

Block Copolymer Nanocomposites With Mono- And Bioriented Structures

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ABSTRACT

Block copolymer nanocomposites are materials with interesting structures and properties. The control of their morphology can be obtained during processing, and anisotropic structures may be oriented in one or two directions, affecting both the copolymer domains and nanoparticle alignments. In this work mono- and bioriented films of SEBS copolymer and its nanocomposites containing nanoclays, carbon nanotubes and silica nanoparticles were prepared by blown tubular film extrusion, by controlling the air pressure inside the bubble, and other processing parameters. The structure of the materials was evaluated by SAXS and their tensile properties were tested. The bioriented samples have balanced mechanical properties, and the nanoparticles may promote faster biorientation of the copolymer domains by cooperative motion during processing.

Keywords: block copolymers, nanocomposites, biorientation, organoclays, carbon nanotubes

1 INTRODUCTION

Block copolymers are materials known to form different ordered structures in the nanoscale. The addition of nanoparticles to these copolymers may form materials with interesting morphologies and properties, depending on the interactions between the particles and block domains, as well as the processing conditions [1-3]. One of the most important strategies to produce nanocomposites is to control the degree of nanoparticle dispersion, and the control of morphological alignment is also desired for many applications [4].

It is possible to align block copolymers with anisotropic structures, such as lamellar or cylindrical using shearing and elongational flows. Shear alignment in one direction can be achieved when the copolymer is in the molten state, using processing techniques such as extrusion [5,6], or in solution, with techniques such as roll casting [7]. The alignment of the copolymer domains can be more effective using elongational flow [8], especially in lower strain rates [9,10]. At large rates, the competition between the alignment of the block domains and copolymer molecules

themselves decreases the overall domain alignment of once highly oriented copolymer domains [10].

The addition of nanoparticles can also affect the shape and orientation of block copolymer ordered domains. Studies show that they can act as templates for the formation or transformation of different morphologies [11,12], or they can promote the alignment of the ordered domains under shear flow [13].

In a previous study, our group prepared styrene-ethylene/butylene-styrene (SEBS)-organoclay nanocomposites by melt extrusion, resulting in the alignment of the cylindrical block domains and the clay nanoparticles in the extrusion direction [6]. We verified that the nanoparticles aligned at different extents with the flow, depending on their dispersion and on the affinity between the clay particles and the copolymer domains. This alignment could be changed by melt elongation of samples in directions parallel and perpendicular to the extrusion flow, as evaluated in another study [10]. We verified that the nanoparticles could either help or disturb the morphological realignment depending on the microstructure and rate of elongation.

In this work nanocomposites of SEBS block copolymers with cylindrical morphology and different nanoparticles were prepared using melt processing techniques in order to promote uniaxial and biaxial alignment of both the block cylinders and the nanoparticles.

2 EXPERIMENTAL

The polymer used as matrix in this study was a polystyrene-*b*-poly(ethylene-*co*-butylene)-*b*-polystyrene (SEBS) triblock copolymer from Kraton Polymers containing 20 wt% PS blocks (Kraton G1643). The main nanoparticles used to prepare SEBS nanocomposites were the organoclay Cloisite 20A from Southern Clay and hydroxylated multiwall carbon nanotubes (CNTs) with an average diameter of 50 nm and average length of 15 μ m. Some samples were also prepared containing halloysite clay nanotubes (average diameter of 100 nm and length of 4 μ m) and silica nanospheres (Aerosil 200, primary particles' average diameter of 12 nm).

In order to have a good dispersion, the nanoparticles were mixed with the copolymer in a Rheomix PTW-16

double-screw extruder attached to a PolyLab 900 torque rheometer from Haake using a temperature profile from 160 to 190 °C and screw speed of 100 rpm. All the samples were then processed in a 16 mm diameter single screw extruder from AX Plásticos using a similar temperature profile and screw speed of 30 rpm. Uniaxial alignment was obtained by preparing samples using an annular die with an inner diameter of 20 mm and a gap of 1 mm. The shear provided by the die was expected to align the copolymer cylindrical domains forming an almost monocystal-like structure, such as the ones observed in a previous study [6] Erro! Indicador não definido., as evaluated by small angle x-ray scattering (SAXS).

