Polymer Testing 70 (2018) 434–440

Contents lists available at ScienceDirect

Polymer Testing

journal homepage: www.elsevier.com/locate/polytest

Material Properties

Impact and flexural properties of polypropylene composites reinforced with multi-walled carbon nanotubes

Ji-Zhao Liang*, Shao-Yi Zou, Qiang Du

Key Laboratory of Polymer Processing Engineering, Ministry of Education, School of Mechanical and Automotive Engineering, South China University of Technology, Guangzhou 510640, PR China

ARTICLE INFO

Keywords:
Polymer composites
Nanoparticles
Mechanical properties
Reinforcement
Morphology

ABSTRACT

The effects of content and size of multi-walled carbon nanotubes (MWCNTs) on the impact and flexural properties of reinforced-polypropylene (PP) composites were investigated at room temperature. The results showed that the flexural modulus and maximum flexural stress increased with increase of the MWCNTs weight fraction, while effects of the diameter and average length-diameter ratio of the fillers on the flexural strength were insignificant. The effects of the size and content of the MWCNTs on the impact fracture toughness were significant, the Izod V-notched impact fracture strength increased roughly with increasing weight fraction and the average diameter of the MWCNTs, while it decreased with increasing length-diameter ratio of the MWCNTs. Finally, the reinforcing and toughening mechanisms of the PP/MWCNTs composites are discussed.

1. Introduction

It is generally believed that carbon nanotubes (CNTs) are widely applied in polymeric materials owing to their good electrical conductivity, thermal conductivity and mechanical properties. This is because CNTs have distinctive geometric structure including special seamless nanometer tube structure, large ratio of length to diameter and large specific surface area. The CNTs as tubes sometimes have open ends and sometimes capped ends [1]. When polymers are filled with CNTs, the mechanical and physical properties of the composites can be improved or some new properties can be obtained [2–6]. Some disadvantages of polypropylene (PP), such as high flammability, low strength, high notch sensitivity etc., can be improved by modification with CNTs to extend its scope of application. Since 2000, several methods for preparing polymer/CNTs composites have been proposed, such as submerged friction stir processing [6]. Dintcheva et al. [7] investigated the effect of elongational flow on morphology and properties of polymer/CNTs nanocomposites, including polyaminde-6 (PA), polystyrene (PS) and ethylene-vinyl acetate copolymer (EVA), and found that extensional flow led to higher mechanical properties and higher melt strength, but only a slightly reduced breaking stretching ratio. For PP/CNTs composites, these preparation methods include melt spinning [8], in situ polymerization [9], shear blending [10], solution blending [11] and melt blending [12,13]. CNTs usually include single wall carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). Because the cost of MWCNTs is much lower than that of SWCNTs, the applications of the former are wider than those of the latter. Chen et al. [14] found that MWCNTs supported by calcium pimelate could change from alpha-nucleation of MWCNT surface to beta-nucleation and induced beta-crystallization in MWCNT-filled PP nanocomposites. Jin and his co-workers [15] observed the different behavior in crystallization and melting temperature of PP/MA-g-PP/diamine-MWCNTs composite compared to PP and PP/neat-MWCNT. The decomposition temperature of the composite was increased by 50 °C compared to PP. PP/MA-g-PP/diamine-MWCNTs composite had the highest complex viscosity. More recently, Liang and his colleagues [1,16] studied the melt extrudate swell behavior of multi-walled carbon nanotube filled-PP composites, and investigated the effects of the size and content of MWCNTs on the melt flow properties of PP composites during capillary extrusion. The results showed that the melt shear viscosity increased with increase of the filler weight fraction, while it decreased with increasing the average diameter of the MWCNTs.

Impact and flexural properties are used to characterize the performance of polymeric materials. However, there have been relatively few studies on the mechanical properties of PP/MWCNTs composite systems, especially for studies on the influence of MWCNT size on the mechanical properties. The objectives in the present study are to investigate the influence of the size and content of MWCNTs on the flexural properties and impact fracture toughness of the PP/MWCNTs composites, and to discuss the reinforcing and toughening mechanisms

* Corresponding author.
E-mail address: scutjzl@sohu.com (J.-Z. Liang).

https://doi.org/10.1016/j.polymertesting.2018.07.029
Received 23 June 2018; Accepted 31 July 2018
Available online 01 August 2018
0142-9418/

Table 1
Major characteristics of MWCNTs.

MWCNTs type	$d_{average}$ (nm)	$l_{average}$ (μm)	l/d	ρ(g/cm³)	Specific surface area (m²/g)
CNT-2	19.12	32.0	1673	2.1	250–300
CNT-3	22.34	21.9	985	2.1	100–200
CNT-4	24.61	34.7	1382	2.1	> 140
CNT-8	45.72	12.7	278	2.1	> 40

of the composites.

2. Experimental

2.1. Raw materials

To identify the influence of the size and content of the fillers on the mechanical properties of the composite systems, four kinds of MWCNTs with different size (e.g. diameter, length-diameter ratio) were used, which were designated as CNT-2, CNT-3, CNT-4 and CNT-8. Table 1 lists the main size characteristics of the four MWCNTs [1]. It can be seen that the ranking of the average diameter of the four MWCNTs is: CNT-2 < CNT-3 < CNT-4 < CNT-8; while the ranking of the length to diameter ratio of the four MWCNTs is: CNT-2 > CNT-4 > CNT-3 > CNT-8. In other words, the values of the average diameter and the length to diameter ratio of the CNT-4 are slightly higher than those of the CNT-3.

