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Tensile Properties of Graphene Nano-platelets Reinforced Polypropylene Composites

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ABSTRACT

The tensile properties of polypropylene (PP) composites filled separately with three kinds of graphene nano-platelets (GNPs) with different size were measured using a universal materials tester at room temperature and rate of extension of 50mm/min. It was found that the values of the Young's modulus of the composites increased, the values of the tensile yield strength and tensile fracture of the composites increased slightly while the values of the tensile elongation at break decreased with increasing the GNPs weight fraction. The reinforcement of the composites could be attributed to the relatively big interfacial area and good interfacial adhesion between the matrix and the GNPs.

Key words: A. polymer-matrix composites; A. Particle-reinforcement; A. Thermoplastic resin; B. Mechanical properties; D. Mechanical testing.

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1 Introduction

Polypropylene (PP) is one of general type thermoplastic resins, and it is used extensively owing to its ease of processing, light-weight, low cost, and high recyclability. However, the applications of PP are certainly limited due to some disadvantages, including high molding shrinkage, low stiffness, and poor impact toughness. PP is usually modified with the introduction of inorganic fillers, such as talcum powder [1], calcium carbonate [2, 3], mica [4], wood powder [5], metallic powder [6, 7], and glass fiber [8], carbon fiber [9] and Graphite-like carbon nitride and functionalized layered double hydroxide [10]. Graphene nano-platelets (GNPs) are a kind of planar thin sheet made of carbon atoms [11]. GNPs are extensively used in industry owing to good physical and mechanical properties, such as high specific strength and excellent conductivity [12, 13]. For instance, a small amount of GNPs can lead to a significant improvement in properties of polymers, including electrical properties [14, 15], thermal properties [16, 17] and mechanical properties [17-20]. Moreover, the thermal stability and flammability of PP can be improved with the addition of GNPs [21-24].

Mechanical properties including tensile, impact and flexural properties are important service performances. There have been a number of studies on the mechanical properties of PP composites, such as PP/glass bead [25], PP/nano-$CaCO_3$ [26], PP/$Mg(OH)_2$ [27] and PP/$CaSO_3$ [28] composite systems. However, there have been relatively few studies on the mechanical properties of PP/GNPs composites. Inuwa et al [18] measured the mechanical and thermal properties of exfoliated graphite nanoplatelets reinforced polyethylene terephthalate/polypropylene composites, and found that the values of the flexural and impact strength of the composites were maximum when the GNPs content was 3 phr.

Wang et al [19] investigated the mechanical properties of graphene/poly (vinyl alcohol) nanocomposites in the grapheme weight fraction range from 0 to 3wt.%, and the results showed that the value of the tensile strength of the nanocomposites was the highest when the grapheme weight fraction was 0.5wt.%. GNPs are thin sheet shape inorganic nanometer particles with different thickness. Then, how does the GNPs size affect the mechanical properties of polymeric materials? However, there have been relatively few studies in this field. Therefore, it is necessary to have an in-depth study on the reinforced mechanisms of polymer/GNPs composite systems. The objective of the present study is to investigate the influence of the size and content of GNPs on the tensile properties of PP/GNPs composites to discuss the reinforced mechanisms of the GNPs in the matrix.

2 Experimental

2.1 Materials

The polypropylene with trademark CJS-700, serving as the matrix material was supplied by the Guangzhou Petrochemical Works in Guangdong province (Guangzhou, China), and the density in solid state was 910 kg/m^3 and the melt flow rate was 10 g/10min (230^{o}C, 2.16 kg).

Three types of GNPs were selected as the fillers for investigating the effects of the size on the thermal stability of the composite systems. They are: (1) trademark SGNP-F01005 was supplied by the Nanjing Kefu Nano-Tech Co. Ldt (Nanjing, China), it was abbreviated as G1; (2) trademark HQNANO-GR-003 was supplied by the Suzhou Hengqiu Graphene Technol. Co. Ltd (Suzhou, China), it was abbreviated as G2; (3) trademark JCGNP-15-10 was supplied by the Nanjing Jichang Kefu Nano-Tech Co. Ldt (Nanjing, China), it was abbreviated as G3.

