4	116,000	1.20	0.65	PS domains in S/B copolymer matrix

Architectures of used block copolymers are shown in Fig. 1. Materials were synthesized and provided by BASF. Synthesis of these materials is described by Knoll et al. [17]. LN4 is a symmetric triblock copolymer having the block sequence S–S/B–S and weight ratios of 16/68/16. The S/B (statistical copolymer PS-*co*-PB) middle block contains about 50 wt% PS. ST2 is an asymmetric star block copolymer with about four arms on average with a PS corona and a PB core, which contains a small PS core. ST2 exhibits a tapered transition from the PB blocks to the PS core (core molecular weight is about 20,000 g/mol). In order to quantify the toughness behavior of the investigated block copolymer 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 using a milling cutter, the specimens were notched with a razor blade. For the measurements of fracture mechanics parameters, an initial crack length of 4.5 mm was used [13]. To minimize the vibration of the specimens, the support span was set to 40 mm, and the pendulum hammer speed was 1 m/s. The determination of dynamic flexural modulus and dynamic yield strength was carried out by applying the procedures described in Ref. [13]. 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*-) curve concept of elastic–plastic fracture mechanics. *R*-curves represent the functional dependence of a loading parameter (*J*-integral or crack-tip opening displacement δ_d) on the stable crack growth Δa. Such 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 [12,13]. The analysis of the *R*-curves measured can been realized by different procedures, whereas two standards were especially developed for plastics [14,15]. Because the kinetics of the crack propagation is not universally clarified up to now, particularly the processes of crack blunting and initiation of stable crack growth (physical crack initiation), the blunting region is often not analyzed. Thus, instead of physical crack initiation values, so-called technical crack initiation values are often used to quantify the stable initiation process, such as $J_{0.05}$ and $\delta_{0.05}$ at $\Delta a = 0.05$ mm. The tearing moduli, T_J and T_δ, calculated by using the slope of the *R*-curves at $\Delta a = 0.1$ mm were determined as resistance against stable crack propagation. Further details on determination and evaluation of *R*-curves under impact loading conditions are given in Refs. [13,16].

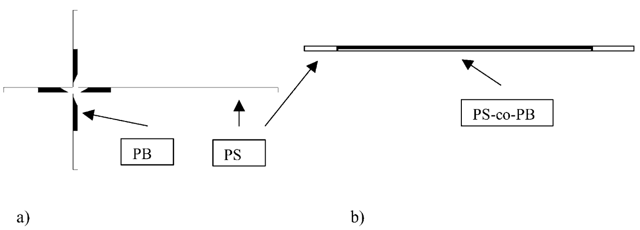

Fig. 1. Schematical representation of molecular architecture of block copolymers used in this study: (a) ST2: asymmetric star block copolymer and (b) triblock copolymer S–S/B–S with a PS-*co*-PB statistical copolymer as middle block.

3. Results and discussion

It is found that sample ST2 reveals unstable crack propagation associated with a considerably small toughness under impact loading conditions. To use this material for applications under dynamic loading, it is necessary to find strategies to increase their toughness without any loss of transparency usually not observed in binary polymer blends. A new way to realize this concept is to use binary block copolymers blends, which show a transparency due to the phase separation on the nanometer scale. We used blends of a thermoplastic star block copolymer (ST2) and a thermoplastic elastomer (LN4). Morphology, synthesis, and tensile properties of a very similar system were described by Knoll et al. [17]. This system did not show any loss of transparency in the whole composition range and a linear dependence of tensile strength and strain at break (uniaxial tensile test at 50 mm/min) on composition.

Samples ST2 and LN4 have equilibrium morphologies comprising of alternating lamellae and randomly distributed cylinders [18] respectively. Morphology of the block copolymers and their blends is strongly influenced by shear stress of injection molding. As shown in Fig. 2(a), lamellar structures of sample ST2 are aligned parallel to the direction of shear stress during injection molding. Macrophase separation of the blends is strongly suppressed by the shear stress in the melt. Basically, two types of morphologies are found. At lower LN4 contents (0–20 wt% LN4; Fig. 2(a) and (b)), a lamellar morphology prevails, which resembles qualitatively the morphology of pure ST2. At higher LN4 content (40–80 wt% LN4; Fig. 2(c)), the morphology of the blends is qualitatively comparable to that of pure LN4 (Fig. 2(d)). The morphological change with increasing LN4 content has a strong influence on the achieved toughness, as it will be shown later. In contrast to microphase-separated morphology of the injection-molded samples, films prepared from solution (toluene) show a macrophase separation with dispersed LN4 domains in the ST2 matrix, which represents the

