PS-*b*-PMMA block copolymer as template for rutile TiO_2 nanoparticles

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Abstract

The still increasing interest of block copolymers lies in their ability to self-assemble into various structures such as spheres, hexagonally packed cylinders and lamellae.[1,2] Owing to that capability of block copolymers, they can act as template to design hybrid inorganic/organic materials with well-organized structures.[1,3,4] The combination of self-assembled block copolymer systems with inorganic components as different types of inorganic nanoparticles can lead to highly ordered nanocomposites that have the potential to be used in a wide range of applications due to the optical,[5,6] magnetic[7] or electrical[8-10] properties of the inorganic nanoparticles. The effect of the nanoparticles on the properties of the hybrid inorganic/organic material depends strongly on the localization of the inorganic nanoparticles in the polymeric matrix.[4,11,12]

In this work, an easy method of fabrication of hybrid inorganic/organic nanocomposites based on polystyrene-*block*-polymethyl methacrylate (PS-*b*-PMMA) diblock copolymer as self-assembled matrix modified with different contents of commercial, hydrophobic rutile TiO_2 nanoparticles was employed. Different amounts of TiO_2 nanoparticles (from 0.5 to 4 wt %) were added to the PS-*b*-PMMA block copolymer in order to study the effect of the TiO_2 nanoparticles content on the final properties of TiO_2/PS-*b*-PMMA nanocomposites.

The final morphologies of the neat PS-*b*-PMMA block copolymer and TiO_2/PS-*b*-PMMA nanocomposites and the confinement of the inorganic nanoparticles in one of the blocks of the block copolymer were studied by atomic force microscopy (AFM, Nanoscope IIIa scanning probe microscope, Multimode™, Digital Instruments). Electrical properties of obtained TiO_2/PS-*b*-PMMA nanocomposites were studied using electrostatic force microscopy (EFM). UV-vis absorption spectroscopy (Jasco V-630) and differential scanning calorimetry (Mettler Toledo DSC 822^e) were used for further characterization of the designed nanocomposites.

As is shown in the AFM image corresponding to PS-*b*-PMMA block copolymer (Figure 1), a microphase separation can be easily observed in the self-assembled diblock copolymer. Bright microphase separated areas corresponded to the PS-block phase, whereas dark areas corresponded to PMMA-block phase. The addition of 0.5 wt % of TiO_2 into the block copolymer did not change the final morphology of the nanocomposite if compared with the morphology of neat PS-*b*-PMMA block copolymer. However, when TiO_2 nanoparticles were added to the block copolymer, the size of the microseparated domains increased confirming the confinement between TiO_2 nanoparticles and PS-block.

The introduction of more than 0.5 wt % of TiO_2 nanoparticles resulted in an increase in the size of PS-block domains, which led to a significant change on the morphology from worm-like to cylindrical structure. This confirmed the location of TiO_2 nanoparticles in the PS-block of the PS-*b*-PMMA block copolymer. The addition of 3 and 4 wt % of TiO_2 nanoparticles into PS-*b*-PMMA matrix deteriorated the final morphology of the systems probably due to the presence of some aggregates of inorganic nanoparticles. However, all investigated nanocomposites showed good dispersion of TiO_2 nanoparticles in the PS-*b*-PMMA block copolymer matrix independent of the content of the inorganic part.

Thermal behavior of the designed materials studied by DSC confirmed that TiO_2 nanoparticles were located in the microseparated PS-block domains. UV-vis spectroscopy and EFM measurements indicated that TiO_2 nanoparticles transferred their optical and electrical properties to the designed TiO_2/PS-*b*-PMMA nanocomposites.

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Figures

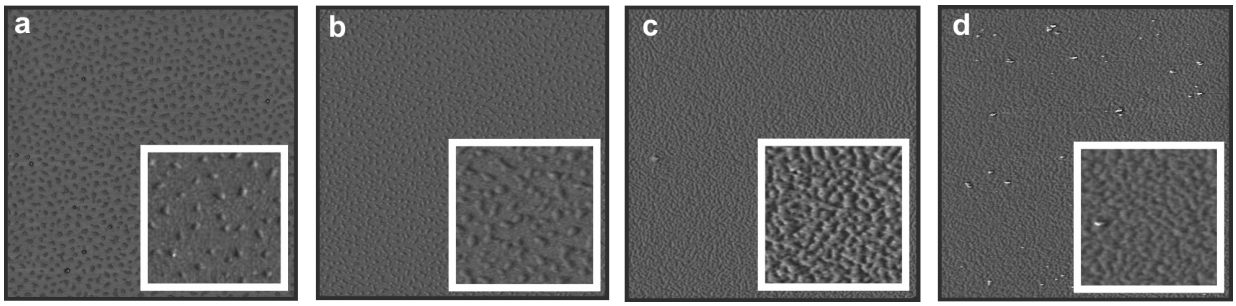

Figure 1. AFM phase images (5µm x 5µm) of a) neat PS-*b*-PMMA block copolymer and TiO_2/PS-*b*-PMMA nanocomposites containing b) 0.5, c) 1 and d) 3 wt % of rutile TiO_2 nanoparticles. The insets correspond to higher magnification AFM images (1µm x 1µm).