All the MWCNTs were supplied by the Chengdu Organic Chemical Co., Ltd. (Chengdu, China), and prepared using a chemical vapor deposition method, with a purity of greater than 90 wt%. A PP with trademark CJS-700 used as the matrix was supplied by the Guangzhou Petrochemical Works in Guangzhou (China). The melt flow rate and density in the solid state were 10 g/10min (230 °C, 2.16 kg) and 910 kg/m^3, respectively. The melting temperature of the resin was 190 °C.

2.2. Preparation

Firstly, the surface of the four kinds of MWCNTs was pretreated applying an activating agent, and then the PP was mixed separately with the surface pretreated-MWCNTs in a high speed compounding machine (model GH-10) at a speed of 1000 rotations per minute starting at room temperature to improve the uniform distribution of the PP and the MWCNTs. The high speed compounding machine was supplied by the Beijing Plastics Machinery (Beijing, China) The weight fractions (ϕ_f) of the MWCNTs were 1, 2, 3, 4 and 5 wt%. To prepare the four PP/MWCNTs composites, the mixtures of the PP/MWCNTs were melt-blended in a twin-screw extruder (model of SHJ-26) supplied by the Nanjing Chengmeng Machinery Ltd. Co. (Nanjing, China) to improve the uniform dispersion of the MWCNTs in the PP matrix. During the melt-blending, the screw speed was 100 rev/min and the temperature range was from 190 to 210 °C. The screw diameter of the extruder was 26 mm, and the screw length-diameter ratio was 40. The four PP/MWCNTs composites were designated, respectively, as PP/CNT-2 system, PP/CNT-3 system, PP/CNT-4 system and PP/CNT-8 system. Finally, the granulated composites were dried at 80 °C for 5 h before mechanical specimen preparation.

The specimens for impact testing and flexural testing were prepared using an injection molding machine (model UN120A), which was supplied by the Yizumi Precision Mechanism Ltd (Foshan city, China). The injection temperature range was varying from 170 to 210 °C, and the mold temperature was from 40 to 50 °C. The specimen size (length × width × thickness for Izod and Charpy impact tests was 80 × 10 × 3 mm, the notch was V type and was at the center of the specimen length, the residual thickness behind the notch was 8 mm. The specimen size (length × width × thickness) for flexural tests was also 80 × 12.7 × 3 mm.

2.3. Instruments and methodology

The flexural tests of the PP/MWCNTs composites were conducted using a universal materials testing machine at room temperature. The tester with model 5566 was supplied by Instron Inc., (Boston, Massachusetts,USA). The span (i.e. the distance between the two supports), was 60 mm and the span to thickness ratio was 20, with the intention of measuring stiffness and maximum flexural stress, but not flexural strength. The center deflection at the end of the test was 16 mm, and the cross-head descending speed was 2 mm/min. Moreover, each group of specimens contained 5 pieces, and the average values of the measured flexural properties (including flexural modulus and maximum flexural stress) under these experimental conditions were used from the measured data.

The impact fracture toughness of the PP/MWCNTs composites was measured at room temperature applying a LCD type plastic pendulum impact testing machine which can conduct both Izod and Charpy tests. The pendulum impact testing machine model PIT501B-2 was supplied by the Wance test equipment limited company (Shenzhen, China). Similarly, each group specimens contained 5 pieces, and the average values of the measured impact fracture strength were used from the measured data.

The fracture surfaces of the specimens after impact testing were examined using a scanning electron microscope (SEM) to observe the impact fracture surface, interlayer structure morphology, interfacial debonding, and the dispersion or distribution of the MWCNTs in the PP matrix. The SEM model S-3700 N was supplied by the Hitachi Co. Ltd. (Tokyo, Japan). The fracture surface of the specimens was gold-coated before SEM examination.

3. Results and discussion

3.1. Flexural properties

3.1.1. Flexural load versus displacement curves

Fig. 1 shows the curves of the flexural load versus flexural displacement for the four PP/MWCNTs composites (i.e. (a) PP/CNT-2; (b) PP/CNT-3; (c) PP/CNT-4; (d) PP/CNT-8). It can be seen that the flexural load increases with increasing flexural displacement when flexural displacement is lower than 12 mm, then it starts to decrease. For the PP/CNT-2 system, the flexural load of the composite with the MWCNTs weight fraction of 5 wt% is the highest, the flexural load of the composite with the MWCNTs weight fraction of 4 wt% is lowest; while the flexural loads of the other composites are close to each other. For the PP/CNT-3 system, the influence of the MWCNTs content on the flexural load is insignificant. For the PP/CNT-4 system, the flexural load of the composite with the MWCNTs weight fraction of 1 wt% is lowest, while the flexural load for the other composite systems decreases slightly with increasing the MWCNTs weight fraction. For the PP/CNT-8 system, the flexural load of the composite with the MWCNTs weight fraction of 4 wt% is the highest, the flexural load of the composite with the MWCNTs weight fraction of 1 wt% is lowest; while the flexural loads of the other composites are close to each other.

3.1.2. Relationship between flexural modulus and MWCNTs content

Fig. 2 presents the relationship between the flexural modulus and MWCNTs weight fraction for the four PP/MWCNTs composites. The flexural modulus (E_f) is defined as follows:

$$E_f = \frac{\sigma_{f2} - \sigma_{f1}}{\varepsilon_{f2} - \varepsilon_{f1}} \tag{1}$$

where $\sigma_{f1}$is the flexural stress at flexural strain ε_{f1}, $\sigma_{f2}$is the flexural stress at flexural strain ε_{f2}, in this study, $\varepsilon_{f1} = 0.0005$, $\varepsilon_{f2} = 0.0025$. It was found that the flexural modulus increases with increasing MWCNTs weight fraction. This illustrates that introducing the MWCNTs into the PP matrix is beneficial to improve the flexural stiffness of the PP