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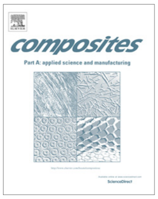

Intercalation structure and highly enhancing tribological performance of monomer casting nylon-6/graphene nano-composites

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ABSTRACT

A series of monomer casting nylon-6 (MC PA6)/graphene (GN) nano-composites were *in situ* synthesized by incorporation of polyethylene glycol (PEG) as a solid lubricant and compatibilizer. Addition of PEG led to more efficient grafting of PA6 molecules on GN surface, while GN was exfoliated and uniformly distributed in the matrix. Compared with neat MC PA6, addition of only 0.5 wt% GN resulted in a roughly 12% increase in tensile strength and 20.6% increase in impact strength, while over 75% reduction in specific wear rate and 13% reduction in friction coefficient were obtained with 0.7 wt% GN addition. The worn surface displayed smooth and flat features with uniform depth distribution, and the annealing degree due to produced friction heat was much lower for the composites. The mechanical and tribological properties of the composites in presence of PEG were superior to those in absence of PEG, further confirming the synergistic reinforcing/lubrication effect of GN-PEG.

1. Introduction

Monomer casting nylon-6 (MC PA6), as a new type of engineering plastics, is synthesized by anionic ring-opening polymerization of ε-caprolactam (CL). Due to its high molecular weight, high crystallinity, superior mechanical and self-lubricating performances [1–4], and ease of manufacturing, MC PA6 has been extensively investigated and widely used to replace metallic materials for production of gears, bearings, slide blocks and structural components in automotive industry [5,6]. However, under high load and harsh PV conditions, the wear rate of MC PA6 parts is high, and the self-lubrication and wear resistance property can't satisfy the application requirement. Many attempts have been made to improve the tribological properties of MC PA6 by adding various fillers such as graphite, lubrication oil, carbon black and fiber [7–11]. However, the mechanical properties of the composites were usually deteriorated due to high fillings.

Graphene (GN), as a typical two-dimensional material with one-atom-thick planar sheet of sp^2 carbon atoms arranged in a hexagonal lattice, has received worldwide interest because of unique properties, such as excellent mechanical strength, high electrical and thermal conductivities [12–16]. Moreover, as a fine solid lubricant, GN exhibits superior self-lubricating and anti-wear properties ascribed to high hardness and low shear resistance through its intrinsic lamellar structure [17]. Recently, the potential value of GN for tribological applications has been explored on micro-scale and macro-scale in the polymer material fields [18–23]. Huang et al. [20] studied the friction behavior of polyimide/-modified graphene composites and the result showed that 2 wt% modified graphene addition only obtained a ~10% reduction in friction coefficient. Shen et al. [24] prepared epoxy/graphene oxide (GO) composites, which exhibited the lowest wear rate but more than 100% increase in friction coefficient at 0.05 wt% GO content. Tai et al. [21] investigated the tribological properties of UHMWPE/GO composites and found that 1 wt% GO addition produced a ~15% increase in friction coefficient and a ~35% reduction in wear rate for UHMWPE. The similar result was also obtained by An et al. [25]. Overall, the wear resistance of the composites was far less than expected, and the friction coefficient even increased in some cases, perhaps due to the poor dispersion of GN in the matrix. In addition, few literatures can be available on the tribological performance and wear mechanism of PA6/GN nano-composites.

Unfortunately, GN nano-sheets, packed into benzene-ring structure, exhibit chemical inertia and suffer from aggregation resulting from strong Van der Waals attractive forces between the GN planes, which gravely restricts the development of such high-performance nano-composites [26–28]. Polyethylene glycol (PEG) with flexible structure of C—O—C bonds is an important lubricant due to self-lubricating property, which has good compatibility with both PA6 and GN by forming hydrogen bonding interactions. The

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opportunity to combine PEG and GN appears as an attractive way to endow with properties that are inherent to both types of the components. Therefore, in this work, MC PA6/GN nano-composites were synthesized via *in situ* polymerization by using PEG as a compatibilizer, and the synergistic lubrication effect of GN-PEG on the nano-composites is expected to be achieved without deterioration of mechanical properties. The intercalation behavior and structure of MC PA6/GN nano-composites in presence or absence of PEG were characterized, and the mechanical and tribological performances were investigated in detail.

2. Experimental section

2.1. Materials

The caprolactam (CL) monomer was supplied by China Petroleum and Chemical Co. Ltd., with a commercial grade product. Sodium hydroxide (NaOH), as the main catalyst with analytical purity was commercially obtained from Kermel Chemical Reagent Co. Ltd. (Tianjin, China). Toluene-2,4-diisocyanate (TDI), as the auxiliary catalyst, was purchased from Kelong Chemical Reagent Co. Ltd. (Chengdu, China). Graphene (GN) powder with a particle size of micron grade was supplied by the Sixth Element Materials Technology Co. Ltd. (Changzhou, China). Polyethylene glycol (PEG) with an average molecular weight of 20,000 was purchased from the Kelong Chemical Reagents Co. Ltd. (Chengdu, China), and used as received without further purification. Other chemical agents are all commercial grade products.

