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# In situ synthesis of monomer casting nylon-6/reduced graphene oxide nanocomposites: Intercalation structure and electrically conductive properties

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## ABSTRACT

Based on the industrialized reduced graphene oxide (RGO) product, MC nylon-6/RGO composites were in situ synthesized through anchoring effect of polyetheramine (PEA). Nylon-6 chains were confirmed to intercalate into RGO layers with high grafting ratio by formation of covalent bond and intermolecular hydrogen bond. By presence of PEA, RGO was well exfoliated by the nylon-6 chains and the average layer thickness increased remarkably. Moreover, the stacking of RGO layers was much more weakened and exhibited almost monolayer homogenous dispersion state in the matrix, resulting in the establishment of the electrically conductive network with a low threshold percolation.

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## Introduction

Monomer casting (MC) nylon-6, as one of the commercially prominent members of polyamides, is synthesized by anionic ring-opening polymerization of caprolactam, using sodium hydroxide as catalyst and diisocyanates as co-catalyst. Compared with ordinary nylon-6, it shows relatively high molecular weight, high crystallinity, resulting in the high mechanical strength, excellent self-lubricating performance and so on [1], which enables it to be widely used to replace metallic materials for the production of gears, bearings and slide blocks [2]. Especially, it is suitable for producing large products that cannot be prepared by injection molding or compression molding.

Graphene, a single-atom-thick sheet of hexagonally arrayed  $sp^2$ -bonded carbon atoms, has been under the spotlight owing to its intriguing and unparalleled physical properties [3]. Because of its novel properties, such as exceptional thermal conductivity, high Young's modulus and high electrical conductivity, graphene has been highlighted in fabricating various micro-electrical devices, batteries, super-capacitors, and composites [4,5].

One of the most fascinating aspects of graphene is the potential for its use in electronic applications due to its very high electrical conductivity [6]. Addition of a small amount of graphene to the

insulating nylon matrix can change it into electrical conductor with a high level of electron delocalization owing to the larger surface area of the graphene sheets [7]. At a certain concentration level, known as the percolation threshold [8,9], the graphene sheets can form a network, allowing charge transport and leading to a rapid rise in the electrical conductivity of the nylon composite [10].

Many studies have been reported on the electrical conductivity improvement of nylon composites with graphene currently. Bouhfid et al. [11] prepared PA6/graphene nanosheets (GNs) nanocomposites by batch system followed by hot compression to get samples for different tests. The electrical resistivity of the composites reached a highest conductivity value of  $3 \times 10^{-7}$  S/m and a lowest percolation threshold of 2 wt% graphene content. Steurer et al. [10] fabricated melt compounding PA6/graphene composites based on thermally reduced graphite oxide. It was found that the composites showing a lowest resistivity value of  $1.4 \times 10^4 \Omega \text{ cm}$  and a lowest percolation threshold of 7.5 wt% graphene content. Kim et al. [12] in situ synthesized PA6/functionalized graphene composites using a thermal reduction of graphite oxide, which exhibited a highest conductivity value of  $6.84 \times 10^{-4}$  S/cm and a lowest percolation threshold of 0.39 wt% graphene content. However, the graphene layers with low polarity without modification or functionalization in the above mentioned composites were difficult to be compatible with the high polarity nylon-6 matrix and were easy to aggregate in the composites, resulting in a low electrical conductivity or high percolation threshold. Moreover, these graphene were small-scale prepared in

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the laboratory, and it is far away from large production and application in industrial scale, although it owns perfect  $\pi$ – $\pi$  conjugate structure.

Reduced graphene oxide (RGO), based on the large production in industrial scale, is usually reduced by the thermal treatment at temperatures up to 1050 °C [13]. Oxygen groups on such RGO surface were difficult to be completely removed during the previous reduction of GO to RGO, and thus the  $\pi$ – $\pi$  conjugate structure of RGO was inevitably influenced by those oxygen groups. However such reactive sites of oxygen groups on its surface were easy to be designed and controlled to obtain the tailored interface by the covalent linkage. In order to exfoliate RGO and improve its dispersion in MC nylon-6 matrix, the surface of RGO sheets needs to be pre-modified by surfactants or polymers before the reduction. Those surfactants or polymers should be compatible with caprolactam well and inhibit the decrease in toughness of the polymer composites resulting from the stress concentration caused by the restacking of RGO sheets, and most importantly, do not inhibit the anionic ring-opening polymerization of MC nylon-6. Polyetheramine (PEA) with the molecular weight of approximately 400–3000 g/mol is composed of flexible chains of C–O–C bond in its molecular chain with primary amine as end group [14], which can easily lead to anchoring effect by formation of covalent bond, intermolecular hydrogen bond or electrostatic interactions between the remnant oxygen groups of RGO and PEA molecular chains. As a result, the exfoliation of RGO is improved and the aggregation of RGO sheets is effectively prevented, resulting in an improvement of electron transfer in the composites. In our previous work, PEA was grafted onto MC nylon-6 to enhance the mechanical toughness and permanently antistatic property [15]. Herein, we prepared MC nylon-6/RGO-PEA composites by in situ polymerization. For the effective intercalation of nylon-6 molecular chains into the RGO layers, PEA with primary amine as end group is anchored onto RGO surface before the polymerization to strengthen the molecular entanglement with nylon-6 molecular chains.

