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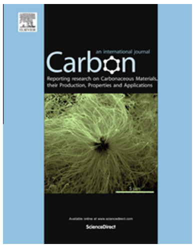

Improved strength and toughness of polyketone composites using extremely small amount of polyamide 6 grafted graphene oxides

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ABSTRACT

Polyketone (PK) composites were prepared by a solution casting method using 1,1,1,3,3,3-hexafluoro-2-propanol as a solvent and polyamide 6 grafted graphene oxides (PA 6-GOs) as filler materials. PA 6-GOs were obtained by in situ polymerization of ε-caprolactam using GOs having different amounts of oxygen functional groups. The PK composites containing only an extremely small amount of the PA 6-GOs (0.01 wt%) showed much improved mechanical properties compared to PK. This could be ascribed to the homogeneous dispersion of the graphene-based filler materials in the polymer and specific interactions such as dipole–dipole interactions and/or the hydrogen bonds between the fillers and the polymer matrix. For example, when 0.01 wt% of PA 6-GO having less oxygen functional groups was used as a filler for the composite, the tensile strength, Young's modulus, and elongation at break of the composite increased by 35%, 26%, and 76%, respectively. When 0.01 wt% of PA 6-GO having larger content of oxygen functional groups and PA 6 was used, Young's modulus decreased, while the tensile strength increased by 37%, and the elongation at break increased tremendously by 100 times, indicating that very tough polymeric materials could be prepared using a very small amount of the graphene-based fillers.

1. Introduction

Polymer composites containing nano-sized filler materials have been widely studied for scientific and industrial purposes over the past few decades because they can have much improved performance [1–5]. The remarkably improved mechanical and thermal properties of the polymer composites have been known to be closely related to the interface structures and good interfacial interactions between nano-sized fillers and a polymer matrix [6–8]. Since the interfacial areas between the fillers and the polymer matrix are very large, a significant load transfer across the interface is possible, if there are large interactive forces between the fillers and the polymers [5]. Normally, the interaction between the polymer

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matrix and the fillers in the polymer composites could be increased by modification of the surfaces of the fillers.

Carbon nanomaterials have been widely applied to improve the performance of polymer composites, because the modified carbon nanomaterials can control the interactive forces between the fillers and the polymer matrix [9–13]. Recently, graphene, a single layered two-dimensional atomic carbon sheet, has been widely applied as a filler due to its extraordinary reinforcing efficiency of the electronic, thermal, and mechanical properties [11,12]. Particularly, much improved composite performance was observed by adding only a very small amount of graphene-based materials (about 0.1–1.0 wt%) to the polymers, because graphene has extremely large surface area and specific interactions between the graphene and the polymer can be expected [14–17]. Therefore, graphene-based polymer composites have been considered as very promising materials for engineering plastic applications [2,11,12,18]. For the polymer composites to have advanced properties, homogeneous dispersion of fillers in the polymer matrix and compatibility between fillers and polymers are strongly needed. When graphene is modified properly, the compatibility with the polymer matrix could be improved, producing polymer composites materials having uniformly-dispersed graphenes [18,19]. In addition, it was possible to control the interface parameters, such as grafting density, grafting chain length, and functional groups on the graphene surface.

Aliphatic polyketones (PK) are alternating olefin/carbon monoxide (CO) copolymers prepared using ethylene and/or propylene with CO as a co-monomer [20,21]. PK could be considered as high-performance thermoplastic polymers because they have good chemical resistance, mechanical properties, and low gas permeability [22]. Accordingly, there has been of great interest in a wide range of possible applications of the PK polymers, while they have not been introduced to the market. We strongly believe that further works on the synthesis, rheology, and processing of PK are necessary to use them in practical applications [23–30]. In particular, the introduction of graphene-based materials as fillers in a PK matrix could produce composite materials with integrated properties for possible applications.

In this work, we tried to prepare PK composites using graphene-based nanofillers. Graphene oxide (GO) having various oxygen functional groups, such as carboxylic acid, hydroxyl, epoxide, and ketone groups were used because they can interact with the ketone groups in PK. However, we could not make any PK composite materials with improved mechanical and physical properties using graphene or GO, because they are not miscible with PK; only phase-separated domains were observed from the PK composite films that contained the graphene or GO. To impart miscibility to GO with PK, polyamide 6 (PA 6) was attached to GO, because PA 6 is known to be miscible with PK [31–33]. It was not possible to attach PK on GO, because PK is prepared by coordination polymerization using a catalyst composed of metallic complexes [20,21]. Surprisingly, we found that the addition of only a very small amount of GO with PA 6, such as 0.01 wt%, to PK improved the mechanical properties of PK significantly.

2. Experimental

2.1. Materials

Polyketone (PK) was kindly supplied by Hyosung (Korea) and used as received. The glass transition and melting temperatures are 10 and 220 °C, respectively. Melt index is 60 g/10 min. The PK used in this study is an alternating copolymer prepared by ethylene, propylene and carbon monoxide as monomers; the molar contents of 1-oxo-trimethylene and 1-oxo-2-methyltrimethylene are 94 and 6 mol%, respectively (Fig. 1a). Graphite powders were received from BASF (Germany). Phosphorus(V) oxide (P_2O_5), sodium nitrate ($NaNO_3$), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2), ε-caprolactam (CL), 6-aminocaproic acid, and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), all from aldrich, were used as received. All other reagents and solvents were used as received from standard vendors.

2.2. Preparation of GO

GO was synthesized from graphite powders through the modified Hummers method [34]. 1.0 g of graphite powders and 0.5 g of P_2O_5 were added to 6.0 mL of 98% H_2SO_4. The mixture was kept at 85 °C for 5 h. Deionized water (200 mL) was added to the mixture and left overnight. Then the mixture was filtered through anode aluminum oxide (AAO) membrane filter with 0.2 μm pore size and washed with deionized water continuously. The solid was dried in vacuum at 35 °C overnight. 1.0 g of the dried product (pre-oxidized graphite) and 0.5 g of $NaNO_3$ were added to 23 mL of 98% H_2SO_4 in an ice bath and kept at this temperature for 40 min without stirring. Then 3.0 g of $KMnO_4$ was slowly added with stirring to keep the temperature below 10 °C. The mixture was heated to 35 °C and stirred for 2 h and then 140 mL of deionized water and 10 mL of 30% H_2O_2 were added. Then the mixture was centrifuged (10,000 rpm for 30 min) and the supernatant decanted. The solid was washed with water and centrifugation with 250 mL of 10% HCl at least 3 times until the pH was 7. After vacuum filtration the solid was dried overnight at 35 °C. The resulting solid was called GO 1 (less oxidized GO). GO 2 (more oxidized GO) was obtained using the same procedure except the amount of $KMnO_4$ (6.0 g) and the reaction time (18 h).

2.3. Preparation of PA 6 grafted GO

PA 6 grafted GO (PA 6-GO) was obtained using GO 1 as follows: 4.5 g of ε-caprolactam (CL) and 50 mg of GO 1 were added into 10 mL of anhydrous DMF and the mixture was sonicated for 1 h. Then 0.5 g of 6-aminocaproic acid was added into the solution and the solution was purged under N_2 for 1 h. The solution was heated at 180 °C for 1 h and heated at 250 °C for 5 h with stirring. After the mixture was cooled to room temperature, the black product was washed with warm water and then dried in vacuum at 35 °C overnight. Then the product was purified by centrifugation with formic acid and washing by 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) to obtain purified PA 6 grafted GO (PA 6-GO1) without separated PA 6

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