Table 1 Major characteristic of three GNPs

GNPs	Purity (%)	Specific surface area (m^2/g)	Flake thickness (nm)	Number of layers	Particle lateral dimension (μm)	Notes
G1	99.50%	> 200	≤5	1-6	< 10	Physical preparation no oxygen groups
G2	99.5%	40-60	5-25	> 10	0.5-20	Physical preparation no oxygen groups
G3	95%	150-200	3.4-7	6-10	10-50	Graphite intercalation production, a small amount of oxygen groups

2.2 Preparation

The PP was separately mixed with the three GNPs with different sizes in the high speed compounding machine (model GH-10) supplied by Beijing Plastics Machinery (Beijing, China), and then the PP/GNPs blends were melt-blended in a twin-screw extruder (model SHJ-26) supplied by Nanjing Chengmeng Machinery Ltd. Co. (Nanjing, China) at a screw speed of 100 rev/min and in a temperature range from 190 to 210°C, to prepare the three PP/GNPs composites: PP/G1, PP/G2 and PP/G3, in which the weight fractions of the GNPs were 0.1, 0.2, 0.3, 0.4 and 0.5 wt.%. The screw diameter was 26 mm, while the length to diameter ratio of the screw was 40. The granules of the fabricated composites were dried at 80°C for five hours before injection of the specimens.

The specimens for tensile test were molded by using a plastic injection machine with model UN120A supplied by Yizumi Precision Mechanism Ltd (Foshan city, China). The temperature was varying from 170 to 210^{o}C, and the mold temperature was from 40 to 50^{o}C.

2.3 Apparatus and methodology

The tensile tests of the PP/GNP composites were conducted at room temperature by means of a universal materials testing machine (model tensiTECH) supplied by Tech-Pro Inc. (Woodstock, USA) at room temperature, and the cross-head descending speeds was 50 mm/min. Each group specimens contained 5 pieces, and the average values of the measured tensile properties were used from the measured data.

3. Results and discussion

3.1 Relationship between tensile stress and strain

Figure 1 displays the relationship between tensile stress and strain of the PP/G1 composites. It can be seen that the values of the tensile strain at break decreases with increasing the GNPs weight fraction. Figure 2 presents the relationship between tensile stress and strain for the PP/G2 composites. When the GNPs weight fraction is smaller than 0.3wt.%, the values of the tensile strain at break are only slightly lower than that of the unfilled PP; while when the GNPs weight fraction is more than 0.3wt.%, the values of the tensile strain at break significantly decrease with increasing the GNPs weight fraction. Figure 3 illustrates the relationship between tensile stress and strain for the PP/G3 composites. Similar to the results shown in Figure 1, the values of the tensile strain at break decreases with increasing the GNPs weight fraction.

Moreover, it can also be seen from Figures 1 to 3 that the maximum values of the tensile stress of the composites are obviously higher than that of the unfilled PP. It means that there is a certain reinforced effect of the GNPs on the PP resin under these conditions.

3.2 Dependence of Young's modulus on GNPs content

Figure 4 shows the dependence of the Young's modulus on the GNP weight fraction of the PP/GNPs composites. It can be found that the values of the Young's modulus of the three composite systems increase with an increase of the GNPs weight fraction. This indicates that the stiffening effect of the GNPs on PP is significant. Under the same GNPs weight fraction, the values of the Young's modulus of the PP/G1 system are the highest, while the values of the Young's modulus of the PP/G3 system are the smallest. When inorganic particles are loaded into polymer materials, they will play a role of skeleton in the matrix, and the movement of molecular chains will be limited due to a number of physical crosslinking points between the GNPs and the matrix, leading to improve the stiffness of the composite systems. For a crystalline polymer, the inclusions will play a role of heterogeneous nucleation, leading to increase the crystalline degree or to change the crystal type structure, and to improve correspondingly the stiffness of the composite systems in this case. When the filler particles uniformly disperse in the matrix, the stiffness of polymer composites will increase with increasing the number of the inclusions. The smaller the particle size, the more number of the particles is under the same filler volume fraction. The lateral dimension of G1 particles is the smallest, while the lateral dimension of G3 particles is the biggest (see Table 1). Therefore, the values of the Young's modulus of the PP/G1 system are the highest, while the values of the Young's modulus of the PP/G3 system are the smallest.

3.3 Dependence of tensile strength on GNPs content

Figure 5 presents the dependence of the tensile yield strength on the GNPs weight fraction of the PP/GNPs composites. It is shown that the values of the tensile yield strength of the PP/G1 and the PP/G3 composite systems increase slightly with an addition of the GNPs weight fraction, and the relationship between them is almost linear. For the PP/G2 composite system, the values of the tensile yield strength also increase with increasing the GNPs weight fraction, and the value of the tensile yield strength is up to the maximum at the GNPs weight fraction of 0.1 wt.%. It is generally believed that the tensile strength including tensile yield strength and tensile fracture of polymer composites depends, to great extent, on the interfacial adhesion between the inorganic particles and resin matrix [29]. Consequently, it can be concluded from the results shown in Figure 5 that the interfacial adhesion between the GNPs and the PP matrix is strong in this case.

