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## Reactive melt processing of polyamide 6/reduced graphene oxide nano-composites and its electrically conductive behavior

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### ABSTRACT

Based on the industrialized reduced graphene oxide (RGO) product, the graphene precursor of RGO-TDI with reactive sites of isocyanate groups was prepared with high grafting ratio, and a series of PA6/RGO-TDI composites were prepared via reactive melt processing. The PA6 molecules were confirmed to reactively intercalate into RGO layers through covalent and hydrogen bonding, which had high grafting ratio and layer thickness, exhibiting almost monolayer dispersion state. The molecular bridge effect of exfoliated RGO-TDI lowered activation energy of electrically conductive network formation, which resulted in a rapid increase of electrical conductivity of the composites with a low threshold percolation. © 2017 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V. All rights reserved.

### Introduction

Polyamide 6 (PA6) is a typical engineering plastic, which displays excellent load bearing capability, resistance to chemicals and self-lubrication property, and widely applied in industry. 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 [1–3], such as exceptional thermal conductivity, high Young's modulus, and high electrical conductivity. And thus graphene has been highlighted in fabricating various micro-electrical devices [4], batteries [5], especially in the field of conductive switching [6], bioimaging [7] and photocatalysis [8], and one of the most fascinating aspects of graphene is the potential for their use in electronic applications [9–11]. The electrical and mechanical properties of PA6 can be further improved by the incorporation of graphene [12]. Addition of a small amount of graphene to the insulating PA6 matrix can change them into electrical conductors with a high level of electron delocalization for its potential use in the electronic applications, owing to the larger surface area of the graphene sheets [13]. At a certain concentration level, known as the percolation threshold [14,15], the graphene sheets can form a network, allowing charge

transport and leading to a rapid rise in the electrical conductivity of the PA6 composite [16].

Most of PA6 based nano-composites were manufactured through melt processing such as injection molding, extrusion and hot pressing due to its advantages, for instance, simpleness of preparation, continuity of production, low cost and energy consumption, short production cycle and friendliness to environment. Studies on the electrical conductivity improvement of PA6 composites with graphene have been reported currently. Bouhfid et al. [17] 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  $3 \times 10^{-7} \text{ S/m}$  and a lowest percolation threshold of 2 wt% graphene content. Steurer et al. [16] fabricated melt compounding PA6/graphene composites based on thermally reduced graphite oxide. It was found that the composites showed a lowest resistivity value of  $1.4 \times 10^4 \Omega \text{ cm}$  and a lowest percolation threshold of 7.5 wt% graphene content. However, caused by the high melt viscosity of PA6 matrix during processing, the graphene layers with low polarity without modification or functionalization in the abovementioned composites were difficult to be compatible with PA6 matrix and were easy to aggregate in the composites, resulting in a low electrical conductivity or high percolation threshold. Moreover, those graphene were small-scale prepared in the laboratory, and it is far away from large production and application in industrial scale, although it owns perfect  $\pi$ - $\pi$  conjugate structure.

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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 [18]. 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.

Due to the effect of cumulated double bond and atoms of N, O on either hand of carbon atom, isocyanate group has high reaction activities and is easy to react with compounds containing active hydrogen [19]. Herein, through the reactive melt processing, PA6 molecular chains were covalently bonded with RGO via molecular bridge effect of toluene-2,4-diisocyanate (TDI). In the first step, the graphene precursor (RGO-TDI) was prepared by introduction of isocyanate groups onto RGO surface via the reaction between isocyanate groups of TDI and hydroxyl groups of RGO. In the second step, PA6 molecules reactively intercalated into RGO layers by the reaction between imino groups of PA6 and isocyanate groups of RGO-TDI in the melt processing of the composites. The interfacial interaction between PA6 molecules and RGO layers, reactive intercalation structure and formation mechanism of electrically conductive network structure of the composites were investigated. The interfacial interaction between PA6 chains and RGO layers, as well as the homogeneous dispersion of RGO, and additionally the formation of electrically conductive network are responsible for the remarkably improved electrical conductivities, which depict a promising method in rapid preparation of PA6/graphene composites as new nanocomposites in industrial production.

