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Processing dependency of percolation threshold of MWCNTs in a thermoplastic elastomeric block copolymer

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ABSTRACT

We prepared carbon nanotube thermoplastic elastomeric block copolymer nanocomposites using a commercial styrene–ethylenebutylene–styrene (SEBS) block copolymer and multiwall carbon nanotubes (MWCNTs) at different filler concentrations. Hereto we applied two different processing strategies, namely direct melt mixing and solution-precipitation. We observe that the mechanical and electrical properties such as storage module and electrical percolation threshold are clearly affected by the processing approach. We studied these effects in detail by means of dielectric spectroscopy, which provided important information about the dispersion state of the MWCNT filler network. It revealed a fractal filler behaviour of the samples independent of the processing method. However, in samples prepared by melt mixing an additional dielectric response related to nanoscopic gap junctions of 1.5 nm was identified. This response was not present in solution-mixed samples, which are characterized by improved polymer wetting. We discuss how the interactions between CNTs and the two phases of the block copolymer matrix are affected by the processing conditions resulting in the important differences in the filler network structure, which directly influence the final electrical and mechanical properties of the composite.

1. Introduction

Block copolymers consist of two or more chemically distinct blocks within the polymer chain. Chemical incompatibility between the constituent blocks leads to microphase segregation restricted to the length scale of the polymer molecules due to the covalent linkage between blocks. This restriction leads to well-ordered self-assembled nanostructures in the order of 5–100 nm dictated by the Flory–Huggins interaction parameter, the volume fraction of the blocks, the molecular weight of the blocks and the time–temperature experimental conditions. Thus, depending on the relative length of the constituents, block copolymers can segregate into microphase lamellae, cylinders and spheres, with several novel microstructures intervening between these broad boundaries [1]. These mesophases can act as structure directors for nanoscopic inclusions. In order to achieve maximum enhancement of effective physical properties of the composite material, control over the phase morphology of the host, the localization of the nano-inclusion and the overall properties of the filler network has to be gained. This in turn allows the much more sophisticated tailoring of the overall properties of the composites [2,3]. In this sense, carbon nanotubes with their unique structure and properties [4] are of increased interest for achieving phase-selective incorporation of in binary microphase separated polymer systems; i.e. blends of immiscible polymers or biphasic systems on the molecular level such as block copolymers.

In polymer blends preferential localization of carbon nanotubes is commonly explained by the differences in interfacial energies of the filler and the respective polymers, which originates from the differing polarities and surface energies [5–8]. This also holds for block copolymers but additionally effects arise from the sensitivity of the system to changes of the relative volume fraction upon segregation of nanotubes in one of the phases, which can cause a change of the phase morphology of the block copolymer matrix. Peponi et al. have demonstrated this with surface-modified single wall nanotubes segregated in the polystyrene phase of b-styrene–b-isoprene–b-styrene. The composites were obtained by dispersion of SWCNT, surface modified with octadecylamine, in toluene with dodecanethiol as surfactant for the tubes and subsequent film casting, finding in dependence of the use of dodecanethiol as surfactant a phase change from cylindrical to lamellar morphology in the dried films [9].

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We focus on the dispersion behaviour of *neat* multiwall carbon nanotubes (MWCNTs) in b-styrene–b-ethylenebutylene–b-styrene (SEBS), an industrial very important thermoplastic elastomer used for compatibilisation of immiscible polymer blends, impact modification, hot-melts and many more [10]. The composites were obtained by direct incorporation of the tubes into the melt of the block copolymer by extrusion and injection molding and for comparisons by means of ultrasound in a solution of the polymer and subsequent co-precipitation, dying and injection molding. We found substantial differences between the composites in dependence of the processing method. Most notably is the higher critical concentration of MWCNTs necessary to achieve percolation, the lower conductivity and the lower modulus of the solution-mixed samples dispersed with the aid of ultrasound in comparison with the melt-mixed samples. Dielectric spectroscopy revealed in the melt-mixed samples two relaxations – one related to the fractal filler network and an additional response, that is not present in the solution-mixed samples. We will demonstrate that this additional relaxation process is related to nanoscopic gaps in the order of 1.5 nm at tube-junctions allowing for quantum-mechanical tunnelling of electrons. The absence of this relaxation in the solution-mixed samples is caused by a stronger separation of the tubes at the junctions. Finally we will explain how the process conditions affect the dispersion state and how it relates to the mechanical behaviour of the composites.

2. Experimental

2.1. Materials and processing

The block copolymer used in this study was b-Styrene–b-ethylenebutylene–b-styrene (SEBS) (Trade name: Kraton G1652), donated by Kraton Polymer LLC. It has a composition of ca. 30 wt% styrene and 70 wt% ethylenebutylene and a molecular weight $M_w = 79{,}400$ g/mol. The diblock content was lower than 1%. Multiwall carbon nanotubes (MWCNTs) of grade NC 7000 obtained from Nanocyl, Belgium were used as received.

