



Improving toughness of ultra-high molecular weight polyethylene with ionic liquid modified carbon nanofiber



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ABSTRACT

Ionic liquids (ILs) with long alkyl substituted groups, including 1-docosanyl-3-methylimidazolium bromide (IL-1) and 1-docosanyl-3-methylimidazolium hexafluorophosphate (IL-2), were synthesized and used to modify the surface of carbon nanofibers (CNF). The nanocomposite film prepared by solution-blending of ionic liquid modified CNF (i-CNF) and ultrahigh molecular weight polyethylene (UHMWPE) displayed better toughness when compared with pure UHMWPE even at very low concentrations (e.g. 0.4 wt%). The effect of ionic liquids on the elongation-to-break ratio of this nanocomposite system was investigated. The ionic liquid with hexafluorophosphate as the anion was more efficient to increase the toughness of UHMWPE due to the improved compatibility of IL with UHMWPE in the polymer matrix than that of the bromide. The rheological behavior of molten nanocomposites revealed that the storage modulus and the complex viscosity decreased with increasing ionic liquid content in the high frequency region. However, a reverse trend was observed when the frequency was less than 0.05 s^{-1} . *In-situ* monitoring in the change of crystallinity of the nanocomposite during tensile deformation suggested a mechanism of sliding between UHMWPE crystal regions and the surface of carbon nanofibers.

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1. Introduction

Ionic liquids, as a new generation of fluid media, have many special properties, such as negligible volatility, non-flammability, high thermal stability, and variable miscibility with organic or inorganic compounds. Thus, they have been served as solvents in synthesis and separation, lubricants in engineering, and additives in materials science [1–3]. The chemical structure of an ionic liquid, i.e., the presence of cations and anions, can have a dramatic effect on its solvent properties. More specifically, the physical and chemical properties can be designed and adjusted by modifying the cationic or anionic properties with functional groups [4]. One example is that by changing the substituted alkyl group of the cation or by changing the nature of the anion, the solubility behavior of the ionic liquid may be tuned. Increasing the length of a substituted group on the cation of an ionic liquid may improve its compatibility with non-polar compounds [5].

Carbon nanofibers (CNF) or carbon nanotube (CNT) is another interesting material due to its good mechanical, thermal and electrical properties [6]. There is a graphite layered structure of CNF (or CNT) that can contain π -electron conjugated carbon atoms. It has been conjectured that the surface of CNF can interact with a poor electronic conjugated plane by π - π interactions [7–9]. An important application of CNF is its ability to improve the toughness of polymer materials [10–13]. However, this ability depends substantially on the CNF surface properties and how CNF is being dispersed in the polymer matrix [14]. Several chemical and physical methods were employed to improve the compatibility between CNF and polymers. For chemical modifications, functional groups were covalently bonded on the surface of CNF. Its advantage is obvious, i.e., the properties of modified CNF can be modified by introducing the desired functional groups. However, modification reactions can be complex and the surface of CNF has to be disrupted. Moreover, modifications tend to decrease mechanical, thermal and electronic properties of CNF [15,16]. For the physical modifications, chemical compounds or polymers can be attached onto the surface of CNF by physical adsorption. For example, pristine CNF could be dispersed in water with the help of surfactants. The interaction between the alkyl chain and the surface of CNF may promote the dispersion of CNF [17–19]. A pioneering work focusing on the interactions between CNF (or CFT) and ionic liquids was

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reported by Aida et al. [8]. Single-walled nanotubes (SWNTs) could form a gel with ionic liquids by the so-called “cation– π ” interaction between the surface of SWNT and the imidazolium ion. The orientation of an ionic polymer, instead of an ionic liquid, could dramatically improve the mechanical property and electrical conductivity of the material. Gilman et al. melt-extruded the multi-walled nanotube (MWNT) with tri-alkyl imidazolium salts into polystyrene [20]. A better dispersion of MWNT in polystyrene was found with the addition of ionic liquids. Furthermore, by using X-ray diffraction (XRD) and infrared (IR), they proposed a physical interaction between MWNT and the long aliphatic chain of an ionic liquid.

Rastogi et al. used the nanofiller of sodium dodecylbenzene sulfonate (SDS) modified SWNTs with the as-synthesized UHMWPE and observed a shish-kebab structure during the drawing process. An unusual rheological behavior of the nanocomposites with different amounts of SWNTs was also studied [21]. However, the surfactant-modified CNT was not stable in thermal or acidic processes, with water being the solvent/suspending medium. Pristine MWNT and high density polyethylene (HDPE) were extruded at 150 °C, where the hierarchical structure of nano-hybrid shish-kebab was formed in the injection-molded composite [22]. In our previous work, 0.6 wt% of IL-1 (see Scheme 1) was used as a plasticizer to improve the stretching property of polyethylene, where a 2–3 times increase of elongation-to-break ratio was observed during the tensile performance. The alkyl-substituted group of IL-1 might interact with polyethylene chains and act like a solvent, which could improve the overall chain mobility during the stretching process [23].

In this study, we demonstrate the use of ionic liquids having the same long alkyl substituted group but different anionic groups and their stable complexes with CNF in order to improve the processing ability, mechanical property (i.e., elongation and toughness) and improved ability to introduce functional groups for the ultra-high molecular weight polyethylene (UHMWPE). The UHMWPE material is well known to be difficult to undergo melt processing, to be highly inert (not easy to color) and to have a relatively low elongation-to-break ratio due to more extensive chain entanglements. We showed that the cationic part of an ionic liquid could form strong π – π interactions with the para-arene surface of carbon nanofibers. Consequently, the surface-modified IL-containing carbon nanofibers could be easily dispersed in the UHMWPE matrix, with significant improvements in toughness of the UHMWPE nanocomposite. It is expected that polyolefin nanocomposites containing surface modified carbon nanofillers can be used to create a new class of functional fibers and films.

2. Experimental

2.1. Materials

1-Methylimidazole, 1-bromodocosane and hexafluorophosphoric acid (60% water solution) were purchased from Aldrich and used as received. The UHMWPE powders were obtained from Basell, USA, having a molecular weight of about 6,000,000 g/mol. The carbon nanofiber (CNF, PR-24-HHT) was purchased from Pyrograf Products, Inc. The typical morphology of the as-received CNFs exhibited an

average diameter of 70 nm and a length of 50–100 μm . It was found that the as-received CNF samples were fairly clean. Therefore, no additional purification procedures were carried out.

2.2. Synthesis of 1-docosanyl-3-methylimidazolium bromide (IL-1) ionic liquid

The new ionic liquids, IL-1 and IL-2 were synthesized using the following procedures and were characterized by ^1H NMR. The synthetic routes are shown in Scheme 1.

Typically, 2.0 g (0.025 mol) of 1-methylimidazole and 10.7 g (0.026 mol) of 1-bromodocosane were dissolved in 20 mL of acetonitrile. The mixture was refluxed at 85 °C for 24 h, and subsequently cooled down to room temperature. The resulting sample (cake-like) was filtered and washed with ethyl ether three times. The final product: 1-docosanyl-3-methylimidazolium bromide was obtained as a white powder after being dried in a vacuum oven. The yield based on this procedure was 81.4%. The spectra of ^1H NMR (CDCl_3 as the solvent, δ , ppm) were: 10.713 (N–CH–N, s, 1H), 7.274 (N–CH–CH, s, 1H), 7.218 (N–CH–CH, s, 1H), 4.310 (N–CH₂, t, 2H), 4.130 (N–CH₃, s, 3H), 1.918 (N–CH₂–CH₂, m, 2H), 1.248 (N–CH₂–CH₂–(CH₂)₁₉, m, 38H), 0.874 (CH₃, t, 3H).

2.3. Synthesis of 1-docosanyl-3-methylimidazolium hexafluorophosphate (IL-2) ionic liquid

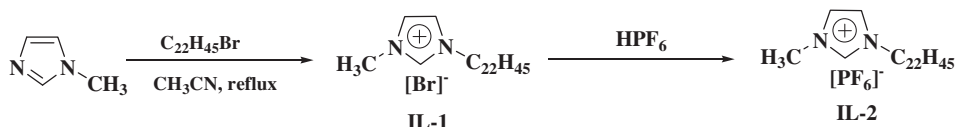
4.0 g (0.008 mol) of 1-docosanyl-3-methylimidazolium bromides were dispersed in 150 mL of water, and then, 2.0 mL (0.014 mol) of hexafluorophosphoric acid aqueous solution was drop-wise added slowly into the suspension under continuous stirring. The mixture was stirred for 24 h at room temperature. CH_2Cl_2 was subsequently added to form a two-layer mixture, allowing the removal of the aqueous layer. After filtration, the white solid was washed with water until neutral. The powdery product was dried in a vacuum oven. The yield based on this procedure was 95%. The spectra of ^1H NMR (CDCl_3 as the solvent, δ , ppm) were 8.541 (N–CH–N, s, 1H), 7.264 (N–CH–CH, s, 1H), 7.228 (N–CH–CH, s, 1H), 4.135 (N–CH₂, t, 2H), 3.920 (N–CH₃, s, 3H), 1.860 (N–CH₂–CH₂, m, 2H), 1.248 (N–CH₂–CH₂–(CH₂)₁₉, m, 38H), 0.875 (CH₃, t, 3H).

2.4. Physical modification of CNF with ionic liquid to produce i-CNF

A proportional mixture of IL-1 (or IL-2) and CNF was prepared in 2.0 mL of decalin, followed by sonicating it at 70 °C for 1 h. Then, the mixture was filtered and washed three times with a large amount of decalin. The final product i-CNF was dried under vacuum for 24 h. A schematic representation of the π -stacking arrangement of IL-1 (or IL-2) head on MWNT surface is shown as Scheme 2.

2.5. Preparation of nanocomposite film based on i-CNF and UHMWPE

The i-CNF sample was mixed with UHMWPE in decalin. The mixture was heated to 140 °C at 0.2 °C/min under stirring conditions and kept at 140 °C for 1 h. After having cooled down to room temperature, the nanocomposite sample was separated by filtration and dried in a vacuum oven at 60 °C to remove most of the



Scheme 1. Synthesis of ionic liquids IL-1 and IL-2.

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