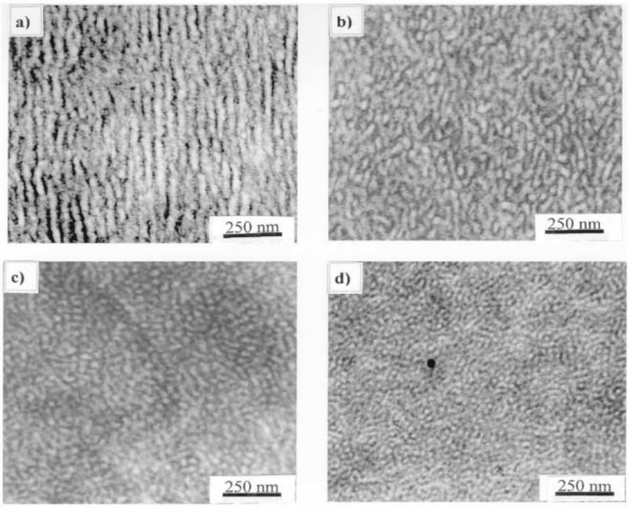

Fig. 2. TEM micrographs of injection-molded ST2/LN4 block copolymer blends: (a) ST2, (b) 20 wt% LN4, (c) 40 wt% LN4, and (d) LN4 (stained with OsO_4); dark areas: PB domains and light areas: PS domains.

equilibrium structure of this blend (Fig. 3). Our investigations clearly show that the phase separation occurs on the nanometer scale and the materials do not show a turbidity and can still be used for applications as transparent materials. It is now important to discuss the fracture mechanics behavior under impact loading conditions.

As shown in Fig. 4, the *R*-curves with *J* or δ_d as loading parameters exhibit a nearly identical dependence with increasing LN4 content represented by almost the same slopes of *R*-curves for *J* and δ_d. The tearing moduli, T_J and T_δ, and also the technical crack initiation values, $J_{0.05}$ and $\delta_{0.05}$, increase up to an LN4 content of 80 wt% (Fig. 5). This indicates that the increasing ductility of the notched samples with increasing LN4 content, associated with a decreasing dynamic flexural modulus and yield strength, also causes an increasing resistance against stable crack propagation. It should be, however, mentioned that this correlation does not have a general validity for other materials.

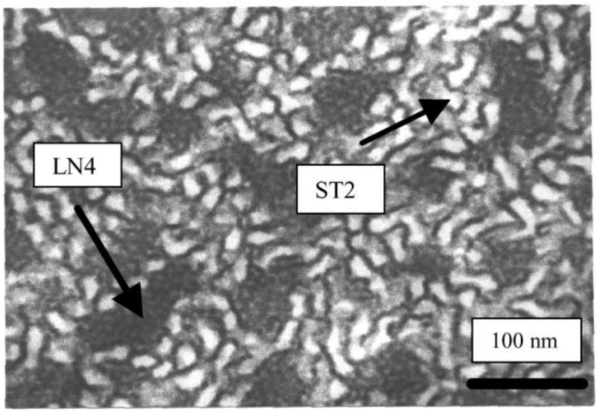

Fig. 3. TEM micrographs of solution cast films of the blend ST2/LN4 with 20 wt% LN4 (stained with OsO_4).

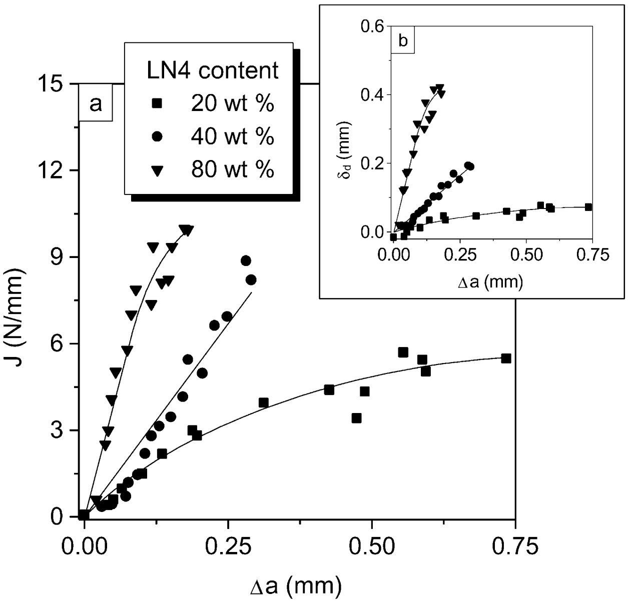

Fig. 4. Crack resistance curves (*R*-curves) for ST2/LN4 blends with (a) *J* and (b) δ_d as loading parameter.