Figure 6 shows the dependence of the tensile fracture strength on the GNPs weight fraction of the PP/GNPs composites. It can be seen that the values of the tensile fracture strength of the PP/G1 and PP/G3 composites increase slightly with increasing the GNPs weight fraction. For the PP/G2 composite system, the values of the tensile fracture strength also increase with increasing the GNPs weight fraction when the GNPs weight fraction is lower than 0.3wt.%, and then decrease slightly with increasing the GNPs weight fraction, but the values of the tensile fracture strength are still higher than that of the unfilled PP.

As stated above, the tensile strength of inorganic particle-filled polymer composites is closely related to the interfacial adhesion between the inclusions and resin matrix. For an inorganic thin sheet shape particle, the interfacial adhesion effect of the composites under tensile load mainly depends, to great extent, upon the particle

lateral area (i.e. length × width) under the same interface adhesion between the inclusions and resin matrix. The sketch of a mechanical model of polymer composite filled with inorganic thin sheet shape particles in tension and the particle lateral size are shown in Figure 7. When a specimen of polymer composite filled with inorganic thin sheet shape particles is under tensile load, the matrix will generate relative deformation while the particles will be no deformation. Thus the interface being perpendicular to the load will bear tensile force, while the interface being parallel to the load will bear shear force. Therefore, the larger the specific surface area of the particle, the higher is the strength of the composite in a case of the same interfacial adhesion state. It is known from Table 1, the order of the specific surface area for three GNPs is: G1>G3>G2. Moreover, there are no oxygen groups on G2, and the interface adhesion between the inclusions and resin matrix is relatively weak. Therefore, the values of the tensile fracture strength of the PP/G2 are lower than those of the PP/G1 and PP/G3 composite systems. More recently, Zare [30] proposed a new model of tensile strength of polymer composites through introducing the specific surface area of the filler into the interfacial interaction parameter "*B*" in the Pukanszky's model. In addition, Zare and Garmabi [31] developed a model to assume the interphase properties in a ternary polymer nanocomposite reinforced with two nanofillers.

3.4 Dependence of tensile elongation at break on GNPs content

Tensile elongation at break is an important parameter for characterizing the ductility (or tensile fracture toughness) of materials. Figure 8 illustrates the dependence of tensile elongation at break on the GNP weight fraction of the PP/GNPs composites. For the PP/G1 and PP/G2 composite systems, the values of tensile elongation at break decrease slightly when the GNPs weight fraction is less than

0.1wt.%, and then decrease outstandingly with increasing the GNPs weight fraction. For the PP/G3 composites, the values of tensile elongation at break decrease with an increase of the GNPs weight fraction, and the values of tensile elongation at break are slightly lower than those of the PP/G1 and PP/G2 composite systems. As discussed above, the reinforcing and toughening effects enhance with increasing the filler specific surface area under the same interfacial adhesion status. Because the specific surface area of the G2 particle is the smallest in the three GNPs, the PP/G2 system has the worse ductility.

Figures 9, 10 and 11 present the pictures of the tensile fractured specimens of the three PP/GNPs composite systems. It can be seen that the values of tensile elongation at break decrease with an increase of the GNPs weight fraction. When the GNPs weight fraction was 0.1wt.%, the stress whitening phenomenon of the specimens for the PP/G1 and G2 composite systems is relatively obvious. These microcracks will absorb tensile fracture energy, to be beneficial to improve the ductility of the PP composites, resulting in increasing the tensile elongation at break of the specimen in this case (see Figure 8).

4. Conclusions

There were certain effects of the content and size of the graphene nano-platelets on the tensile properties of the filled polypropylene composites. The results showed that the values of the Young's modulus of the composites increased, and the values of the tensile yield strength and the tensile fracture of the composites increased slightly while the values of the tensile elongation at break decreased with increasing the GNPs weight fraction. The interfacial area between the GNPs and the matrix is relatively big owing the thin sheet shape of the inclusions. The reinforcement of the composites could be attributed to the good interfacial adhesion and relatively big interfacial area

between the GNPs and the PP matrix. This study provided a basis for further development of grapheme reinforced polymer composites with desirable mechanical performance and good damage behavior.

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Figure captions

Figure 1 Relationship between tensile stress and strain of PP/G1 composites.

Figure 2 Relationship between tensile stress and strain of PP/G2 composites.

Figure 3 Relationship between tensile stress and strain of PP/G3 composites.

Figure 4 Dependence of Young's modulus on GNPs weight fraction.

Figure 5 Dependence of tensile yield strength on GNPs weight fraction.

Figure 6 Dependence of tensile fracture strength on GNPs weight fraction.

Figure 7 Sketch of a tensile model of polymer filled with inorganic thin sheet shape particles.

Figure 8 Dependence of tensile elongation at break on GNPs weight fraction.

Figure 9 Pictures of tensile fractured specimens of PP/G1 composite.

Figure 10 Pictures of tensile fractured specimens of PP/G2 composite.

Figure 11 Pictures of tensile fractured specimens of PP/G3 composite.