



# Changes of morphology and properties of block copolymers induced by carbon nanotubes

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## ABSTRACT

Carbon nanotubes have been extensively used in isotropic polymer media as mechanical reinforcements or as conductive fillers. New phenomena arise when the polymer matrix is made of an ordered block copolymer. Dispersions of nanotubes stabilized by block copolymers in selective solvents can be used to cast composite films in which the nanotubes are segregated in microdomains of the structured polymer. This concept is here investigated for the case of carbon nanotubes in a poly(styrene)-*b*-poly(butadiene)-*b*-poly(methylmethacrylate) terpolymer (SBM). It is observed that casting films of SBM from different solvents in the presence or absence of nanotubes can lead to different morphologies with distinct mechanical and electrical properties. In particular it was found that neat SBM cast from a mixture of cyclohexane and acetone exhibits a cylindrical microstructure. This metastable form is mechanically weak and brittle. But the polymer adopts a stable lamellar morphology in the presence of nanotubes. This phase exhibits much better mechanical properties. The capability of nanotubes to alter the morphology of a block copolymer and to lead to large improvements of mechanical properties appears therefore as a new mechanism of mechanical reinforcement beyond the already reported mechanisms of direct reinforcement and network formation.

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## 1. Introduction

Block copolymers exhibit a rich phase behavior and the capability to adsorb at interfaces. They have been used over the last years as stabilizers of various colloids, including carbon nanotubes in aqueous or organic media [1–11]. Block copolymers can undergo microphase separations [12–17] and be used as self-organized matrices for nanoparticles; offering thereby the possibility to develop novel nanocomposite structures. Depending on the relative size of the constituents, block copolymers can segregate into microphase lamellae, cylinders and spheres, with several other microstructures between these boundaries. In addition to this rich phase behavior at equilibrium, it is also known that the properties of block copolymers depend on their processing. In particular, metastable microstructures can be quenched via different thermal or casting treatments, resulting in materials with potentially different properties in spite of a similar chemical composition. Embedding colloids in such matrices is reminiscent of the approach which consists in dispersing carbon nanotubes in thermotropic or lyotropic liquid crystals [18,19] to achieve anisotropic functional

materials. Several examples of carbon nanotube-block copolymer composites have been reported in the last years. This class of materials holds a great promise for potential applications in organic electronics, optics, biotechnologies and reinforced polymers [9,20–28]. Most studies in the field have focussed on diblock copolymers or ABA type triblock copolymers. More recently, Pieré et al. reported pioneering studies of the inclusion of multiwall carbon nanotubes (MWNTs) in ABC triblock copolymers [8,9]. Such polymers offer a greater degree of complexity associated to a large potential of properties and possible functionalities. Pieré et al. investigated poly(styrene)-*b*-poly-(butadiene)-*b*-poly(methyl methacrylate) systems (SBM). The properties of such polymers depend on their microstructure, in their neat state [13–17,29] and also on the dispersion of the inclusions [9]. In particular, it was observed that well dispersed MWNTs can induce a direct mechanical reinforcement due to the stress transfer from the polymer to the nanotubes. This type of reinforcement can be described by micromechanical models of particle reinforced composites, such as the Halpin–Tsai equations [9,30]. Instead at high temperature the observed increase of Young's modulus with the particle fraction was ascribed to the formation of a nanotube network in the softened polymer. Regardless the physical mechanisms of reinforcement it was observed that the presence of MWNTs did not affect the SBM polymer morphology in the conditions of investigation. The

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addition of carbon nanotubes to block copolymers, and to polymers in general, is an effective approach to provide electrical conductivity. Conductive composites can find applications from simple antistatic materials to more sophisticated components of organic electronics. Pieré et al. demonstrate that the addition of MWNTs in SBM terpolymers led to conductive composites [9]. The materials were found to be conductive when the weight fraction of nanotubes was above 1 wt%. Actually the so-called percolation threshold was estimated just below 1 wt%. The same electrical behavior and percolation threshold were observed for different SBM materials [9]. The experimentally measured percolation threshold was consistent with the percolation threshold theoretically expected considering the aspect ratio of the used MWNTs [31,32].

