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Reinforcing nylon 6 via surface-initiated anionic ring-opening polymerization from stacked-cup carbon nanofibers

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ABSTRACT

This article reports the preparation of nylon 6/stacked-cup carbon nanofiber (CNF) nanocomposites via in situ anionic ring-opening polymerization partially initiated from caprolactam-functionalized CNFs. As a result of the successful functionalization of CNF surface, good dispersion of the CNFs was observed by transmission electron microscopy (TEM). Moreover, with the addition of a very small amount of CNFs, significant enhancements in tensile modulus and yield strength were achieved together with slightly improved impact resistance. The enhanced stiffness may be attributed to effective filler–matrix stress transfer induced by interfacial covalent bonds. On the other hand, SEM micrographs provided evidence for the possible unraveling of the stacked-cup CNF, which may allow the CNFs to bridge the matrix during crack propagation, hence resulting in the toughening of the nanocomposites.

1. Introduction

Nylon 6 is a versatile thermoplastic that finds applications in a broad range of products owing to its good physical and mechanical properties. There has also been considerable interest in recent years to replace thermosets with nylon 6 in light-weight composite products, such as turbine blades [1]. This is because compared with thermosets, nylon 6 potentially provides higher resistance to fatigue and the composites can be remolded upon melting, thus presenting a prospective environmentally friendly manufacturing process. Anionic polymerization of ε-caprolactam has been employed to directly fabricate parts via vacuum infusion or reaction injection molding [1–3]. This is possible since the anionic polymerization occurs at a fairly fast rate (i.e. in a few minutes) and relatively low temperature (i.e. 150 °C). This reactive processing method hence allows composites to be easily processed in a way similar to their thermoset counterparts, and with short mold cycle times.

Despite the attractiveness of using nylon 6 for the manufacturing of high-performance and light-weight composites, some challenging issues remain when processing composites on a large scale. A critical issue is that non-uniform crystallization may happen in the preparation of large parts by vacuum infusion process, leading to embrittlement in some regions. Moreover, although the incorporation of some inorganic nanofillers, such as clay, can further enhance the stiffness of nylon 6, it frequently leads to poorer toughness of the system [4]. Therefore, it becomes imperative to improve the stiffness of nylon 6 without sacrificing its toughness.

The toughness of a polymer can be improved by adding soft components, such as elastomers, into the system. However, a disadvantage of this approach is that it is often accompanied by a reduction in stiffness. Another technique to potentially impart toughness to polymers is by incorporating carbon nanofillers such as carbon nanotube (CNT), carbon nanofiber (CNF) and graphene [5–8]. Among these fillers, CNF is gaining appeal as it can be produced in large quantities at a much lower cost. It also contains more reactive carbon edges that can be functionalized to interact with the matrix. This facilitates filler dispersion and interfacial stress transfer. In particular, the unique structure of stacked-cup CNF, which is composed of helically coiled graphene sheets with weak π–π interactions between stacked layers, had been demonstrated to impart significant toughening effect in epoxy systems [6,9,10]. Under impact the weak π–π interactions between the stacked graphene layers may be overcome to dissipate significant amounts of energy.

Currently, there is no reported work on anionic polymerized nylon 6/CNF nanocomposites/composites and very limited literature on the use of stacked-cup CNFs to reinforce/toughen thermoplastics [9,11,12]. We hypothesized that with adequate surface chemistry, stacked-cup CNFs could act as not only efficient reinforcing fibers, its ability to unravel and bridge cracks could also aid the toughening of nylon 6 to some extent. To promote dispersion of the CNFs in nylon 6 and achieve adequate interfacial interactions, there is a need for chemical modification of the CNF surface. Thus, in this work, initiation sites were built on the surface of the CNFs for in situ anionic ring-opening polymerization of

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ε-caprolactam (CL) to yield covalently bonded nylon 6 chains on the surface of CNFs. It is aimed at reinforcing nylon 6 by aptly adding stacked-cup CNFs at very low loadings without sacrificing toughness of the system; ultimately benefiting the advancement of fabrication of large thermoplastic composites via reactive processing. Herein, the results on the functionalization of stacked-cup CNFs, morphology and properties of the nylon 6/stacked-cup CNF nanocomposites prepared via the in situ anionic ring-opening polymerization will be discussed to demonstrate the effectiveness of our approach.

2. Experimental

2.1. Materials

Pyrograf-III carbon nanofibers (CNFs, PR-24-XT-LHT) with diameter of 70–200 nm and length of 50–200 μm were obtained from Applied Science Inc. (USA). ε-Caprolactam, hexamethylene diisocyanate (HMDI), sodium, and nitric acid were purchased from Aldrich (Singapore). Dimethylformamide (DMF, ACS grade) were obtained from Tedia. Ultrapure Milli-Q water was used throughout all the experiments.

2.2. Synthesis

2.2.1. Preparation of caprolactam-functionalized CNFs

Typically, pristine CNFs were ultrasonicated for 30 min and then refluxed in a 9 M HNO_3 aqueous solution in a flask at 100 °C for 12 h. After cooling to room temperature, they were vacuum-filtered through a 0.22 μm Millipore PTFE membrane and washed with deionised water until a neutral pH of the filtrate was reached. The product was then dried overnight at 50 °C.

