



Interfacial molecular dynamics of styrenic block copolymer-based nanocomposites with controlled spatial distribution



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ABSTRACT

The dielectric properties of nanocomposites of polystyrene-*b*-poly (ethylene-*co*-butylene)-*b*-polystyrene (SEBS) triblock copolymers containing organically modified clay nanoparticles featuring controlled spatial orientation at the nanoscale: isotropic, totally oriented and partially oriented, have been investigated and correlated with the nanocomposite morphologies. A slow dielectric relaxation process attributed to elastomer chains with reduced mobility confined at nanoparticle/polymer interphase was observed in all the nanocomposites and was found to be dependent on the orientation of nanoclay and polystyrene (PS) domains, the location of clay tactoids as well as the PS block fraction. A dielectric “interfacial” glass transition temperature T_{gi} assigned to this characteristic relaxation was estimated to occur at temperatures ranging between 6 °C and 35 °C depending on the nanocomposite, which is much higher than the bulk rubber phase glass transition temperature, normally lower than -40 °C for the studied block copolymers. Interestingly, the highest T_{gi} were associated with the nanocomposites featuring random or partial orientation and/or selective location of nanoparticles in the rubber phase.

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1. Introduction

In nanocomposite materials, controlled orientation of certain anisotropic nanoparticles such as nanoclay [1,2], carbon nanotubes [3] and recently boron nitride nanotubes and nanosheets [4,5] is very beneficial for a wide spectrum of applications requiring excellent mechanical, electrical and/or thermal properties. For example, in the case of mechanical reinforcement, the alignment of nanoclay was reported in several publications to induce an improved mechanical strength in the alignment direction [6]. In the specific case of nanodielectrics, more efficient electron scattering and consequently higher breakdown strength perpendicular to the nanoparticles alignment direction were reported [2,7,8,9]. Simultaneously, nanoparticle alignment was shown to reduce dielectric losses in the direction perpendicular to the main plane of the

aligned nanoparticles [2]. This controlled orientation can be obtained using a wide range of techniques [3] although spatial alignment of nanoparticles according to 2D and 3D patterns is still a challenging field of study [10].

In applications requiring tuned spatial distribution of nanoparticles, the use of block copolymers can be really an asset due to the different nanoscale morphologies these materials present [11–16]. To probe the effect of tailored morphology and orientation of such designed nanocomposites on their polymer-filler interactions and implicitly on their final performance, techniques such as broadband dielectric spectroscopy (BDS) are often required [17].

In fact, the performance of polymer nanocomposites in general is governed by the interphase region [18,19] which consists mainly of a bound layer where the motion of macromolecular chains is strongly restricted affecting several properties including dielectric and mechanical properties [19–22]. The thickness and volume fraction of this interphase usually depend on the geometry of the nanoparticles and their compatibility with the polymer matrix [23–26]. It was estimated using both experimental techniques [23,25] and molecular dynamics simulations [27,28]. Furthermore,

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an additional glass transition corresponding to the interfacial polymer chains with restricted mobility was observed in some nanocomposites featuring strong attractive interfacial interactions [20,21,23–32] and predicted by modeling and simulations [33] as well, for relatively thick bound layers.

The reduced mobility of polymer chains in the interphase region of homopolymer-based nanocomposites has been well investigated during the last years, especially the effect of interaction strength between nanoparticles and the polymer matrix. However, to the best of our knowledge, there is only little literature regarding the interphase region in block copolymer based nanocomposite systems and specifically the effect of the orientation of nanoparticles and block copolymer nanodomains on polymer dynamics in this interphase region. In fact, in the case of nanocomposites prepared from multicomponent polymer matrices, an additional degree of complexity is added to the system as the nanofillers can interact differently with the constitutive components [15,20]. These interactions are usually interdependent and hard to quantify separately. Few studies investigated the dielectric behavior of copolymers and its dependence on chemical and structural factors such as sulfonation [34] and compatibility with different nanofillers. In this context, Vo et al. [20] studied the dielectric behavior of styrene-butadiene rubber (SBR) random copolymer filled with three different nanoparticles: nanoclay, silica and carbon black. They reported a new relaxation mode for all three systems attributed to the segmental motion of rubber chains with reduced mobility at the polymer-nanoparticle interface. Moreover, they evaluated an interfacial glass transition temperature T_{gi} associated with this relaxation process. The highest T_{gi} was attributed to the SBR/clay system indicating stronger interaction and better compatibility compared to the two other fillers.

