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Influence of melt processing induced orientation on the morphology and mechanical properties of poly(styrene-b-ethylene/butylene-b-styrene) block copolymers and their composites with graphite

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ABSTRACT

The effect of orientation induced during the manufacturing process on the self-assembled morphology and mechanical properties of poly(styrene-b-ethylene/butylene-b-styrene) block copolymer (SEBS), maleated SEBS (SEBS-MA) and their composites with graphite was examined in this paper. The roll milling process induced higher stiffness along the rolling direction, emphasized by the increase of Young's modulus with 645% in this direction relative to the perpendicular one and the increase of storage modulus at room temperature with one order of magnitude. The addition of graphite particles diminished the anisotropy of static and dynamic mechanical properties but contributed to the increase of the total energy absorbed till break. The different self-assembled morphologies and degree of order observed by polarized optical microscopy (POM), scanning electron microscopy (SEM) and atomic force microscopy (AFM) in SEBS and SEBS-MA explained some of the differences in their static and dynamic mechanical behavior. For the first time the anisotropy was emphasized by the different glass transition values obtained on the two stretching directions.

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1. Introduction

Block copolymers undergo microphase separation into self-assembled ordered morphologies as a result of the incompatibility between the different blocks constituting the copolymer. Manipulation of these morphologies in nanometers range is a hot topic because of the huge potential application value [1–6]. The microphase separated morphology can be controlled through the variation of composition, molecular weight and history of processing conditions [5,7–9]. The influence of specific morphologies (spherical, cylindrical, lamellar and gyroid) on the rheological properties of block copolymers has been widely studied [10–12].

SEBS block copolymer shows very high elongation at break, high rigidity and linear elastic response at low deformation and important strain energy absorption [13,14]. The microdomains resulted from microphase separation in SEBS may form, in certain conditions, regular arrangements with local periodicity, most frequently cylindrical or lamellar, with high effect on the mechanical properties [8,15,16]. These microdomains disappear only at high temperature, giving rise to an isotropic phase. The order–disorder transition temperature of SEBS is high, values between 220 °C and 240 °C being reported [8,15,16].

The known advantages of SEBS can be manipulated to design new materials by controlling the deformation conditions. Preferred molecular orientation because of the plastic deformation during processing has as main result the increase in material's toughness and strength and is widely applied in industry: blow molding, thermoforming, hydrostatic extrusion, rolling, plane strain compression, fiber spinning and others [17,18]. In their pioneering work, Seguela and Prud'homme studied the influence of the morphology of SEBS films (styrene weight fraction 0.29), prepared by solvent casting, on mechanical behavior [19,20]. They demonstrated that toluene-casted SEBS film showed a lamellar two-phase morphology [19] and a mechanical behavior involving yield point and neck propagation [20], the overall deformation resulting mainly from the rubbery microphase deformation with small contribution of ductile deformation of the glassy microphase. Moreover, studying the microstructural transitions during the deformation of styrene–butadiene–styrene (SBS) roll-cast films, Cohen et al. showed that the deformation mechanism was dependent on the initial orientation of the lamellae relative to the deformation axis:

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stretching parallel to the lamellae resulted in yielding and high strain by propagation of a stable neck, and stretching perpendicular to the lamellae led to layer undulation and "chevron" morphology [7]. At very high strains, the stress–strain curves coincided, regardless the orientation of the applied stress, showing similar morphology consisting of highly stretched rubber matrix with glassy blocks mainly oriented along the deformation axis [7].

Several conditions were applied during the processing of block copolymers to obtain self-assembled ordered morphologies, such as low temperature extrusion (100–120 °C) followed by annealing [21] or shear using different types of rheometers [22]. Common polymer processing methods including extrusion [8], injection molding [9,23], and plane strain compression processing using a channel die [24] were also applied to create long-range morphology alignment in block copolymers. Different degree of orientation was achieved in SBS star-block copolymers by compression molding followed by rapid cooling (high orientation of lamellar microdomains), and by injection molding (small degree of lamellar orientation) [13].

The influence of the orientation on the properties of block copolymers in high-rate processes such as injection molding has been widely investigated both in the bulk [9,10,23] and for the surface [25], but limited information is available for low-rate processes, where the induced orientation can be better controlled. Previous information on the orientation of polystyrene (PS) cylinders (21 wt%) dispersed in a poly(ethylene butylene) (EB) continuous matrix by roll processing of SEBS was reported by Kotaka et al. using elongational flow opto-rheometry [16]. Micro and nano-fillers have been tested to improve the properties of SEBS for specific applications [12,26–29] but, to the best of our knowledge, no data were reported on the influence of graphite (G), a filler which can lead to anisotropic properties in materials, on the morphology and mechanical properties of block-copolymers with preferred orientation. Therefore, the combined effect of orientation induced during roll milling processing and graphite, a layered structure filler, on the morphology and mechanical properties of two block copolymers, SEBS and SEBS-MA is discussed in this paper. Specimens were collected parallel and perpendicular to the rolling direction and characterized by mechanical tests and dynamic mechanical analysis (DMA). The morphology and orientation at micro and nanoscale were investigated by optical and electron microscopy and by AFM. AFM enabled precise information regarding surface morphology without the need for special preparation techniques to enhance contrast [30,31] and was used in this study to provide real-space observation of nanophase separated patterns in SEBS and SEBS/G composites.

