Dynamical mechanical analysis of multiwall carbon nanotubes-styrene-isoprene-styrene block copolymer nanocomposite

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ABSTRACT

DMA investigations on polystyrene-*block*-polyisoprene-*block*-polystyrene three block copolymer containing with 17 wt%. styrene, loaded by various amounts of multiwall carbon nanotubes are reported. The wrapping of the soft phase around the nanofiller is demonstrated through the splitting of the glass transition assigned to the soft phase. The nanofiller has a weaker effect on the hard phase (polystyrene) of the block copolymer and did not destroy completely the self-assembly features of the block copolymer as the order to disorder transition was still observed in all investigated nanocomposites. A model for the morphology of this nanocomposites is suggested.

1. Introduction

The dispersion of nanometer-sized nanoparticles within polymeric matrices affects dramatically the physical properties of the matrices enhancing mechanical features (such as tensile strength [1] and Young modulus [2,3]), thermal stability [4,5] reducing the gas permeability [6], flammability [7], modifying phase transitions (glass transition [8,9] melting transition temperatures [10]), and degree of crystallinity [11,12]. The nanofiller may add new physical properties such as thermal conductivity [13–15], antistatic features [16,17] electrically conducting characteristics [18–20,1] and non-linear optical features, leading to multifunctional, heterogeneous, and eventually smart nanocomposites. It is generally accepted [21,22] that these outstanding modifications are controlled by the thin interface between the nanofiller and the macromolecular chains, reflecting the huge surface area of the nanoparticles dispersed within the polymeric matrix. The naïve picture of a polymer-based nanocomposite implies the wrapping of macromolecular chains around the nanofiller, providing an intuitive understanding of the mechanism responsible for these modified or new properties. Multilayers of such nanocomposites can improve both the mechanical and the electrical features [23].

The assembly of nanometer-scale nanoparticles within polymeric matrices expresses the fine competition between entropic and enthalpic contributions [24,25] revealing the effect of filler's size [26,27] on the morphology [28] and thermodynamic features of block copolymers,

and reflecting a wide range of cooperative interactions [29,30] that can be exploited to obtain better materials [25] and biomaterials [31] structured at nanometer scale.

Recent research in polymer-based nanocomposites concentrates on block copolymers and polymeric blends, due to their self-assembly capabilities [32]. Several authors speculated the possibility to exploit these features to achieve an ordered distribution of nanoparticles within block copolymers by simply confining the nanofillers in a specific phase of the block copolymer [33,34]. This theoretical and experimental endeavor focused at Van der Waals interactions [34], dissimilar hydrophilic-hydrophobic interactions [32] including Janus particles [29]), hydrogen bonding [35,36], and covalent bonding [29]. Experimental data regarding the effect of submicron fillers/confinement on the glass transition of the polymeric matrix are contradictory. In certain cases, it was reported that the loading of polymeric matrices with carbon nanotubes increased the glass transition temperature of the pristine polymeric matrix [9], while some authors reported a decrease in the glass transition temperature as the loading with submicron particles was increased [37]. Such a complex behavior is not unique; experimental data on polymeric films confined to a thickness smaller than the radius of gyration of the polymer (typically equal or smaller than 100 nm) revealed an analogous behavior [38]. For example, the glass transition of polystyrene is decreased as the thickness of the polymeric film is reduced below 200 nm or eventually the diameter of polymer nanofiber is decreased to the submicron range

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[39,40].

In the case of homopolymers, such behavior reflects the nature of the interactions between polymeric segments and nanometer-sized fillers such as carbon nanotubes (CNTs) at two extremes:

Firstly: *Attractive interactions between carbon nanotubes and polymer segments*. This interaction reduces the amount of free volume available to polymeric segments, contracts the polymer coil, and increases the glass transition temperature. Phenomenonlogically, attractive interactions build wetting interfaces and can be associated with the formation of the interface between the nanometer-scale filler and the polymer. In this case, macromolecular chains are wrapped around carbon nanotubes. At macroscopic scale the attractive interactions between carbon nanotubes and polymeric segments are responsible for surface tension effects, which are increasing the pressure exerted on the polymeric chain coil. These attractive interactions favor the growth of polymer crystallites at the interface with the nanofiller and shifts upwards the glass transition temperature of the interfacial material.

Secondly: *Repulsive interactions between polymer segments and carbon nanotubes*. At this extreme the macromolecular chain does not wet (does not wrap around) the nanofiller. Strong repulsive interactions push the polymeric segments away from the nanofiller, bulging the isotropical spherical random coil. Eventually, some atoms or groups of atoms belonging to the macromolecular chains are anchored (captured) by the surface of the nanofiller. Accordingly, the free volume available to polymeric segments is increased and consequently the glass transition temperature is shifted downwards. Such interactions generate nanometer-scale voids at the interface polymer-nanofiller that can be occupied by the filler or by polymeric segments. Due to the increased volume the interface repulsive interactions do not favor the polymer crystallization, and hence just a "volume" or bulk crystallization is expected in such nanocomposites.