In the first step, the graft of RGO by PEA was realized by ultrasonic dispersion of both RGO and PEA in melting caprolactam matrix at 80 °C, and a stable colloidal suspension of RGO-PEA in caprolactam was obtained. In the second step, the MC nylon-6/RGO-PEA composites were in situ synthesized by using the obtained caprolactam/RGO-PEA mixture without the aid of solvents. The interfacial interaction, intercalation structure and electrically conductive network structure of MC nylon-6/RGO-PEA composites were investigated. The interaction between nylon-6 chains and RGO layers, as well as the uniform dispersion of RGO, and additionally the formation of conductive network are responsible for the improved electrical conductivities.

## Experimental

### Materials

The RGO powders were supplied by Sixth Element Materials Technology Co., Ltd. (Changzhou, China) with an average diameter of 50  $\mu$ m. The CL (caprolactam) monomer was supplied by China Petroleum and Chemical Co., Ltd. (Yueyang, China), with a commercial grade product. NaOH (sodium hydroxide), as the catalyst with analytical purity was purchased from Kernel Chemical Reagent Co., Ltd. (Tianjin, China), and TDI (toluene-2,4-diisocyanate), as the co-catalyst with analytical purity was purchased from Kelong Chemical Reagent Factory (Chengdu, China). PEA with average molecular weight of 2000 g/mol was purchased from Huntsman Polyurethanes Ltd., Guangzhou Branch (Guangzhou, China).

### In situ synthesis of MC nylon-6/RGO-PEA composites

Firstly, 400 g of CL monomer was put into a three-necked flask and heated to about 80 °C. After completely melting, 8 g of PEA and 4 g of RGO powders were added. The mixed melt was stirred for 20 min and sonicated for 30 min. Then, the melt was refluxed under vacuum conditions for 30 min to remove water from it. 0.6 g of NaOH was added under vigorous stirring. The melt was refluxed under vacuum again and 2.3 g of TDI 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 of MC nylon-6/RGO-PEA composites were obtained. The resultant MC nylon-6/RGO-PEA composites were designated as MC nylon-6/x RGO-PEA, where x indicates the weight ratio of RGO in the composite. For comparison, the neat MC nylon-6 and MC nylon-6/RGO samples in absence of PEA were synthesized with the same method. The synthesis process of MC nylon-6/RGO-PEA composites is depicted in Fig. 1.

### Measurements

#### FT-IR analysis

The structures of RGO, g-RGO and g-RGO-PEA samples were analyzed with a Nicolet-560 Fourier-transform infrared spectrometer (FT-IR) (U.S.A.). The scanning rate was 20  $\text{min}^{-1}$ , and the differentiate rate was 4  $\text{cm}^{-1}$ .

#### Raman analysis

The skeletal structures of the RGO, g-RGO and g-RGO-PEA and MC nylon-6 samples were analyzed at room temperature with a RENISHAW Invia Raman microscope (UK) over the range of 300–3000  $\text{cm}^{-1}$ . Laser excitation source at 532 nm was used.

#### X-Ray diffraction analysis (XRD)

The interlayer spacing of the samples of RGO, g-RGO and g-RGO-PEA and MC nylon-6/RGO-PEA composites was measured at room temperature over the scanning range approximately of 2  $\theta$  = 3–30° with Rigaku D/max III B X-ray diffraction equipment (XRD) (Japan). Copper (Cu)  $K_{\alpha}$  radiation ( $\lambda$  = 0.154 nm) was used at a generator voltage of 40 kV, current of 35 mA, and the scanning speed was 2.4°/min. The  $d$ -spacing of the PEA-GO layers was calculated with the Bragg equation:

$$2d \sin \theta = n \lambda \quad (1)$$

where  $\theta$  is the diffraction angle;  $n$  is the order of diffraction, and  $\lambda$  is the incident wavelength.

#### X-ray photoelectron spectroscopy analysis (XPS)

The XPS analysis of the RGO, g-RGO and g-RGO-PEA was performed with a XSAM 800 spectrometer (KRATOS Co., UK), using AlK $\alpha$  radiation (1486.6 eV) at a pressure of  $2.0 \times 10^{-7}$  Pa.

#### Atomic force microscopy analysis (AFM)

The sheet dimensions and thickness of RGO, g-RGO and g-RGO-PEA were characterized with a Shimadzu SPM9700 atomic force microscopy (AFM) (Japan) and recorded in tapping mode. Samples for AFM imaging were prepared by depositing diluted alcoholic dispersion of RGO, g-RGO and g-RGO-PEA (0.1 mg/ml) on freshly cleaved mica surface.

**2.3.6 Thermal gravimetric analysis (TGA)**  
The thermal stability and grafting ratio of RGO, g-RGO and g-RGO-PEA were measured with a TA 2950 thermo gravimetric analyzer (TGA) (U.S.A.) with the flow rate of 50  $\text{ml min}^{-1}$  under nitrogen atmosphere. The granulated samples of about 10 mg were heated from ambient temperature to approximately 800 °C at a rate of 10 °C  $\text{min}^{-1}$ . Calibration of the instrument was

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