## Experimental

### Materials

The RGO powders were supplied by Sixth Element Materials Technology Co., Ltd., (Changzhou, China) with an average diameter of 50  $\mu\text{m}$ . *N,N*-Dimethylformamide (DMF) with analytical purity was purchased from Kermel Chemical Reagent Co., Ltd., (Tianjin, China). Stannous octoate, as the catalyst with analytical purity was

purchased from Kermel Chemical Reagent Co., Ltd., (Tianjin, China), and TDI (toluene-2,4-diisocyanate) with analytical purity was purchased from Kelong Chemical Reagent Factory (Chengdu, China). Commercial PA6 resins (YH-800) were obtained from the China Petroleum and Chemical Co., Ltd., (Yueyang, China).

### Synthesis and preparation

#### Preparation of graphene precursor (RGO-TDI)

RGO (0.1 g) was dispersed and exfoliated in DMF (200 ml) by ultrasonication at 70 °C. After TDI (0.4 g) and stannous octoate (0.04 g) as catalyst were added, the RGO-TDI mixture was sonicated again for 4 h. The obtained mixture was centrifuged and rinsed in DMF and then filtrated to remove the physically adsorbed TDI. The filter cake was dried in an oven at 80 °C for 24 h, and the RGO-TDI powder was obtained.

#### Preparation of PA6/RGO-TDI nano-composites

For a typical preparation of nanocomposites, 30.0 g of PA6 resin with different content of RGO-TDI powder, conveniently dried in vacuo at 80 °C overnight, were pre-mixed at the solid state for 3 min, fed to a Brabender Plasticorder PLE300 batch mixer and then processed for 10 min at constant rotor speed (50 rpm) and temperature ( $T=250$  °C). Thereafter, the materials fed out of the batch mixer were rapidly cooled to room temperature, ground into pellets, compression molded for about 5 min at 250 °C and finally cut into specimens for further characterizations. The resultant PA6/RGO-TDI composites were designated as PA6/x RGO-TDI, where x indicates the volume ratio of RGO in the composite. For comparison, the PA6/RGO samples in absence of TDI were prepared with the same method. The preparing process of PA6/RGO-TDI composites is depicted in Fig. 1.

### Measurements

#### FT-IR analysis

The structures of RGO, RGO-TDI, PA6-RGO, PA6-RGO-TDI and neat PA6 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  $\text{cm}^{-1}$ .

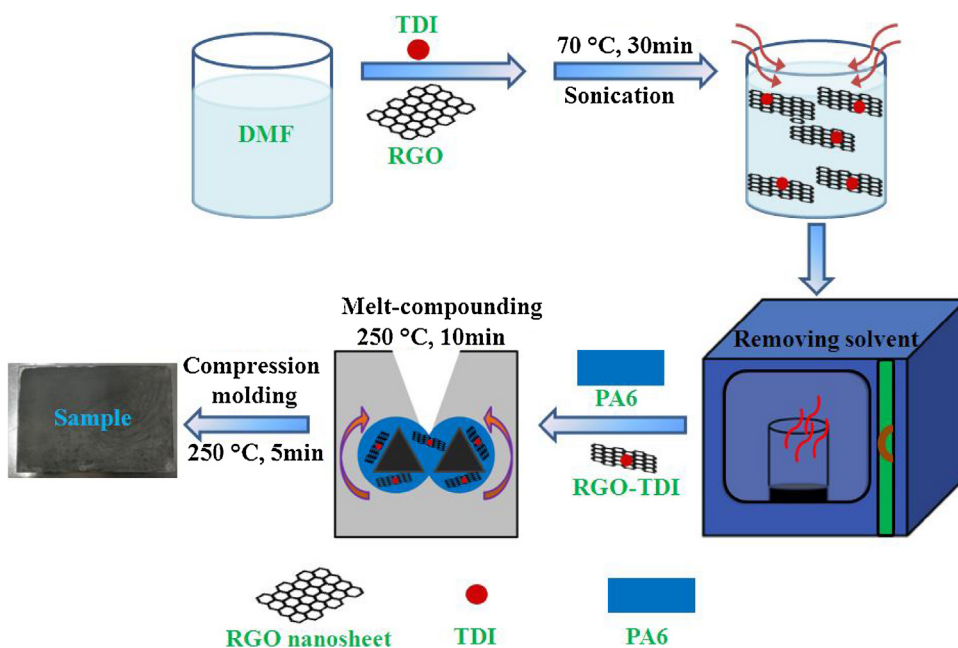


Fig. 1. Schematic representation of preparation of PA6/RGO-TDI composites.

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