The same annular die was used to prepare extruded blown tubular films, in order to promote biaxial alignment of the copolymer domains and nanoparticles, which is a non conventional process for this kind of material. By increasing the air pressure inside the tube, it was possible to adjust the blow-up ratio (BUR = bubble diameter/die diameter), in order to increase the circumferential elongation. The mechanical properties of the extruded samples were then tested under uniaxial tension at a crosshead speed of 5 mm/min. The structure of the samples was evaluated by SAXS using a Bruker NanoStar setup, with a CuK α X-ray beam and a sample-to-detector distance of 650 mm.

3 RESULTS AND DISCUSSION

Figure 1a shows the tensile stress-strain curves for pure SEBS for three different BURs. It is possible to see that when the BUR = 1, the sample has a much stiffer behavior in the longitudinal (extrusion) direction, because of the alignment of the cylinders. In the transverse direction the sample is much softer and has a high value of elongation at break. By increasing the bubble diameter, the stretching of the sample in the transverse direction ends up equilibrating the properties in both directions at a BUR value around 3.

This behavior occurred in a similar way for the samples containing nanoparticles. Figures 1b and 1c show the tensile stress-strain curves of the nanocomposites containing 5% 20A and 0.5% CNT, respectively. The addition of clay has a subtle effect on the mechanical properties, and it decreases the maximum elongation of the samples in comparison to the pure copolymer at similar values of BUR. The samples containing CNT, on the other hand, have a positive effect on the elongation, showing a consistent increase in the values of elongation at break, an effect that becomes even more evident from the average results presented in Figure 2. For the pure copolymer, the maximum elongation slightly increases with BUR in the longitudinal direction, but decreases in the transverse direction, both reaching a common value around BUR = 3. After the addition of nanoclay 20A, the elongation at break decreases in both directions with increasing BUR. On the other hand, the addition of CNT makes the elongation reach its maximum value at the highest BUR for both directions.

The structure of the copolymers and nanocomposites was evaluated by SAXS. The results showed that the block copolymer domains have cylindrical structure, as expected for the PS content. The addition of nanoparticles did not significantly alter this morphology. Bidimensional SAXS images were taken along the direction perpendicular to each film surface. Figure 3 shows azimuthal plots of the SAXS results for selected samples around the first order peak corresponding to the cylindrical structure of the copolymer.

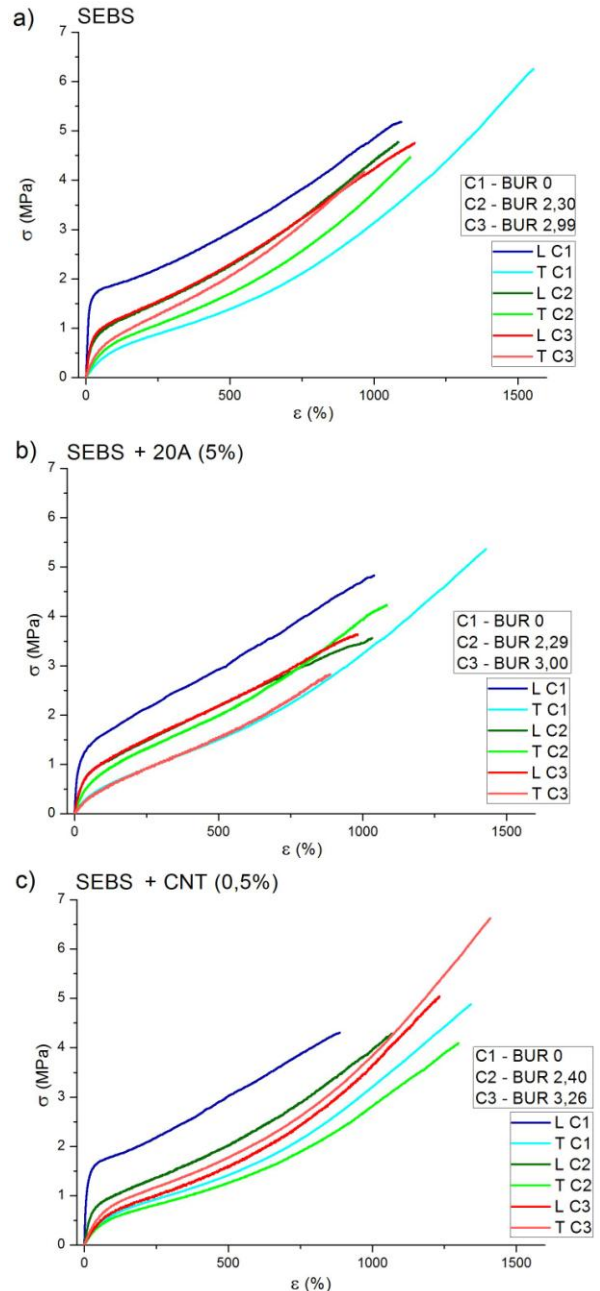


Figure 1: Typical stress-strain tensile curves for extruded blown films of a) SEBS; b) SEBS+5% 20A and c) SEBS+0.5% CNT prepared at different blow-up ratios (BUR) and tested in the extrusion (longitudinal – L) and perpendicular (transverse – T) directions.

