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Morphological evolution of oriented clay-containing block copolymer nanocomposites under elongational flow

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ABSTRACT

We have studied the effects of elongational flow on the morphology of nanocomposites of polystyrene-*b*-poly(ethylene-*co*-butylene)-*b*-styrene (SEBS) triblock copolymers – with aligned cylindrical morphologies – containing organoclays. These nanocomposites were elongated along two perpendicular directions at varied Hencky strain rates. Small angle X-ray scattering measurements indicate that the different types of deformation induce very different microstructural changes during the elongation processes. When elongated along the direction parallel to the extrusion direction, pure copolymers under low strain rates exhibit an increasing alignment of the cylinder axes while under high strain rates a disorientation effect prevails. When elongated at low strain rates along the transversal direction, the axes of the cylinders rotate an angle close to 90°, thus becoming parallel to the elongation direction, while under high strain rates the rotation is incomplete. The addition of clay causes different effects on the final morphology after elongation depending on the sizes and degree of clay dispersion and on the predominant interactions between clay and copolymer domains.

1. Introduction

Block copolymers, polymer blends and polymer nanocomposites are examples of multiphase polymeric materials with interesting engineering and physical properties highly dependent on their morphology. In turn, the morphology of these materials depends on composition, physicochemical (thermodynamical) affinity between components, rheological properties of phases, and history of processing conditions. In the case of block copolymers, the blocks usually phase segregate at a nanometric scale leading to different types of morphologies, the most common being named as spherical, cylindrical and lamellar [1]. These different morphologies can be useful to interact selectively with other materials, such as nanoparticles, which form nanocomposites with controlled morphologies according to the interactions between the nanoparticles and the block domains [2–5]. In particular, clay-containing nanocomposites consist of polymeric materials in which dispersed clay nanoparticles are embedded [6–8]. Depending on the state of dispersion of the clay, the morphology of these composites has been traditionally classified in three categories: microcomposites (not truly nanocomposites), intercalated and exfoliated nanocomposites [6,9]. The actual morphology, however, may be any intermediate

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combination of these three main types. In the case of block copolymer/clay nanocomposites, the final morphologies are complex because they depend on the structure of the block copolymer and on the particular affinities of the clay with the different phases of the copolymer [10–12].

During processing, polymeric materials are submitted to strong flows, both shearing and elongational, which alter their morphologies and therefore their properties. Many studies have been published on the effects of shear flow on the evolution of morphologies of block copolymers [13–16], and clay-containing nanocomposites [17–21]. The effects of elongational flows on the morphology of block copolymers were extensively investigated [22–32]. Most of these studies have been carried out at temperatures below the glass transition of the hard domains. In this case, although at high strains the molecular connectivity between the phases alters the morphology of the copolymers, at small strains they behave mechanically as typical composites [22]. Most of these studies demonstrate that, when subjected to large strains, the morphology of copolymers presents kinks due to the buckling of the hard domains and connectivity between phases [22–25]. Copolymers with spherical morphology arranged in a body-centered cubic lattice can have their structures aligned as well, and elongational tests show that the structure has an affine deformation up to a certain strain, and then the morphology exhibits a certain de-correlation from the cubic arrangement [26].

As mentioned above, only a few studies regarding the effects of elongational flows on the morphologies of block copolymers in the ordered state and above the glass transition temperature (T_g) of the harder domain have been reported. In this case block copolymers under elongation usually exhibit strain softening behavior [27,28]. During elongation, samples consisting of aligned domains held above the glass transition temperature might lose their anisotropy [29], but surprisingly this effect not always occurs. As a matter of fact, some copolymers under elongational flow retain their microstructural alignment, their rheological response being different according to the testing direction. This is more likely to occur when the viscosity of the molten copolymer is high enough, showing long relaxation times. Particularly, a previous study on the effects of elongation on a triblock copolymer with an aligned cylindrical structure [30] demonstrated that the morphology does not considerably change when the sample is deformed parallel to the cylinder direction.

However, when the copolymer is extended along the direction perpendicular to the cylinder axes, small angle X-ray scattering (SAXS) analysis revealed that the cylinder axes rotate and eventually become aligned with the elongation direction. Similar results were observed for a lamellar block copolymer [31]. Lee et al. [32] also carried out elongational rheological experiments on a triblock copolymer with spherical structure above the glass transition temperature of the hard blocks [32]. This material exhibits a strain hardening behavior, and SAXS and microscopic observations showed that after deformation the spherical morphology transformed into an isotropic arrangement of short cylinders. Due to restrictions imposed by the rheometers used, most of these previous studies have been carried out at rather low strain rates (up to 1.0 s^{-1}).

Flows also affect the morphology of clay-filled polymer nanocomposites, which in turn affects their rheological behavior. When subjected to shear flow, the clay platelets become parallel to the flow direction [17,19,21] resulting in a strong shear thinning behavior. This "flow thinning" effect has also been observed in samples of ethylene–vinyl acetate (EVA) nanocomposites deformed by elongational flows [33,34], the clay particles having even decreased the strain hardening effect on the polymer matrix [33].

On the other hand, Okamoto et al. [35] observed a strong strain hardening effect caused by exfoliated clay embedded in a polypropylene matrix modified with maleic anhydride (MA). This study showed that the clay particles form a "house of cards" structure with the clay planes aligned perpendicular to the flow direction. According to these authors, this unexpected morphology occurs because it presents a minimal energy dissipation rate due to the viscous resistance between clay surface and polymer under elongational flow, and/or because of the effects of strong interactions between MA modifier and clay surface.

This work aims at evaluating the effects during elongation processes of the complex anisotropic microstructures of pre-aligned and clay-filled triblock copolymer nanocomposites [36] on (i) the variation of their rheological properties and (ii) the evolution of their morphology at namometer scale.

2. Experimental

2.1. Preparation and elongation procedure

Samples of polystyrene-*b*-poly(ethylene-*co*-butylene)-*b*-styrene (SEBS) triblock copolymers with a morphology of aligned polystyrene (PS) cylinders within a matrix of poly(ethylene-co-butylene) (PEB) as well as their clay-containing nanocomposites were prepared by extrusion processing and then submitted to elongational flow.

Rheological measurements under elongation were carried out above the glass transition temperature of the PS domains (100 °C), but below the order–disorder transition of the block copolymers, which is above 220 °C, according to SAXS measurements [36]. In order to study the effect of the microstructural alignment on the rheological properties and on the evolution of morphology during flow, the samples were elongated along two perpendicular directions, parallel and perpendicular to the extrusion direction.

The structural alignments of block domains and clay particles were characterized by small angle X-ray scattering (SAXS). Details about the materials used in this work and experimental procedures are reported below.

2.2. Materials

The two SEBS copolymers used for nanocomposite preparation were Kraton G1652 (SEBS) and Kraton FG1901 (SEBS-MA), both having 30 wt.% PS blocks, and the latter also containing 1–2 wt.% maleic anhydride attached to the middle poly(ethylene-*co*-butylene) (PEB) block. The Cloisite 20A and 30B organoclays added were purchased from Southern Clay. The samples were prepared