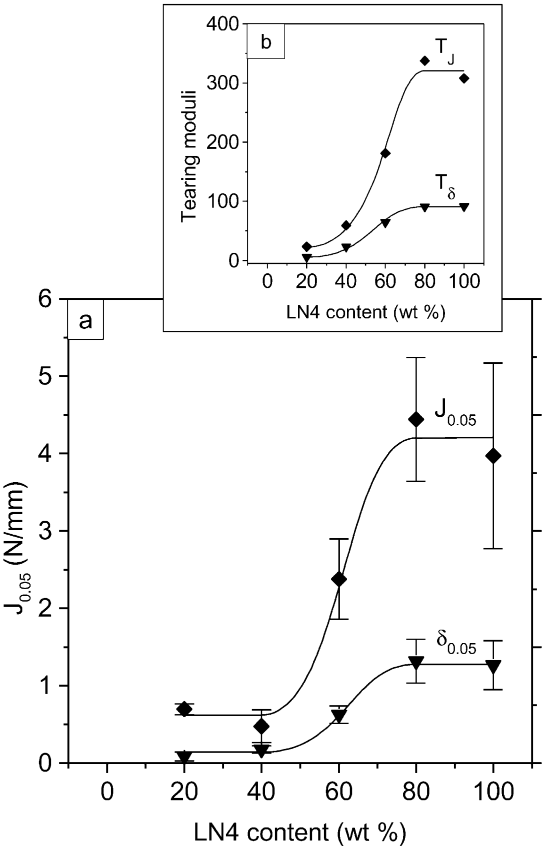

Fig. 5. (a) $J_{0.05}$ and $\delta_{0.05}$ and (b) tearing moduli T_J and T_δ for ST2/LN4 blends as a function of weight fraction of LN4.

It is found that the block copolymer blends with <20 wt% LN4 show unstable crack propagation. With increasing content of LN4, a transition to stable crack propagation is observed, which makes it possible to determine *R*-curves (Fig. 4). The increasing toughness of these blends with increasing LN4 content indicates that samples with ≥20 wt% LN4 have a sufficient resistance against unstable crack propagation. The materials investigated show a maximum stable crack speed ranging from 0.12 m/s for 40 wt% LN4 to 0.6 m/s for 20 wt% LN4 (the crack speed is determined as time derivation $d(\Delta a)/dt$ of the stable crack growth Δa). This demonstrates that the increasing toughness is correlated with a decreasing stable crack speed.

While the transition from unstable to stable crack propagation is found at 20 wt% LN4, corresponding to a common brittle/tough transition, at higher LN4 contents an additional transition can be observed. In Fig. 5, 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 at 60 wt% LN4 indicating a 'tough/high-impact' transition, BTT 2, as a measure for the resistance against stable crack initiation. Because fracture mechanics parameters represent a conservative estimation of the toughness behavior of materials under impact loading conditions, the blends containing LN4 contents equal or higher than 60 wt% do not show a brittle failure, and only stable crack propagation is observed. The maximum stable crack speed of blends having equal or more than 60 wt% LN4 is only 0.05 m/s. This value is much smaller than that of the materials with lower LN4 contents and corresponds to the increasing toughness at the BTT 2.

For the materials investigated in this study and for other heterophase polymers [19,20], two different brittle/ductile transitions were observed, the BTT 2 and the conventional 'brittle/tough' transition (BTT 1). In contrast to the BTT 1 as a measure for the safety against unstable crack propagation, the BTT 2 can be described as a measure for the safety against stable crack propagation. As demonstrated in recent studies [10,21], a BTT 1 occurs if the crack growth mechanism shifts from stable towards unstable. However, the BTT 2 should also be correlated to a change in deformation mechanism. As discussed in Ref. [19], differences in deformation mechanisms leading to BTT 1 and BTT 2 may be explained by Wu's percolation theory [22] and Margolina's theory [23] respectively. In other words, Wu's percolation theory is valid in the region of predominant stable crack growth and the theory by Margolina in that of stable crack growth. This classification is, however, impossible in the system investigated, where the structural heterogeneity lies in the nanometer scale in contrast to a particle-matrix structure of conventional polymer blends, where particle sizes are usually in the micrometer scale. The morphological changes in the ST2/LN4 blends only occur on the nanometer scale and have a strong influence on the achieved toughness level and underlying crack propagation mechanisms. However, the nature of deformation mechanisms at the BTT 2 observed in these materials studied via SEM (fracture surface) will be discussed elsewhere [24].

4. Conclusion

This study represents an investigation of crack resistance behavior of binary block copolymer blends. In contrast to current trends in developing novel polymeric materials based on binary polymer blends, such as PP/EPDM, ethylene–propylene copolymers and other high-impact PP materials, the binary SB block copolymer blends, comprising of a thermoplastic block copolymer (ST2) and a thermoplastic elastomer (LN4), investigated in this study combine the high-impact behavior with an excellent transparency and allow to adjust the stiffness–toughness ratio in a wide range, demonstrating new concepts for toughening of polymers. Two transitions are observed with increasing LN4 content, the conventional brittle/tough transition, and the tough/high-impact transition. While the former is caused by the transition from unstable to stable crack propagation, the tough/high-impact transition should be caused by a transition in deformation mechanism. In contrast to sample ST2, materials with about 60 wt% LN4 reveal a sufficiently high toughness for application under impact loading and still maintain their high level of transparency. It should be mentioned that the morphology–toughness correlation observed in the system investigated is fundamentally different from that found in conventional impact-modified or reinforced polymeric systems with matrix-particle morphology due to its nanometer-structured morphology.

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