2.2. In situ synthesis of MC PA6/GN-PEG nano-composites

The synthesis procedure for the MC PA6/GN-PEG nano-composites was carried out as follows: firstly, the caprolactam monomer (CL) with 4 mol in stoichiometric amount was put into a three-necked flask and heated to about 80 °C. After completely melting, PEG and GN powders with different contents (0.1–1.0 wt %) were added. The mixed melt was stirred for 10 min and sonicated for another 1 h. Then, the melt was refluxed under vacuum conditions for 30 min to remove water in it. Afterwards a proper amount of NaOH (0.05 mol) was added under vigorous stirring. The melt was refluxed under vacuum again and TDI (0.05 mol) was added. Finally, after quickly well mixed up, the melt was cast into a preheated mould at 170 °C. The reaction lasted for 60 min and the product were demolded [29]. The resultant MC PA6/GN-PEG nano-composites were denoted as MC PA6/x GN-PEG, where x indicated the weight ratio of GN in the composite. For comparison, the neat MC PA6 and MC PA6/GN samples in absence of PEG were synthesized with the same method. The synthesis process of MC PA6/GN-PEG nano-composites is depicted in Fig. 1.

2.3. Measurements

2.3.1. FTIR analysis

The structure of GN samples was analyzed with a Nicolet-560 Fourier-transform infrared spectrometer (FTIR) (U.S.A). The scanning rate was 20 min^{-1}, and the resolution was 4 cm^{-1}.

2.3.2. Raman spectra analysis

The structure of GN samples was investigated by Raman spectra analysis. Raman spectra were recorded from 1000 to 3500 cm^{-1} on a Renishaw Invia Raman Microprobe (Britain) using a 532 nm argon ion laser.

2.3.3. X-ray photoelectron spectroscopy (XPS) analysis

The XPS analysis of GN samples was performed on a XSAM 800 spectrometer (KRATOS Co., UK), using AlKa radiation (1486.6 eV) at a pressure of 2.0×10^{-7} Pa.

2.3.4. Thermo-gravimetric analysis (TGA)

TGA was used to characterize the grafting ratio of PA6 on GN surface. It was performed with a TA2950 thermobalance from TA Co. (USA) under nitrogen atmosphere with the flow rate of 50 ml/min. The granulated samples of about 10 mg were heated from ambient temperature to approximately 800 °C at a heating rate of 10 °C/min.

2.3.5. X-ray diffraction (XRD) analysis

The X-ray diffraction (XRD) analysis of GN samples was performed with a Rigaku D/max IIIB X-ray diffractometer (Japan) using Cu Kα radiation (λ = 0.154 nm) at an accelerating voltage of 40 kV and current of 40 mA. XRD data were collected from 5° to 40°.

2.3.6. Atomic force microscopy (AFM) analysis

The morphologies of GN samples and the worn surfaces of MC PA6/GN-PEG samples were examined by Atomic force microscopy (AFM) analysis. It was performed with a SPM-9700 Scanning Probe Microscope (Japan) in a tapping mode. The samples for AFM imaging were prepared by drop-casting the GN dispersion onto freshly cleaved mica substrates, which were then allowed to dry in air at ambient temperature and pressure.

2.3.7. Scanning electron microscopy analysis (SEM)

The morphologies of the cryogenically fractured surface, the impact and tensile fractured surfaces, and the worn surfaces of MC PA6/GN-PEG nano-composites were observed with a JEOL JSM-5900LV SEM (Japan). The operating voltage was 15 kV. The samples were ion beam sputter-coated with gold and thin layer thickness was about 1–20 nm.

2.3.8. Transmission electron microscopy (TEM) analysis

Transmission electron microscopy (TEM) images were recorded on a JEOL JEM 100CX II TEM equipment (Japan). It was operated at an acceleration voltage of 200 kV to observe the micro-morphology of the samples of MC PA6/GN-PEG nano-composites.

2.3.9. Viscosity average molecular weight

The viscosity average molecular weight of MC PA6/GN-PEG nano-composites was measured with an Ubbelohde viscometer. The formic acid was used as a solvent of the composites. Sample of MC PA6 nano-composites of 0.5 g was dissolved in 100 ml formic acid. The time of outflow of the solution was measured with an Ubbelohde viscometer in a water bath at 25 °C, according to ISO 307-1984. Then the specific viscosity (η_{sp}) can be calculated with the following formula:

$$\eta_{\text{sp}} = \frac{t - t_0}{t_0} \tag{1}$$

where t is the flow time of a polymer solution through a capillary tube with known diameter and length, and t_0 is the flow time of the neat solvent through the same capillary tube.

The intrinsic viscosity ($[\eta]$) is described as the limit of the ratio between the specific viscosity (η_{sp}) and the polymer concentration (c), as the polymer concentration approaches zero:

$$[\eta] = \lim \frac{\eta_{sp}}{c} (c \to 0) \tag{2}$$

By measuring the intrinsic viscosity of polymer solutions, the viscosity average molecular weight (M_η) of MC PA6 can be predicted through the Mark–Houwink empirical equation, as described by: