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# EFFECT OF TiO<sub>2</sub> ON THERMAL STABILITY, FLAME RETARDANCY PROPERTIES OF REDUCED GRAPHENE OXIDE/POLYPROPYLENE NANOCOMPOSITES

**Keywords:** RGO -TiO<sub>2</sub> /PP nanocomposites, Thermal stability, Flame retardancy,

## ABSTRACT

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This paper presents a preliminary research on the effects of incorporating TiO<sub>2</sub> modified graphene oxide (TiO<sub>2</sub>-GO) into polypropylene (PP) on thermal stability, flame retardancy properties. TiO<sub>2</sub> functionalized reduced graphene oxide reinforced polypropylene nanocomposites with different loadings were prepared using a master batch based melt mixing approach. TiO<sub>2</sub>-rGO/PP nanocomposites were characterized by different techniques, namely: Fourier-transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM) , Thermal gravimetric analysis (TGA) and Cone calorimeter test. As a results,compared with no modified GO , the dispersion stability of TiO<sub>2</sub>-GO in PP was enhanced significantly which can explained by SEM. TGA showed an enhancement in thermal stability property of PP with TiO<sub>2</sub>-GO modified. HRR were decreased 10% .

## 1 INTRODUCTION

It is well acknowledged that nanofillers reinforced polymer composites get outstanding properties include mechanical enhancement, improved thermal conductivity, gas barrier, and flame retardancy. Polypropylene is a semi-crystalline engineering thermoplastic and is known for its balance of strength, modulus and chemical resistance[1]. Polypropylene has many potential applications in automobiles, appliances and other commercial products in which creep resistance, stiffness and some toughness are demanded because the weight and cost savings[2]. However, the products fabrication from neat PP resin cannot reach the industrial requirements due to its low thermal stability, flame retardancy and mechanical properties. In order to improve the integrated performance of products, various types of nanofillers (such as clay, TiO<sub>2</sub> , graphene, and CNT) have been incorporated into the PP resin[3-6]. Among the various inorganic nanofillers that are used to improve the properties of polymers, graphene is an important one. Graphene nanosheets are considered to be the most promising alternative to simultaneously improve the mechanical properties and barrier properties as well as thermal properties[7]. Due to the existence of strong cohesive interactions between graphene nanosheets, it is difficult to effectively disperse and effectively exfoliate graphene in polymer matrices, especially in polyolefin materials. Effective dispersion is the key requirement for maximizing the enhancement potential of graphene[5]. TiO<sub>2</sub> is one of the most important materials because of its excellent mechanical properties, light density, reduction of UV, and thermal degradation[8]. In this work, we incorporated TiO<sub>2</sub> modified graphene oxide (TiO<sub>2</sub>-GO) nanosheets into polypropylene (PP) matrix with subsequent melt-blending method. TiO<sub>2</sub> can be successfully grafted on the graphene oxide (GO) nanosheets

using the tetrabutyl titanate hydrolyze method. It was expected that the grafted  $\text{TiO}_2$  would improve the dispersion and flame retardant effect of the RGO. In this study, The work concentrated on the experimental determination of the thermal stability, flame retardancy and mechanical properties of the  $\text{TiO}_2$ -GO/PP nanocomposites. The results reveal that a given weight of  $\text{TiO}_2$ -GO content of 10wt.% plays a major role to improve mechanical property of nanocomposites. The enhanced mechanical property of the nanocomposites are attributable to the reinforcing effects of  $\text{TiO}_2$ -GO. The increase of the thermally reduction temperature is benefit for the removal of the oxygen groups form GO layers, and thus lead to an expanded disordered structure. The dispersion stability of  $\text{TiO}_2$ -GO in PP was enhanced significantly which can explained by SEM. TGA showed an enhancement in thermal stability property of PP with  $\text{TiO}_2$ -rGO modified. HRR were decreased 10% .



**Fig. 1.** Fabrication process of  $\text{TiO}_2$ -GO/PP nanocomposites

## 2 EXPERIMENTAL

### 2.1. Materials

GO (granularity 0.5-5 $\mu\text{m}$ ), Nanjing XFNANO Materials Tech Co.,Ltd., Hydrazine hydrate ( $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ ), Tetrabutyl titanate (TBT), Sinopharm Chemical Reagent Co.,Ltd., ethyl alcohol absolute, Sinopharm Chemical Reagent Co.,Ltd., Ammonium chloride ( $\text{NH}_4\text{Cl}$ ), Sinopharm Chemical Reagent Co.,Ltd., Polypropylene (PP, KP503), a granulated product with a melt flow index of 60.0 g/10 min (230  $^\circ\text{C}$ , 2.16 kg), China Petroleum and Chemical Corporation. MAPP, CMG9801, a granulated product with a melt flow index of 12.0 g/10 min (230  $^\circ\text{C}$ , 2.16 kg), Fine-blend Compatilizer Jiangsu Co.,Ltd.. deionized water, obtained in our laboratory.

### 2.2. Synthesis of $\text{TiO}_2$ -GO

0.1 g GO was dispersed into 200 ml deionized water solvent in a 500 ml three-necked flask, then the mixture was refluxed in an ultrasonic bath. The dispersion was mixed with 0.5mol  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  solvent with stirring at 98 $^\circ\text{C}$  for 30min to get solvent A. 500mg TBT was dispersed into 3ml ethyl alcohol absolute and 2ml  $\text{NH}_4\text{Cl}$  solvent, then mixture with 2.5ml deionized water to get solvent B. Then solvent B was dispersed into solvent A under 160 $^\circ\text{C}$  for 4 h. Then the solvent was filtered and dried in vacuum at 50 $^\circ\text{C}$  overnight.

### 2.3. Preparation of $\text{TiO}_2$ -GO/PP nanocomposites

PP, MAPP and  $\text{TiO}_2$ -GO were dried in a vacuum oven at 80  $^\circ\text{C}$  for 3 h before use. Then PP ,

MAPP and TiO<sub>2</sub>-GO were melt-blended on a two-roll mill (XM1F, Jiangdu Jinrui Chemical Machinery Fittings Factory, China) at 170 °C for 15 min. The prepared mixtures were molded under compression (15 MPa) at 180 °C for 6 min and cooled to room temperature naturally to obtain TiO<sub>2</sub>-GO/PP nanocomposites sheets with standard size for further testing.

## 2.4. Characterization

### 2.4.1. Fourier transform infrared spectrometry (FTIR)

Fourier transform infrared (FTIR) studies were recorded on a Nicolet FTIR 6700 apparatus (Nicolet, US) in the wavenumber range of 4000-400 cm<sup>-1</sup>. The powdered samples were mixed with KBr,

### 2.4.2. Thermogravimetric analysis (TGA)

The TGA was carried out with a TGA thermal analyzer (Discovery TGA., American ) from 30°C to 800°C at a linear heating rate of 20 °C/min under an nitrogen flow of 50 ml/min. Each sample was measured in an alumina crucible with a weight about 10 mg.

### 2.4.3. Scanning electron microscope (SEM)

Morphological studies on the residual chars were conducted using a JSM-IT300 scanning electron microscope (SEM) at an acceleration voltage of 20 kV.

### 2.4.4. Cone calorimetric test (CCT)

The CCT was carried out by using a cone calorimeter (Fire Testing Technology Co., UK) according to ISO5660. Each specimen, with the dimensions of 100mm×100mm×4.0 mm, was wrapped in aluminum foil and exposed horizontally to an external heat flux of 50 kW/m<sup>2</sup>. All samples were run in duplicate and the average value was reported.

## 3. RESULTS AND DISCUSSION

### 3.1 Characteration of TiO<sub>2</sub>-GO

Fig.2 gives the FTIR spectra of the pristine GO and TiO<sub>2</sub>-GO. For GO, the bands at 1730 and 1217 cm<sup>-1</sup> are the characteristic peaks of COOH and C-O-C, respectively. The peak at 1612 cm<sup>-1</sup> in the spectrum of TiO<sub>2</sub>-GO is attributed to the skeletal vibration of graphene nanosheets. These peaks of the oxygen functional groups almost disappear in TiO<sub>2</sub>-GO, confirming the effective reduction effect of hydrazine. The peak at 544 cm<sup>-1</sup> in the spectrum of TiO<sub>2</sub>-GO is the stretching vibration of Ti-O-Ti. 1612 cm<sup>-1</sup> is attributed to the C=C stretching vibrations of the TiO<sub>2</sub>-GO.

