European Polymer Journal 49 (2013) 3770–3777

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Macromolecular Nanotechnology

Polymerized ionic liquid functionalized multi-walled carbon nanotubes/polyetherimide composites

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ARTICLE INFO

Article history:
Received 19 February 2013
Received in revised form 16 July 2013
Accepted 4 August 2013
Available online 19 August 2013

Keywords:
Carbon nanotubes
Polymer–matrix composites
Ionic liquids
polyetherimide

ABSTRACT

Thin polyetherimide (PEI) films containing 0.1–3 wt.% multi-walled carbon nanotubes (MWCNTs), have been prepared from three types of MWCNTs, namely pristine, oxidized and polymerized ionic liquid (PIL) functionalized CNTs. Oxidized and PIL functionalized CNTs (CNT–PIL) showed better dispersion in the matrix compared to pristine CNTs. For CNT–PIL, alignment of CNTs has been observed in the matrix. Regardless of the type of CNTs, their incorporation led to an increased thermal stability of the polymer matrix. Dynamic mechanical analysis showed that storage modulus increased by up to 25% (3 wt.% CNT–PIL) and an increase in the height of the damping peaks ($\tan\delta$). The addition of CNTs did not have any significant influence on the tensile properties and T_g of the polymer, and the electrical conductivity did not decrease in the case of modified CNTs.

1. Introduction

Carbon nanotubes (CNTs) are ideal candidates as reinforcing and electrically conducting fillers for high strength and light-weight multifunctional polymer composites. However, there are several challenges for developing such composites, including homogeneous dispersion of CNTs in the polymeric matrix and strong interfacial adhesion [1]. In that context, many efforts have been devoted during the last two decades to surface modification of CNTs using covalent or non-covalent approaches [2]. The non-covalent route is particularly attractive due to its ease of operation and to the fact that it does not alter CNT structure. Ionic liquids (ILs) can provide an easy way to prepare CNT–IL hybrids, owing to cation-π, π–π or van der Waals interactions [3]. These hybrids can be further processed to prepare polymer composites using solution- or melt-processing methods. Due to their high-thermal stability, these hybrids can withstand the high temperatures used during the processing of polymers, and their solubility can be tuned by selecting the appropriate IL counter anion. Polymerized ionic liquids (PILs), have recently attracted attention as a new class of CNT modifiers. The thin PIL layer on the CNT surface can provide stable binding sites for polymer matrices to attach. The number of studies devoted to polymer composites filled with PIL-functionalized CNTs is still very limited [4]. Polyetherimide (PEI) is a high-performance thermoplastic, which has extensive uses in many fields such as medicine, electronics, automotive and aerospace. The extremely high viscosity of this polymer makes the nanocomposite preparation by melt-processing challenging [5]. Solution-based processing methods offer advantages of lower viscosities, which facilitate dispersion, provided highly stable dispersions of CNTs are used. Different surface modification approaches, including acid-oxidation and use of surfactants, have been applied to CNTs in order to obtain stable dispersions in suitable solvents for

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http://dx.doi.org/10.1016/j.eurpolymj.2013.08.007

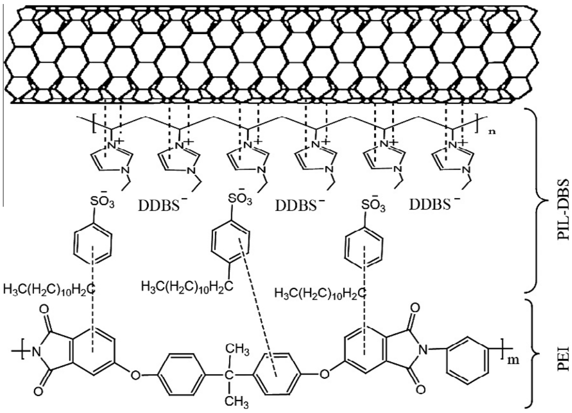

Fig. 1. Illustration of the possible non-covalent interaction between poly([VEIM]DBS) functionalized CNTs and PEI.

PEI processing [6–8]. In these studies, thermal stabilities of the composites improved significantly while improvements in mechanical properties are not remarkable; and in some cases [7,8] negative effects of CNT addition have been observed on the tensile strength. We anticipated that coating a thin film of PIL on CNT surface could result in a better adhesion between CNT and the PEI matrix. The PIL layer could act as a linker between the CNT and the matrix by possible π–π stacking interactions (Fig. 1). We report herein the introduction of multi-walled CNTs (MWCNTs) non-covalently functionalized with poly(1-vinyl-3-ethyl imidazolium) dodecylbenzene sulfonate (poly[VEIM]DBS) into PEI matrix and its effect on the morphological, mechanical, thermal and electrical properties of the composites.

2. Experimental details

2.1. Materials

Polyetherimide in pellet form was supplied by SABIC Innovative Plastics TM. Graphistrength® MWCNTs (average number of walls 5–15, length 0.1–10 µm, diameter 10–15 nm, purity >90%) were supplied by Arkema, France. Sodium dodecylbenzene sulfonate was purchased from Aldrich. Oxidized CNTs were prepared from pristine CNTs by: (i) purification in boiling concentrated H_2SO_4 followed by filtration and washing with water and (ii) refluxing purified CNTs in concentrated nitric acid (69%) for 3 h [9,10]. The surface acidic group concentration on oxidized CNTs was estimated to be 0.234 mmol/g CNT by acid–base titration [11]. Synthesis and polymerization of 1-vinyl-3-ethyl-imidazolium bromide ([VEIM]Br) were carried out as reported in literature [12]. Poly(1-vinyl-3-ethyl-imidazolium dodecylbenzene sulfonate) (poly[VEIM]DBS) was prepared using an anion exchange method previously reported [13]. Their structures were confirmed by ^1H NMR analysis (Fig. S1 in Supplementary Data (SD)). The glass transition temperatures (T_g) of poly[VEIM]Br and poly[VEIM]DBS were found to be 229 °C and 114 °C, respectively, as determined by DSC (20 °C min^{-1}).

2.2. Preparation of PIL functionalized CNTs

The non-covalent functionalization of CNTs was carried out using the following procedure: pristine CNTs (4 g) were added to a solution of [VEIM]Br (73 g) in ethanol (100 mL). After sonication with an ultrasonic bath cleaner for 1 h, azobis(isobutyronitrile) (AIBN, 1.5 g) was added to the mixture, which was stirred vigorously at 65 °C for 24 h under a N_2 atmosphere. The resulted CNTs were washed several times with distilled water in order to thoroughly remove physically adsorbed polymer and unreacted monomer from their surface. To prepare CNT–poly[VEIM]DBS, 500 mg of CNT–poly[VEIM]Br were added to 75 mL of distilled water, and the solution was ultrasonicated at 25% amplitude for 10 min. Then, a solution of sodium dodecylbenzene sulfonate (500 mg) in distilled water (25 mL) was added dropwise to the CNT suspension. The dispersion was stirred overnight and the resulted CNTs were thoroughly washed with distilled water and dried at 115 °C for 3 days.

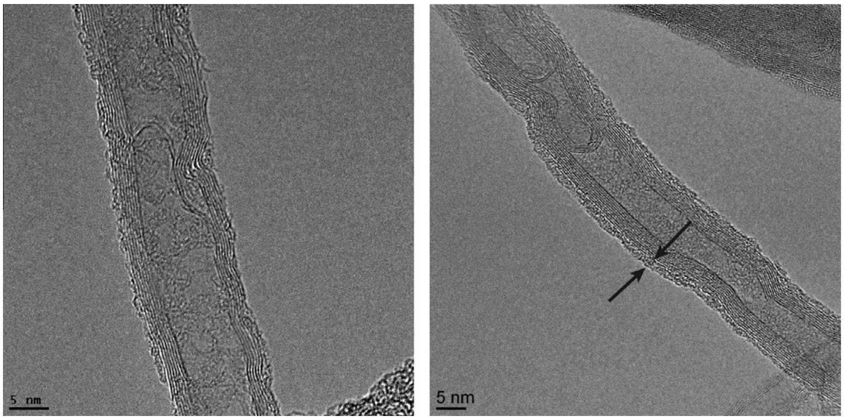

Fig. 2. TEM micrograph of pristine CNT used in this study (left) and CNT–poly[VEIM]DBS (right).