Direct incorporation of the MWCNTs into the melt of the polymer matrix was carried-out by extrusion using a DSM-Xplore 15 cm^3 microextruder with recirculation channel permitting the variation of the mixing time. Processing temperature in all cases was 275 °C. To minimize thermo-oxidative degradation, processing was performed under nitrogen. For the assessment of the mixing time the overall process time is separated into a feeding stage, which was in all cases about 2 min, and a mixing stage. For the concentration series the mixing stage lasted about 5 min. Tensile bars, according to ISO 37 Type 2, and discs with a diameter of 15 mm and a thickness of 1 mm were formed by injection molding using the DSM-Xplore 12 cm^3 injection-molder. The compound was extruded directly into the pre-heated barrel of the injection mold machine maintaining the temperature of the melt within ± 5 °C of the processing temperature. Temperature of the mold was 40 °C in all cases.

One sample series was prepared by a predispersion method in solution. The procedure was as follows: a) SEBS was dissolved in chloroform under stirring with a concentration of 0.02 g per 1 ml solvent, b) MWCNTs of desired quantity were dispersed in 50 ml chloroform and tip-sonicated for 10 min, c) MWCNT dispersion was added drop-wise under stirring to 50 ml of the chloroformic solution of SEBS, d) The mixture was precipitated with 100 ml ethanol, e) The precipitate was filtered and subsequently dried at 100 °C under vacuum for 1 h, f) The prepared powder was melt-mixed at 275 °C in the extruder for 2 min (+2 min for feeding) and injection molded under the same conditions as the samples with direct incorporation of the MWCNTs.

Concentration of MWCNT in the composites has been confirmed thermo-gravimetrically using a Perkin–Elmer TGA Pyris 1. The measurements were performed on samples taken from the injection-molded pieces by heating under nitrogen from room temperature until 600 °C to selectively combust the SEBS followed by heating under oxygen from 600 °C until 950 °C to burn the MWCNTs. The thermograms of the samples prepared by the solution-precipitation method did not show any residual solvent. Further details on the thermogravimetric analysis can be found in the Appendix (electronic supplement).

2.2. Dynamic mechanical measurements

Dynamic mechanical measurements were performed with a MetraviB DMA +450 at room temperature varying the amplitude of the sinusoidal deformation corresponding to the sample strain from 10^{-3} to 1 with a logarithmically equidistant increment of 9 measurement points per decade. The measurement geometry was double sandwich shear with specimen diameter 10 mm and thickness between 1 and 2 mm. The specimens were glued onto the aluminium supports using the cyano-acrylate adhesive Loctite 480. The flat surfaces of the specimens were pre-treated with primer Loctite 770 promoting adhesion of the cyano-acrylate adhesive. The glued specimens were allowed to dry for at least 24 h before any mechanical load was applied. The edges were carefully polished with a fine sand paper to remove excessive adhesive.

2.3. Dielectric measurements

The measurement of the dielectric properties of the specimens prepared by direct melt mixing was performed with a broadband dielectric spectrometer, BDS 40 system, manufactured by Novocontrol GmbH Germany. The measurement frequencies ranged from 1 Hz to 10 MHz. For the measurements of the samples prepared by predispersion in solution an impedance analyser 6505B, from Wayne Kerr, with a frequency range from 20 Hz to 5 MHz was used. The measurement geometry was a disc shaped plate-capacitor formed by the 15 mm diameter disc specimen placed between two electrodes. The thickness of the sample was ca. 1 mm. Thin gold layers were sputtered onto the flat surfaces of the specimens to ensure electrical contact to the electrode plates. All measurements were performed at room temperature.

2.4. Transmission electron microscopy

Thin films of the composites were prepared by ultra-microtomy (service of Centro de apoyo tecnológico, Microscopía de transmisión de electrons, of the University Rey Juan Carlos, Madrid, Spain) under cryogenic conditions at −90 °C using a diamond knife. The thicknesses of the films were about 40 nm. TEM was performed at the Servicios de apoyo de la investigacion, servicio de microscopia electronica.

3. Results

Fig. 1 depicts the shear storage modulus as function of the strain amplitude measured under dynamic conditions at a frequency of 5 Hz for the different concentrations of the melt-mixed and predispersed samples. With increasing filler content the small strain modulus increases. Quite remarkable is the small strain modulus increase observed at the lowest tested concentrations of the two sample series, which already amount to ca. 100%. The reinforced samples show a decrease of the module with increasing strain amplitude down to about the level of the pure