In this work, we investigated polystyrene-*b*-poly (ethylene-co-butylene)-*b*-polystyrene (SEBS) thermoplastic elastomer as the block copolymer matrix since it presents excellent features suitable for many applications, such as good mechanical properties [35,36], good resistance to water treeing [37,38] as well as good electro-mechanical coupling [39]. It is a symmetric triblock copolymer composed of two polystyrene (PS) end-blocks of the same length at the extremities and a poly (ethylene-co-butylene) (PEB) rubber mid-block. Organically modified nanoclays, known for their beneficial effect on mechanical and dielectric properties of polymer nanocomposites including breakdown strength, resistance to surface erosion and reduction of space charge accumulation [2,6–9,19,40], were added to the thermoplastic elastomer. Four sets of block copolymer nanocomposites containing three different weight fractions of PS phase (0.13, 0.20 and 0.30) were investigated in total. Depending on these ratios and using several fabrication processes, different morphologies were successfully prepared: isotropic vs. totally oriented vs. partially oriented polystyrene nanodomains and clay nanoparticles. Moreover, the degree of exfoliation and location of clay particles inside PS or PEB domains were tailored using a specific SEBS grade with a maleic anhydride (MA) grafted on the PEB block.

In a first step, the orientation of nanoclay and PS nanodomains in the different samples as well as the state of order of the block copolymer were fully characterized by SAXS and TEM. In a second step, the dielectric response was studied as a function of frequency and temperature in order to investigate the influence of the block copolymer tuned architecture on the polymer dynamics, which may affect implicitly the engineering properties such as dielectric losses, breakdown strength and mechanical stiffness, to name a few. The dielectric spectroscopy results were correlated to SAXS and TEM results in order to come up with a template of block copolymer nanodielectrics [41] with controllable morphology and properties suitable for different dielectric applications. In

particular, a slower dielectric relaxation mode compared to the main relaxation responsible for the bulk glass transition of the rubbery phase was observed in all nanocomposites and attributed to the segmental motion of rubber chains with reduced mobility located at the polymer-nanoparticle interphase. An interfacial glass transition T_{gi} associated with this new relaxation mode was estimated and used to quantify the interaction strength between the nanoparticles and the polymer chains depending on the configuration, the styrene block content and the location of the nanoparticles in one block or another. Besides, this new dielectric relaxation process, attributed to rubber chains located at the interfacial layer, was also observed in the dynamic mechanical responses of samples prepared from SEBS grade containing 30 wt% of PS block. Finally, the thickness of the interfacial layer was estimated in the range 7–10 nm.

2. Processing

2.1. Materials and methods

Four grades of symmetric triblock copolymer SEBS donated by Kraton were used: G1643, G1645, G1652 and FG1901. These grades contain different fractions of PS block ranging from 13 to 30 wt%. Besides, the FG1901 grade contains 1.4–2 wt% of maleic anhydride (MA) group attached to its elastomeric PEB block. All the grades contain 0% of diblocks. More details regarding the physical properties and morphologies of these polymers are reported in Table 1. Montmorillonite clay grade Cloisite 20A purchased from Southern Clay (Gonzales, USA) and modified with dimethyl di (hydrogenated tallow) quaternary ammonium salt, was used as nanofiller for the nanocomposites preparation. More details regarding the physical properties of the polymers as well as the modification and size of clay particles were provided in the previous studies published by co-authors in the same context of research [1,2,42,43]. All the materials studied in this paper were used as received.

The nanocomposites were prepared by solvent casting, sheet die extrusion or film blowing extrusion to achieve different morphologies. In the case of solvent casting process, the SEBS powder and the nanoparticles were mixed in toluene by magnetic stirring at 60 °C. The mixture was subsequently poured into a Petri dish and left in open air under the fume hood for several days until complete evaporation of solvent. They were subsequently dried in a vacuum oven and annealed according to specific temperature profiles selected depending on the styrene content, in order to reach equilibrium morphologies [44]. For SEBS-13 and SEBS-20, the sequence: 10 min at 50 °C, 30 min at 110 °C, 2 h at 150 °C and 24 h at 60 °C was used while for SEBS-30 and SEBS-30-MA, the sequence 20 min at 60 °C, 20 min at 100 °C, 20 min at 150 °C and 10 min at 200 °C was used as published in Ref. [2]. The samples prepared by sheet die extrusion were obtained according to references [1,43]. In a typical procedure, clay nanoparticles were mixed with SEBS in a twin screw extruder equipped with a sheet die, at a temperature profile ranging from 160 to 190 °C for SEBS-20, equal to 150 °C for SEBS-13 and equal to 200 °C for SEBS-30 and SEBS-30-MA and a screw speed of 100 rpm. The films prepared from SEBS-20 by film blowing extrusion were processed in a first step following the same procedure of sheet die extrusion. Subsequently, the samples were processed in a single screw extruder using the same temperature profile and a screw speed equal to 30 rpm. The latter was connected to an annular die with controllable air pressure inside the tube in order to induce lateral elongation and promote biaxial orientation of the block copolymer. In this study, the resulting films were inflated with air at two blow-up ratios: $R1 = 1$ and $R3 = 3$ in order to initiate respectively uniaxial and biaxial orientation directions. More details regarding this processing method are available in

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