In this work, we study the behavior of single wall carbon nanotubes (SWNTs) or MWNTs stabilized by SBM polymers in two distinct selective solvents. The achieved dispersions are used to produce nanotube-SBM composites by solvent casting. Different morphologies are achieved depending on the solvent. In particular non equilibrium structures can be quenched during solvent evaporation [29]. Surprisingly it is observed in the present work that carbon nanotubes strongly alter the casting behavior. The block copolymers indeed exhibit distinct microstructures in the absence or presence of nanotubes. A related phenomenon was reported for poly(styrene-*b*-isoprene-*b*-styrene) triblock copolymer [28]. However, in this case, the nanotubes were functionalized and a surfactant was added to stabilize the system. Changes of morphologies were ascribed to interactions of the nanotubes with the polystyrene (PS) blocks. Here different solvents are used to modify their selectivity towards the blocks of the terpolymer. In particular mixing solvents that exhibit different rate of evaporation allows the selectivity of the medium to vary during film casting. As a result different morphologies can be obtained. A cylindrical morphology is achieved in the absence of nanotubes or any other additive when a mixture of acetone and cyclohexane is used. This metastable morphology results from the segregation of poly-(methyl methacrylate) (PMMA) blocks in the cores of cylindrical micelles. Mechanical characterizations show that the cylindrical morphology is particularly brittle. By contrast the same polymer forms a stiff and thermodynamically lamellar morphology in presence of unmodified nanotubes. The role of the nanotubes is discussed by considering their capability to act as nucleating agent for the most stable phase of the block copolymer. Indeed the nanotubes onto which polybutadiene (PB) blocks are anchored hinder the segregation of the PMMA blocks as observed in the absence of nanotubes. The capability of nanotubes to alter the morphology of a block copolymer and to lead to large improvements of mechanical properties appears therefore as a new mechanism of mechanical reinforcement beyond the already reported mechanisms of direct reinforcement and network formation. The electrical properties were also found to strongly depend on the solvent used to cast the composites. Systems that are expected to be well above the percolation threshold were found to be insulating if the films were cast from the solvent mixture of acetone and cyclohexane (A/C). By contrast systems with exactly the same final chemical composition are conductive if they are cast from solutions in dichloromethane (DCM). This strong difference is qualitatively discussed by considering the variable degree of ordering in systems cast from distinct solvents.

## 2. Experimental section

Raw block copolymer material was provided by ARKEMA. The product contains approximately 70% wt of triblock SBM copolymer, and 30% wt of SB diblock copolymer impurity. The product was purified following a method developed by Di Cola et al. [33]. Raw

material was put in a 60 wt%/40 wt% mixture of cyclohexane/n-heptane at 90 °C during 2 h. By contrast to SB, SBM molecules are not soluble in this solvent mixture which is a bad solvent for the PMMA block. The non-dissolved fraction which is solely comprised of SBM was collected after centrifugation. The process was repeated twice in order to optimize the purification of the material. Purity was checked using <sup>1</sup>H NMR and exclusion chromatography. The purified terpolymer has the following composition: 32% wt of PS (molar fraction 24%), 36% wt of PB (molar fraction 51%) and 32% wt of PMMA (molar fraction 25%). Its average molecular weight is 64,000 g mol<sup>-1</sup>. Chromatography indicates a polydispersity of 1.4. The glass transition temperature of each block is respectively 96 °C, -86 °C and 144 °C for PS, PB and PMMA. Multiwalled carbon nanotubes were provided by ARKEMA (Graphistrength® C100 batch 6068). The nanotubes are synthesized by a catalyzed chemical vapor deposition process. Their external diameter lies in the 10–15 nm range. Their length exceeds several microns before sonication. Raw nanotubes contain catalytic iron nanoparticles supported by alumina particles. The total weight fraction of impurities is about 15 wt%. The nanotubes were purified via the following treatment: 9 wt% of MWNTs were added to a 15 wt% sulfuric acid aqueous solution. After 5 h under reflux at *T* = 105 °C, the materials were washed with deionized water, filtered and kept in water under the form of a wet-cake that contains 10 wt% of carbon nanotubes. Lastly, this cake was freeze-dried. Freeze-drying leads to a fluffy powder that can be easily processed and mixed with liquid and polymer materials [34]. Thermal gravimetric analyzes showed that the weight fraction of impurities in purified and dried nanotubes was decreased down to 3 wt%. Single walled carbon nanotubes (SWNTs) were provided by Thomas Swan (Elicarb® batch K3772). These tubes are also made by a catalyzed chemical vapor deposition process. They are directly provided as purified materials by the provider.

Nanotube dispersions were prepared as follows for both MWNTs and SWNTs: purified nanotubes were put in a given organic solvent and the solution was sonicated at a power of 20 W during 60 min. A Branson sonifier, model S-250D operating at a 20 kHz and associated to a 13 mm disruptor horn and a 3 mm tapered microtip was used. Two different solvents were used during this study: dichloromethane (DCM) and a mixture of acetone and cyclohexane 50 vol%/50 vol% (A/C). The volume of the sonicated dispersion was 10 mL. Cooling the samples in a water-ice bath prevented the suspension from overheating during sonication. Purified SBM was then added to the dispersion which was again sonicated during 60 min in the same conditions. The amount of added SBM is chosen in order to achieve a desired composite composition after evaporation of the solvent. Table 1 shows the Hildebrand solubility parameters  $\delta$  of the three SBM blocks, compared to that of DCM, acetone and cyclohexane. The Hildebrand value of a solvent mixture can be determined by averaging the Hildebrand values of the individual solvents by volume. The used mixture of acetone and cyclohexane has thus a solubility parameter of about 9.1 (cal cm<sup>3</sup>)<sup>1/2</sup>. The components are compatible when their solubility parameters are similar. By contrast dissimilar values yield limited solubility.

**Table 1**

Hildebrand solubility parameters  $\delta$ , in (cal cm<sup>3</sup>)<sup>1/2</sup> of the PS, PB and PMMA blocks and of DCM, acetone and cyclohexane (values extracted from the Handbook of Polymers).

|          | SBM blocks |     |      | Solvents |         |             |
|----------|------------|-----|------|----------|---------|-------------|
|          | PS         | PB  | PMMA | DCM      | Acetone | Cyclohexane |
| $\delta$ | 9.1        | 8.4 | 9.3  | 9.8      | 9.8     | 8.3         |

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