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Nanocomposites of polystyrene-*b*-polyisoprene copolymer with layered silicates and carbon nanotubes

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Abstract

Nanocomposites of polystyrene-*b*-polyisoprene (PS-*b*-PI) copolymer with layered-smectite clays (organically modified montmorillonite) and nanostructured clay-carbon nanotube hybrids were prepared. The diblock copolymer was synthesized by anionic polymerization using high-vacuum techniques and was molecularly characterized by size exclusion chromatography. Carbon nanotubes were developed on clay-supported nickel nanoparticles by the CCVD method. Nanotubes attached on the clay platelets were then chemically modified to create ester groups on their surfaces. PS-*b*-PI nanocomposites at various polymer to reinforcement loadings were prepared by solution intercalation. The final nanocomposites were characterized by powder X-ray diffraction, FT-IR spectroscopy, thermal analysis, and scanning electron microscopy. The experiments complemented with viscometry measurements reveal the successful incorporation of the reinforcements in the polymer mass.

Keywords: Clay-polymer nanocomposites; Montmorillonite; Carbon nanotubes; Diblock copolymer; PS-*b*-PI

1. Introduction

In polymer nanocomposite research, the basic aim is to enhance several properties of polymeric components using molecular or nanoscale reinforcements. Polymers have been filled with several synthetic and/or natural compounds in order to increase tensile strength, modulus, heat resistance, impact resistance and electrical conductivity [1]. One area of research has focused on using layered-smectite clays as the reinforcing part of the matrix [1–3]. The presence of two dimensional platelike silicate layers in the matrix of a polymer was of major interest due to the significant gains in thermal

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stability [4], mechanical [5,6] and barrier properties of the resulting nanocomposites [7,8]. Depending on the strength of interfacial interactions between the polymer matrix and the layered silicate (modified or not), three different types of nanocomposites are thermodynamically achievable: (1) conventional composites, where packages of silicate layers, keep their stacking, creating a conventional phase separated composite (microcomposite), (2) intercalated nanocomposites, where the polymer chains are intercalated between the silicate layers, therefore increasing their gallery height but maintaining their layered stacking, resulting in a well ordered multilayer with alternating polymer/silicate layers, (3) exfoliated nanocomposites, in which the individual clay layers lose their stacking and are exfoliated and dispersed in the continuous polymeric matrix [9]. Typical preparation methods of these nanocomposites include solution, melt intercalation, and in situ polymerization [9]. Solution intercalation has been very effective in incorporating exfoliated clays into polymers[10].

Equally promising reinforcement, for the creation of polymer nanocomposites, are carbon nanotubes. Since their discovery [11], carbon nanotubes (CNTs) have attracted unlimited attention due to their unique properties such as extremely high mechanical strength, high electrical and thermal conductivity [12,13]. This superior properties offer many opportunities for new composites. In this field of carbon nanotubes-based composites belong polymer/CNT composites, which combine exceptional mechanical, surface and multi-functional properties and strong interactions with the matrix resulting from the nano-scale microstructure and the large interfacial area [14,15]. However, CNTs are generally insoluble in common solvents and polymers, easy to agglomerate, bundle together and entangle, leading to many defect sites in the composites [16]. Several techniques have been applied to achieve homogeneous dispersion of CNTs in the polymer matrices such as: optimum physical blending, in situ polymerization and chemical functionalization [17]. Side-wall chemical functionalization is one of the most effective techniques for homogeneous dispersion of CNT in polymer matrices since strong interface adhesion is achieved between the functionalized carbon nanotubes and the surrounding polymer chains [18–22].

In addition, carbon nanotubes rooted on smectite layers are particularly attractive for polymer reinforcing applications. One would expect that the combined action of clay-carbon nanotubes in polymer matrixes would provide outstanding functionalities to the resulting composite materials. Towards this aim, Zhang et al. [23] demonstrated that the incorporation of CNT–clay hybrid system into nylon-6 by simple melt blending lead to exfoliated nanocomposites with excellent mechanical properties. Compared with neat polymer, the tensile modulus and the tensile strength of the composite were greatly improved, by about 290% and 150% respectively, by the incorporation of only 1 wt% CNT–clay hybrid reinforcement.

In the present study, we developed nanocomposites of polystyrene-*b*-polyisoprene with organically modified montmorillonite and hybrid systems of clays with functionalized carbon nanotubes at various polymer to reinforcement loadings. The block copolymer used in this research work was chosen to be a diblock copolymer of the PS-*b*-PI type, since such materials have been extensively studied and their molecular and morphological behavior is widely known [24,25]. The resulting nanocomposites were characterized by a combination of powder X-ray diffraction, FT-IR spectroscopy, thermal analysis, size exclusion chromatography, scanning electron microscopy, and viscometry measurements.

2. Experimental

2.1. Synthesis of diblock copolymer (PS-b-PI)

The diblock was prepared by anionic polymerization using high-vacuum techniques in evacuated, *n*-BuLi-washed, benzene-rinsed glass vessels. The purification of styrene (Merck), isoprene (Fluka), and benzene (Merck) to the standards required for anionic polymerization have been described elsewhere [26,27]. Additions were made through break seals and removals were accomplished through heat sealing of constrictions. *sec*-BuLi, prepared in vacuum from *sec*-butyl chloride and a lithium dispersion, was the initiator.

2.2. Organic modified clay (C_{16}-SWy)

The clay used in this work was a natural Wyoming montmorillonite (SWy-1) obtained from the Source Clay Minerals Repository, University of Missouri, Columbia with a cation-exchange capacity (CEC) of 76.4 meq/100 g clay. The clay was fractionated to <2 μm by gravity sedimentation and purified by standard methods in clay science [28].