



Macromolecular Nanotechnology

Ionic liquid tailored interfaces in halloysite nanotube/heterophasic ethylene–propylene copolymer nanocomposites with enhanced mechanical properties



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ABSTRACT

In this study, imidazolium ionic liquids (IL) were investigated as novel compatibilizers to improve the dispersion of halloysite nanotubes (HNT) in heterophasic ethylene-propylene copolymer (EPP) matrix to enhance the mechanical properties of the EPP/HNT nanocomposites prepared by melt-blending approach. The results highlight that the dispersion of HNT nanotubes and consequently the mechanical properties of nanocomposites depends on the surface modification of HNT with IL, which in turn strongly depends on the chemical structure of IL, i.e. anion and cation N-alkyl chain length, as well as on the adsorption conditions, e.g. solvent polarity and IL concentration adopted for the modification of HNT surface. In details the nanocomposites with HNT modified by IL (**m-HNT**) exhibited a more homogeneous HNT dispersion above all when the IL surface modification was conducted in less polar solvents as dichloromethane. Furthermore, the IL allowed to tuning the stiffness and the toughness with a right compromise. The EPP/**m-HNT** nanocomposites with bis(trifluoromethylsulfonyl)imide [NTf₂] anion and 1-methyl-3-*n*-octadecylimidazolium cation-based IL, exhibited an improvement of elastic modulus of about 34% with respect to the pristine polymer, without loss of the impact properties at 23 °C. The morphological and mechanical results confirm the IL acted effectively as compatibilizer, improving both the interfacial interaction and HNT dispersion into the EPP matrix.

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1. Introduction

Polypropylene (PP) is a thermoplastic polymer widely applied because of its versatile properties, including low density and cost, good processability and recyclability [1]. However, its low fracture toughness currently represents a limitation for some specific applications. In this scenario, the heterophasic ethylene-propylene copolymers (EPP) consisting of a semi-crystalline isotactic PP homopolymer matrix with a dispersed soft ethylene-propylene rubber (EPR) phase [2] represent a valid approach to overcome some PP limitations and expand its range of applications. In fact, the elastomeric phase, when

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opportunistically dispersed in the polypropylene matrix improves the toughness and low-temperature impact resistance. Unfortunately, the elastomeric component has a detrimental effect on the stiffness of the material [3]. Thus, in order to achieve the desired balance between toughness and stiffness, small amounts of rigid nanoparticles have been used to modify the polymeric matrix [4].

Polymer nanocomposites have been extensively studied due to the premise of better mechanical, electrical and thermal properties compared to pure polymer [5,6]. In general, the key factors for obtaining the enhancement of performances of polymer nanocomposites are both the homogeneous dispersion and the strong interfacial adhesion between polymeric matrix and nanofiller [7]. Nevertheless, the chemical affinity between inorganic fillers of hydrophilic nature and nonpolar hydrophobic polymers is very low and it can be improved through a preliminary modification of the nanofiller surface [8,9]. Several approaches have been proposed for the compatibilization of the filler that consists of chemical functionalization with suitable organic moieties [10], silylation [11], self-assembling or adsorption of ionic liquids [12].

Among the broad variety of inorganic fillers commonly used for the preparation of polymer nanocomposites, halloysite nanotubes (HNT) have received much attention in the last years [13] since it is a natural aluminosilicate and cheap filler, and it exhibits the 1D shape that, in contrast to the widely used 2D phyllosilicate materials, offers interesting opportunities in the designing of the nanocomposites. In fact, the HNT have predominantly hollow tubular structures and their dimensions are in the range of 1–15 μm for lengths, 10–30 nm for inner diameters and 50–70 nm for outer diameters [14]. The internal surface of the HNT consists of aluminol groups, whereas the outer surface is composed of silicate with a few silanols/aluminols groups exposed at the edges and defects of the sheets [15]. Due to the presence of these polar groups, the organofunctionalization of hydrophilic HNT surfaces through the utilization of well selected IL represents a promising strategy to improve the dispersion and interfacial interaction between HNT nanoparticles and apolar polymeric matrix [13].

The use of IL as dispersant of clays, i.e. montmorillonite into polymer matrix has already been widely studied [16–19]. Livi et al. [20] demonstrated that ionic liquids based on phosphonium and imidazolium salts behave as a compatibilizer helping the dispersion into the PE matrix and improving the clay/matrix interface quality. They also observed that the nature of the anion plays a key role on the properties of both the modified montmorillonites and the nanocomposites [21].

On the other hand, the modification of HNT surface with IL [22] has been explored only in a few studies to improve dispersion in polymer matrices, thus increasing the final properties of the resultant polymer nanocomposites [23,24]. Lei et al. [25] investigated the effect on the mechanical properties of HNT modification with 1-methylimidazolium mercaptopropionate and bis (1-methylimidazolium) mercaptosuccinate as interfacial modifiers in the production of styrene butadiene rubber/HNT nanocomposites. The presence of these modifiers promoted a more uniform nanoparticle dispersion that resulted in a significant improvement of mechanical properties. Soheilmooghaddam and Wahit [26] used 1-*n*-butyl-3-methylimidazolium chloride for the preparation of regenerated cellulose/HNT nanocomposites with significantly improved thermal stabilities and mechanical properties. The enhancement of properties was attributed to the increased hydrogen bonding interactions between cellulose and HNT.

In this work, three complementary imidazolium IL were investigated as surface modifiers of HNT for the preparation of compatibilized EPP/HNT nanocomposites. The nanocomposites were prepared through a two-steps procedure: (a) modification of HNT nanotubes with the IL by surface adsorption and (b) melt-blending of IL modified HNT with EPP by means of a two screws extruder. The correlation between chemical structure of IL and thermal and mechanical performances of the final nanocomposites was elucidated through a comprehensive chemical, morphological and mechanical characterization of the nanocomposites comprising both pristine HNT and IL modified HNTs.

2. Experimental

2.1. Materials

Braskem S.A. (Brazil) provided EPP with a melt flow index of 27.7 g/10 min (230 °C/2.16 kg) and total ethylene content of approximately 14 wt.%. HNT was acquired from Sigma-Aldrich. The IL (Table 1) 1-*n*-decyl-3-methylimidazolium tetrafluoroborate [C_{10}MIm][BF_4], 1-*n*-decyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C_{10}MIm][NTf_2] and 1-methyl-3-*n*-octadecylimidazolium bis(trifluoromethylsulfonyl)imide [C_{18}MIm][NTf_2] were purchased from Ionic Liquids Technologies GmbH.

2.2. Surface modification of HNT with IL

Approximately 20 g of HNT were dispersed in 120 mL of dry solvent (acetone or dichloromethane) in presence of 3.2 mmol or 6.4 mmol of IL. The suspension was refluxed under an inert argon atmosphere at 60 °C for 20 h and constant stirring. The solid sample was collected in a Buchner funnel, filtered and washed with dry solvent (acetone or dichloromethane) to remove non-adhered IL. Finally, the modified HNT (**m-HNT**) was dried at room temperature for 24 h and, subsequently, under vacuum at 70 °C until a constant weight was reached. The surface modification conditions, i.e. solvent and IL content adopted in the production of the **m-HNT** as well as their respective sample codes are summarized in Table 2.

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