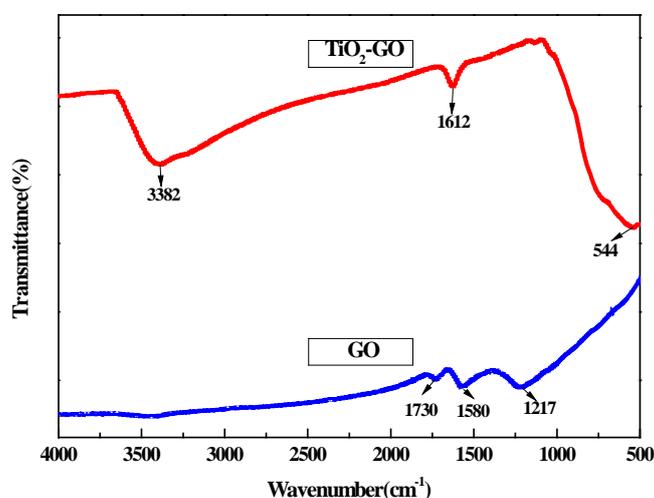
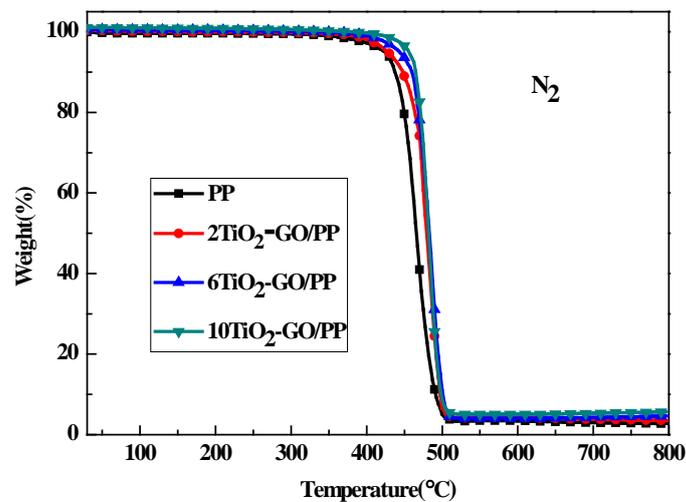


Fig. 2. FTIR spectra of GO and TiO<sub>2</sub>-GO.

### 3.2 Thermal behavior of TiO<sub>2</sub>-GO/PP nanocomposites

Fig. 3 presents the TGA curves of neat PP and its nanocomposites under a flow of N<sub>2</sub> atmosphere at a heating rate of 20 °C/min. The relevant thermal decomposition data are listed in Table 1, including T<sub>0.1</sub><sup>a</sup>, T<sub>0.5</sub><sup>b</sup> which defined as the temperature at which 10% and 50% weight loss occurs, respectively, T<sub>max</sub><sup>c</sup> which defines as the temperature at maximum weight loss rate. It can be seen from Table 1 that the T<sub>0.1</sub><sup>a</sup> of neat PP is 437.3 °C and material decomposes completely at 466.2 °C under nitrogen atmosphere. Adding TiO<sub>2</sub>-GO increases the T<sub>0.1</sub><sup>a</sup> of the TiO<sub>2</sub>-GO/PP composites because of the comparatively good thermal stability of TiO<sub>2</sub>-GO. Adding TiO<sub>2</sub>-GO improved the T<sub>max</sub><sup>c</sup> of the TiO<sub>2</sub>-GO/PP composites.