2. Experimental details

2.1. Materials

The two block copolymers, SEBS (Kraton G1652) and SEBS-MA (Kraton FG1901X) containing 2.0% grafted maleic anhydride (MA) were supplied by Kraton Polymers (USA). Both have about 30 wt% styrene, and a density of 0.91 g/cm^3. The melt flow index of SEBS and SEBS-MA are 5 g/10 min and 22 g/10 min respectively (230 °C/5 kg). G powder, with particles smaller than 75 μm, was supplied by Georg H. Luh. Gmbh (Germany). Sterically hindered phenolic antioxidant, Irganox 1010, provided by Ciba-Geigy (Switzerland), was used as melt processing stabilizer.

2.2. Preparation of composites

Composite materials from block copolymers (SEBS and SEBS-MA) and 5 wt% graphite were obtained by melt mixing in a Brabender LabStation (Germany) equipped with a 60 cm^3 mixing chamber, at a temperature of 180 °C for 7 min after melting, with rotor speed of 60 rot/min. Neat block copolymers were also processed on the Brabender LabStation in the same conditions as the composites. Block copolymers and composites were then molded on a laboratory two-roll-mill for 90 s, ratio of the peripheral speeds 1.3, to induce preferred orientation by the compressive shear forces involved in rolling. Samples were then compression molded into sheets of 1 mm thickness at 185 °C, 3 min preheating (0.5 MPa) and 2 min under pressure (15 MPa).

2.3. Characterization

Tensile properties of block copolymers and composites were determined according to ISO 527 under standard laboratory conditions (21 °C, 65% relative humidity) on specimens type 5B using an Instron 3382 testing machine. Specimens were cut from the compression molded plates, parallel (II) and perpendicular (L) to the rolling direction. Young's modulus was determined from the slope of stress–strain curves using the software of the Instron 3382 (Bluehill 2) at a crosshead speed of 0.5 mm/min and the ultimate mechanical properties at a test speed of 100 mm/min. Ten specimens were used for each direction and sample, five for the determination of Young's modulus and five for tensile strength and elongation at break. The standard deviation was less than 3% for tensile strength and modulus and ~4% for the elongation at break.

DMA experiments were performed in tensile loading mode using a DMA Q800 (TA Instruments) at a constant frequency of 1 Hz with oscillation amplitude of 4 μm. The storage modulus, loss modulus, and loss factor ($\tan\delta$) were recorded as a function of temperature from room temperature (RT) to 150 °C with a heating rate of 3 °C/min and force track of 125%. The samples, 18 × 6.5 × 1 mm (length × width × thickness) were cut from compression molded plates, parallel (II) and perpendicular (L) to the rolling direction. All samples were equilibrated at RT for 5 min. The percentage error in the measurements was found to be less than 1.5%.

AFM images (256 × 256) of specimens' surface were captured in Scanasyst mode by a MultiMode 8 atomic force microscope equipped with a Nanoscope V converter from Bruker (USA). Real time scanning was performed in air at room temperature with scan rates of 1–1.4 Hz and scan angle 90°. A silicon tip (nominal radius 2 nm, from Bruker) with a cantilever length of 115 μm and a resonant frequency of about 70 kHz was used in this test. The surface of annealed samples (110 °C for 24 h) was investigated using Peak force (PF) Quantitative Nanomechanical Mapping (QNM) mode of MultiMode 8 and a silicon tip from Bruker with nominal radius of 8 nm, having aluminum reflective coating on the backside of the cantilever (220 μm) and resonant frequency of 75 kHz.

SEM analysis of graphite powder, block copolymers and their composites (samples taken from the same plates as those used for mechanical characterization) was performed using FEI Quanta 200 Environmental SEM, with tungsten electron source, accelerating voltage 15–20 kV, without prior metallization of samples.

Polarized optical microscopy was performed using the Nikon inverted microscope (Eclipse Ti-U, Nikon Corp., Japan) equipped with DS-Fi1 (5 megapixel) CCD video camera and dedicated software (NIS Elements, Nikon) for image acquisition and processing. A beam of light from a 2 W He–Ne laser (wavelength = 632.8 nm) was directed through the polarizer followed by the sample and the analyzer. Images were acquired on samples of block copolymers taken from the same plates as those used for mechanical characterization and on thin films (60–70 μm) of block copolymers and composites obtained by further compression molding of plates in an electrically heated press (Dr. Collin) at 180 °C, 180 s preheating at 0.5 MPa and 90 s compression at 15 MPa. The samples were placed between crossed polarizer and analyzer with the optical

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