The acid-treated CNFs (500 mg) were dispersed in DMF (500 mL), and then HMDI (2.5 g, 0.015 mol) was added. After stirring in a nitrogen atmosphere at 80 °C for 24 h, isocyanate-functionalized CNFs (CNF-HMDI) were obtained.

ε-Caprolactam (5.1 g, 0.045 mol) was added into the mixture containing isocyanate-functionalized CNFs and unreacted HMDI, and stirred vigorously at 90 °C for 12 h in nitrogen atmosphere. In this step, excess ε-caprolactam would guarantee that the isocyanate groups on the CNFs surface and unreacted HMDI were completely consumed. After cooling to room temperature, the resulting suspension was diluted with DMF (250 mL) and filtered through a PTFE (200 nm pore size) membrane. The collected solid was washed with DMF to completely remove ε-caprolactam. The yielded product (CNF-HMDC) was then dried in a vacuum oven at 55 °C for 72 h.

2.2.2. Preparation of sodium caprolactam

ε-Caprolactam (100 g) was loaded in a three-neck round bottom flask and purged with nitrogen for 10 min. Sodium pellets (9.2 g) were then added into flask. Subsequently, the mixture was heated to 90 °C with vigorous stirring. Both ε-caprolactam and sodium melted after 20 min, and a large amount of hydrogen gas was evolved. After cooling down to room temperature in nitrogen atmosphere, a light yellow solid product (NaCL) was obtained.

2.2.3. Preparation of caprolactam-capped hexamethylene diisocyanate

HMDI (84 g) and ε-caprolactam (179.5 g) were added to a round bottom flask at room temperature and stirred at 90 °C for 12 h in a dry nitrogen atmosphere. The product was dissolved in acetone and then precipitated using water. The mixture was vacuum filtered and the residue was vacuum dried at 50 °C for 3 days. The caprolactam-capped hexamethylene diisocyanate obtained is denoted as HMDC.

2.2.4. Preparation of nylon 6/CNF nanocomposites

The polymerization was prepared in a three neck glass flask under nitrogen atmosphere. ε-Caprolactam (102 g) was melted at 80 °C, and a desired amount of caprolactam-functionalized CNFs (CNF-HMDC) was added, followed by vigorous stirring at 15,000 rpm for 20 min using a homogenizer. Subsequently, NaCL (2.5 g) was added and dissolved with magnetic stirring. Finally, HMDC (1.8 g) was added quickly. The temperature was rapidly raised to 150 °C, and held isothermal for 0.5 h. After cooling to room temperature, a dark solid product was obtained. The yielded nanocomposite was mechanically crushed, soaked in boiling water for 10 h to extract any unreacted monomers and oligomers, and dried at 90 °C under vacuum for 48 h. Neat nylon 6 was synthesized under the same experimental conditions as reference material.

2.3. Characterization

Transmission electron microscopic (TEM) images were recorded on a Philips CM300 FEG TEM instrument operated under an acceleration voltage of 300 kV. Fourier transform infrared (FTIR) spectra were obtained from a Perkin Elmer Instruments Spectrum GX FTIR spectrometer at room temperature in a wave-number range from 600 to 4000 cm^{-1} using KBr method. The thermal stabilities of the specimens were determined by thermogravimetric analysis (TGA) using TA Instrument TGA Q500. They were heated from 25 °C to 850 °C at 10 °C/min in an inert atmosphere. Tensile properties were measured using an Instron 5567 machine according to ASTM D638 type V at a crosshead speed of 50 mm/min using injection-molded dog-bone specimens (ASTM Type V in 1 mm thickness, 30 kN load cell). At least six specimens were tested for each material. The Izod pendulum impact resistance tests were performed in accordance to ASTM D256 on pre-notched injection-molded specimens with dimensions of 4 × 8 × 50 mm and depth under notch of 6 mm. At least six individual determinations of impact resistance were recorded, for which all were "complete break" samples. Scanning electron microscopic (SEM) measurements were carried out on a JEOL 7600 SEM to observe the morphologies of impact-fractured surfaces. The samples were coated with platinum prior to the experiments. Intrinsic viscosity (η_{in}) was measured using an Ubbelohde viscometer. For the nanocomposites, the solid samples were dissolved in formic acid and the supernates were collected; the solutions obtained from repeated centrifuging-washing the precipitates were also collected. The solutions collected were then precipitated into water. The dried samples were re-dissolved in formic acid (85%) to obtain clear solution at a concentration of 5 g/L. The viscosity-average molecular weight (M_η) was calculated based on Mark–Houwink equation, $\eta_{in} = K[M_\eta]^\alpha$ (where $K = 2.26 \times 10^{-4}$ and $\alpha = 0.82$ [13]). Wide angle X-ray scattering (WAXS) patterns were recorded on a Bruker GADDS X-ray diffractometer using Cu Kα radiation. Differential scanning calorimeter (DSC) measurements were carried out on a TA Instrument DSC Q10 under nitrogen atmosphere at a heating and cooling rate of 10 °C/min. The samples were firstly heated to 250 °C and maintained for 5 min to remove any previous thermal history. The crystallization and melting thermograms were taken from subsequent cooling and heating cycles unless otherwise stated.

3. Results and discussion

3.1. CNF functionalization

The reactions involved in the surface modification are illustrated in Scheme 1. Herein, caprolactam functional groups were