**Fig. 3.** TGA curves of PP and its nanocomposites under N<sub>2</sub> atmosphere

**Table1** TGA data for PP and TiO<sub>2</sub>-GO /PP composites

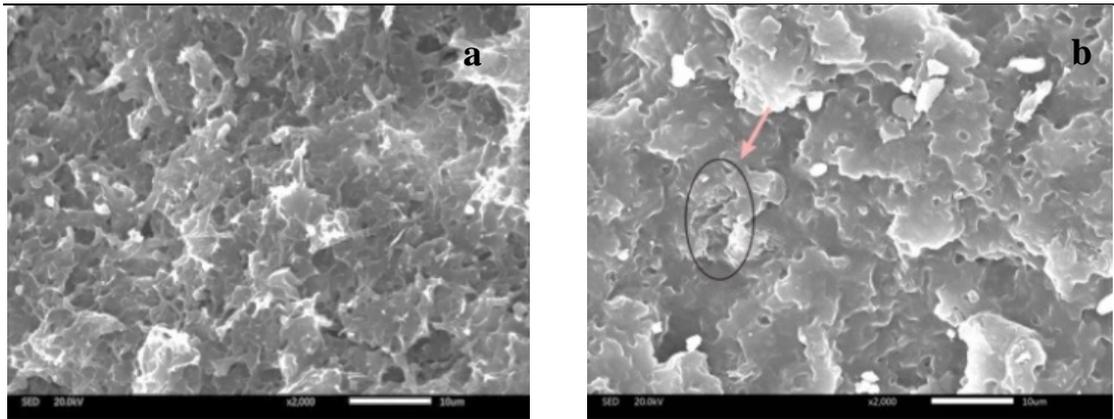
sample	T <sub>0.1</sub> <sup>a</sup> /°C	T <sub>0.5</sub> <sup>b</sup> /°C	T <sub>max</sub> <sup>c</sup> /°C
PP	437.3	465.6	466.2
2% TiO <sub>2</sub> -GO/PP	437.7	479.4	471.3
6% TiO <sub>2</sub> -GO/PP	459.5	482.9	484.5
10% TiO <sub>2</sub> -GO/PP	463.1	484.2	486.4

a-Temperature of 10% mass loss; b- Temperature of 50% mass loss;

c- Temperature of maximum mass loss.

### 3.3 Morphology analysis of the nanocomposites

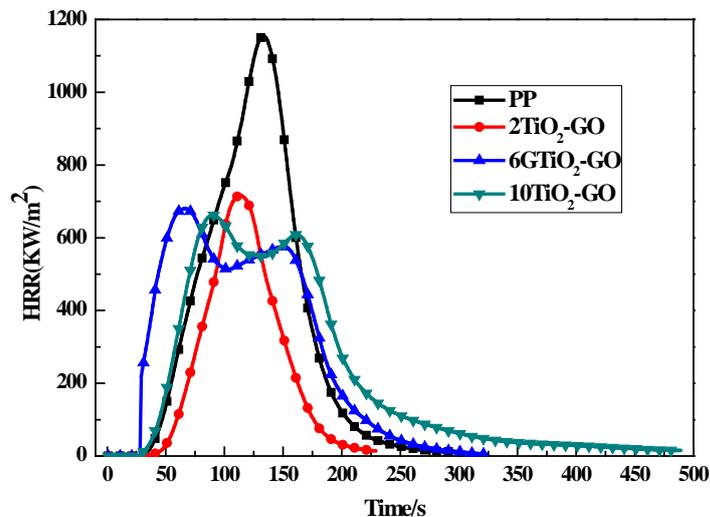
The dispersion state of nanofillers in a matrix is critical to the mechanical, thermal, and other properties of the composite. To investigate the morphological features of TiO<sub>2</sub>-GO in the PP matrix, SEM was used. Pure PP represents a smooth fracture surface, indicative of a typical brittle failure feature (Fig. 3a). With the introduction of 10 wt% TiO<sub>2</sub>-GO, the surface of TiO<sub>2</sub>-GO/PP composite will not become rough (Fig. 3b).



**Fig. 4.** SEM analysis of the freeze-fractured surface of (a)PP and (b) 10% TiO<sub>2</sub>-GO

### 3.4 Flame-retardation properties

Fig.4. shows the values of heat release rate (HRR) collected from the cone calorimeter. It is observed that the larger reduction of peak values of HRR was obtained in neat PP and TiO<sub>2</sub>-GO/PP exhibits the decline 10% in HRR compared with neat PP. The results can be attributed to the explanation that TiO<sub>2</sub>-GO nanosheets have better physical barrier effect. The cone results indicate that the TiO<sub>2</sub>-GO is potential as flame retardant.



**Fig. 4.** HRR curves of PP and its nanocomposites

## 4. CONCLUSIONS

In order to address the issue of the poor dispersion of graphene in PP resin, GO has been modified with TiO<sub>2</sub> and its TiO<sub>2</sub>-GO/PP composites have been fabricated using a master batch-based melt mixing method. The thermal stability of PP composites is improved to a certain extent. As a results, compared with no modified GO, the dispersion stability of TiO<sub>2</sub>-GO in PP was enhanced significantly which can explained by SEM. TGA showed an enhancement in thermal stability property of PP with TiO<sub>2</sub>-GO modified. HRR were decreased 10% .

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