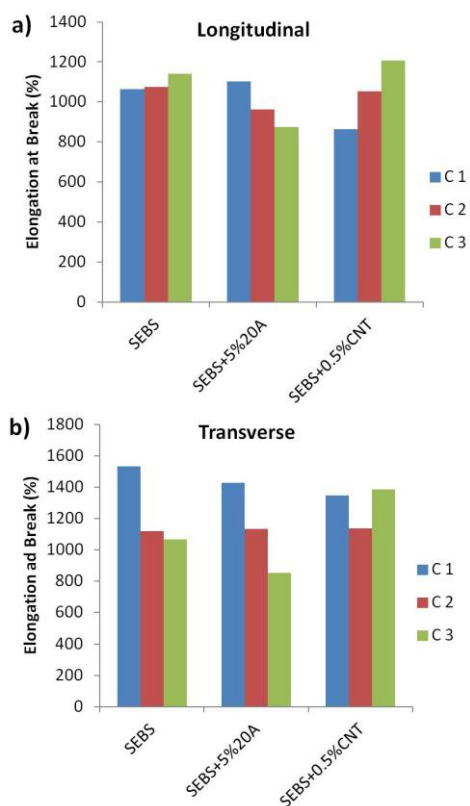


Figure 2: Average elongation at break for the samples tested in the directions: a) longitudinal and b) transversal. The processing conditions C1, C2 and C3 correspond to the BUR values indicated in Figure 1.

The curves and bidimensional images presented in the insets show that for an initial BUR = 1 the materials leave the extruder with the PS cylinders aligned parallel to the extrusion direction, as expected [6]. The copolymer cylinders show a considerable decrease in orientation during the blow film processing, rotating to other directions and forming a more isotropic material, which reflects the mechanical properties presented above.

The nanoparticles in the nanocomposites are also affected by the circumferential stretching, and they influence the rotation of the block copolymer domains. It is possible to notice from the inset in Figure 3b, for BUR = 1, that 20A clay particles form a circular diffraction halo indicating the presence of some non oriented clay particles in the initial condition. As the BUR increases, this clay halo disappears, indicating that all clay particles became parallel to the film plane.

The sample containing CNT shows an interesting behavior, as at BUR = 3.26 the circumferential stretching made the cylinders rotate about 90°, possibly aided by the long nanotubes that easily change their orientation with the flow.

Blown film nanocomposites were prepared using other nanoparticles as well, and Figure 4 shows the angle of the azimuthal peaks, which reflect the orientation of the cylinders during processing. All samples show an initial angle around 0°, which correspond to the extrusion direction. As BUR increases, there is a tendency for cylinder rotation, but different samples have different