An investigation that questions the role of macromolecular chain flexibility on the physical features of polymer-based nanocomposites is reported. The study aims to a better understanding of the physical features (including the self-assembly) of polymer-based nanocomposites, where the polymeric matrix is a block copolymer. A detailed analysis of the interactions between polymeric segments and multi walled carbon nanotubes (MWCNTs), is presented. The final goal is to better understand the stress transfer from the polymeric matrix to the filler by using a model block copolymer consisting of dissimilar chains; soft chains (polyisoprene) covalently attached to stiff chains (polystyrene) in a macromolecular chain with self-assembly capabilities. As the polystyrene content for this block copolymer is 17% wt., the self-assembly results into a cylinder-like morphology, with a continuous phase of cylinder hard segments within a soft matrix of polysoprene. The glass transition temperature of polyisoprene is ranging between -35 °C and -70 °C [41], depending on the average molecular mass and on the microstructure (cis, trans composition) of the polymer. For the three block copolymer containing 17% polystyrene, the reported glass transition temperature for soft segments (polyisoprene) is -55 °C [42] and the glass transition temperature of the hard phase was reported at 72 °C [42]. The glass transition temperatures for the isolated homopolymers of same average molecular mass and morphology are -63 °C and 92 °C [42]. The discrepancies suggest strong interactions between the soft and hard phases and/or confinement effects. It was estimated [42] that by assuming the additivity of free volume (using Fox equation for a blend of 2 homopolymers) and assuming only 2 components (hard and soft), the soft phase would contain about 8% hard phase (PS). The three block copolymer may eventually present an order to order transition at about 170 °C associated to a transition from cylinder of PS to discontinous spheres of PS and an order to disorder transition at 210 °C, which leads to an isotropic fluid (melt) above this temperature [43].

Owing to the qualitative analogy between polymeric ultrathin multilayer and polymer-based nanocomposites, a shift in the glass transition temperature is expected as the concentration of the filler is changed [44]. The direction and amplitude of this shift (increasing or decreasing the glass transition from the glass transition of the bulk homopolymer) depends on many parameters such as the nature of the surface, wetting details, and thickness of the polymeric film [38,39,44,45].

The design of the investigated composite assumed a segregation of the soft and hard segments at nanometer scale triggered by the wrapping of soft chains around MWCNTs, as an efficient way to enhance the mechanical properties of the polymeric matrix. The research dissects the glass transition in a complex polymeric system (styrene-isoprene-styrene block copolymer) filled with MWCNTs and provides unique information regarding the dynamics of polymeric segments and the interaction between polymeric segments and MWCNTs. Formallly, the system investigated contains both soft and hard phases to which a filler with cylinder-like symmetry has been added and may be modeled as described in [46–48].

2. Experimental methods

Multi wall carbon nanotubes (MWCNTs) from Nanostructured and Amorphous Materials Inc. and Polystyrene-*block*-polyisoprene-*block*-polystyrene with 17%wt. styrene (SIS) from Sigma Aldrich were used as received. The block copolymer (SIS) was dissolved in toluene (Sigma Aldrich). MWCNTs have been added to the solution. The as obtained mixture has been stirred for 4 h at room temperature and sonicated 2 h by using a high power sonicator (Hielscher) at an output electrical power of 1000 W and 50% power. The homogeneous solution was cast on microscope glass slides and the solvent has been removed by evaporation in an oven at 80 °C, during 30 h. The sonication was kept within the above mentioned parameters to prevent the degradation of macromolecules (samples of pristine SIS sonicated in similar conditions and not sonicated showed no shift of their glass transition temperatures). The viscoelastic properties of the SIS copolymers were evaluated by DMA on a Rheometric Scientific DMTA IV instrument. Calibration was performed as per manufacturer recommendations included in the Rheometric OrchestratorTM software. The tests were conducted with a shear sandwich geometry. A strain sweep test was performed at room temperature in order to find experimental conditions in the viscoelastic linear region for subsequent experiments. This was done by varying the strain amplitude while keeping the frequency at 1 Hz. A strain amplitude of 0.1% and 1 Hz frequency were chosen. A constant heating ramp of 2 °C min^{-1} was applied in all the experiments.

3. Experimental results and discussions

The dependence of the storage and loss modulus on temperature for sample loaded with various amounts of MWCNTs is shown in Fig. 1. The storage modulus represents the energy stored in the sample as elastic energy while the loss modulus reflects the energy loss due to the friction among polymer segments and nanometer-sized filler and also by the polymer molecules themselves. Due to the complex nature of the investigated system, the dependence of both storage and loss moduli on temperature and concentration of MWCNTs is complex.

The loss tangent, defined as the ratio of loss modulus to storage modulus is traditionally used to determine the main relaxations such as glass transition in polymeric materials (the maxim of the dependence of loss tangent on temperature occurs at the glass transition temperature).

Fig. 2 depicts the temperature dependence of the loss tangent for SIS-MWCNT composites in the low temperature range. The dependence of the loss tangent on temperature for the pristine polymer is almost identical with the dependence of the loss tangent on temperature for the sample filled by 0.38% MWCNTs. The gradual broadening and finally the splitting of the glass transition of the soft phase (polyisoprene) as the concentration of MWCNTs is increased is