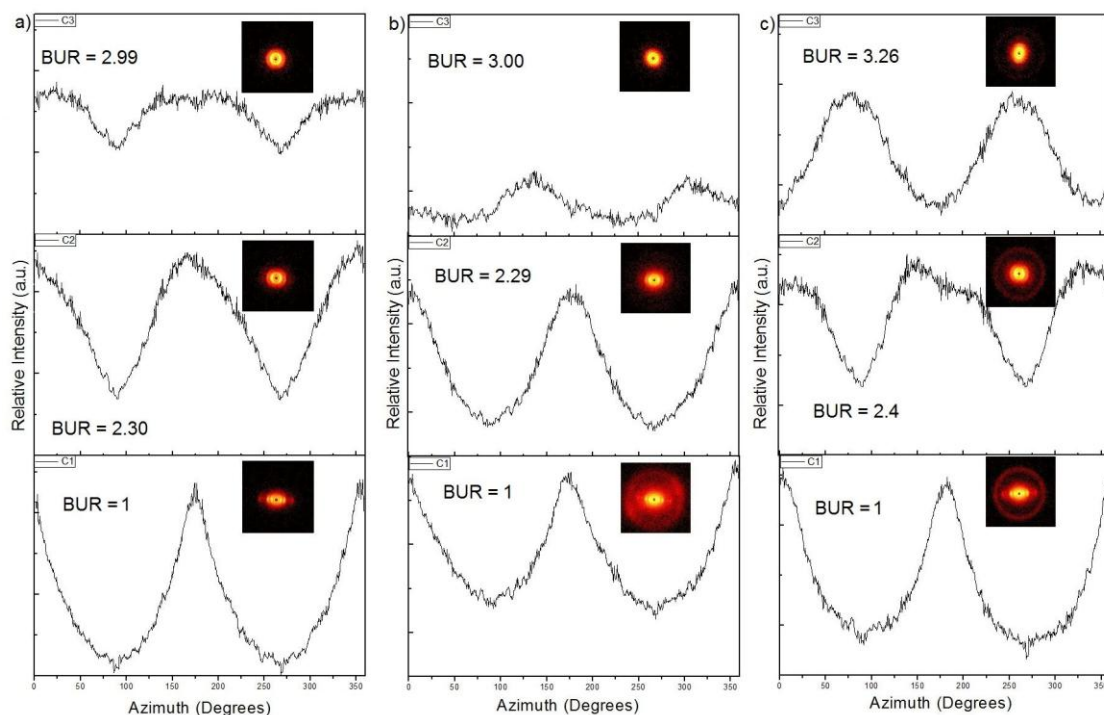


Figure 3: Azimuthal plots along the (10) cylinder peaks from the SAXS patterns shown in the insets of the extruded films (the vertical direction is the extrusion direction): a) SEBS; b) SEBS+5% 20A; SEBS+0.5% CNT.

behavior. The pure copolymer, the sample containing 5% 20A and the one with 5% halloysite nanotubes show a rotation to about 45° at a BUR around 3. This is an intermediate situation, where the samples show a more isotropic structure after stretching in both directions. The rather large concentration of these clays possibly resulted in a coarse morphology, and these nanoparticles do not significantly affect the microstructure during blow molding.

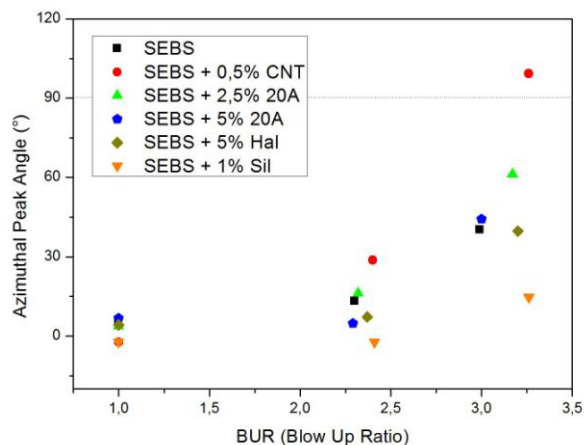


Figure 4: Angular variation of the center of gravity of the (10) Bragg peaks from the azimuthal plots of SAXS intensity for SEBS and its nanocomposites. Hal stands for halloysite, and Sil for silica nanoparticles. All compositions in wt%.

The addition of silica nanoparticles prevents the main rotation of the cylinders, as they are spherical and probably form a network structure within the copolymer. They apparently increase the viscosity and make it more difficult for the cylinders to realign with the circumferential strain. The sample containing 20A clay in a smaller concentration (2.5%), which probably has a more exfoliated structure, helps the cylinders to rotate to about 60° . The very anisotropic CNTs have the most extreme morphology change, as the cylinders rotate about 90° , showing the beginning of an inversion in morphology orientation.

Carbon nanotubes, with a fibrillar morphology, probably have a favorable interaction with the PS cylinders, which helps to keep the cohesion of the material, increasing the elongation at break. Clay particles such as 20A, which have lamellar structure, have a less compatible shape if compared to the cylindrical PS domains, and end up reducing the total elongation of the copolymer.

4 CONCLUSIONS

In this study an SEBS block copolymer and different nanocomposites were processed by blown film extrusion in order to evaluate the effect of shear and elongational flows on the structural alignment of block copolymer cylindrical

domains and the different nanoparticles studied. Depending on the composition and the blow up ratio of the films produced, the samples presented mono- and bioriented structures. The control of processing can therefore affect the orientation of the block copolymer domains and nanoparticles, and there is an important interaction between the nanoparticles and the domains, that defines the final morphology.

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