Polymer 55 (2014) 1745–1755

Contents lists available at ScienceDirect

Polymer

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

Influence of ultrasonic treatment in PP/CNT composites using masterbatch dilution method

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A R T I C L E I N F O

Article history:
Received 7 December 2013
Received in revised form
1 February 2014
Accepted 3 February 2014
Available online 11 February 2014

Keywords:
Polypropylene
Ultrasound
Carbon nanotube

A B S T R A C T

Composites of polypropylene (PP) filled with multiwalled carbon nanotubes (CNTs) of various concentrations were prepared by a twin screw extruder using direct compounding (DC) method without and with ultrasonic treatment. In addition, a masterbatch of 20 wt% PP/CNT composites were prepared without and with ultrasonic treatment and diluted to the same concentrations as in the DC method without ultrasonic treatment. This is called the masterbatch dilution (MD) method. The rheological, electrical and mechanical properties were investigated. The microdispersion was determined using optical microscopy to correlate the processing, properties and structure. It was shown that the MD method provided better dispersion of CNT in PP matrix than the DC method. This was indicated by an increase of the storage modulus, viscosity, electrical and mechanical properties. The fractal dimension of CNTs, *D*, and the backbone fractal dimension, *x*, of the CNT network were determined by fitting the rheological data to the scaling model. The lower fractal dimension of CNT and higher backbone fractal dimension of CNT network in composites prepared by the MD method compared with composites obtained by the DC method indicated a better dispersion. Additionally, a lower *D* and a higher *x* values as well as the favorable effect on the morphology and mechanical properties were achieved when the ultrasonic treatment at an amplitude of 13 μm was applied in the MD method, indicating an advantage in use of the ultrasonic treatment in preparing the PP/CNT masterbatch.

1. Introduction

Since the report of Iijima's discovery of CNT in 1991 [1], CNTs were widely studied by the scientific community and used in many applications. One of the important applications is to reinforce the polymer materials to increase their modulus and tensile strength. However, during their synthesis process, CNTs grow to a ball of interconnected threads in scale of about hundreds of micrometers [2], termed as the primary agglomerate. Due to the highly attractive strength of the primary CNT agglomerates, it is very hard to obtain a uniform dispersion of individual nanotubes in the polymer matrix, which seems to be an unsolved problem [3], especially in the melt mixing.

The mechanism of dispersion of nano-filler agglomerates in polymer melts includes "onion peeling" mechanism [4,5] and "rupture" mechanism [6]. The rupture mechanism dominates when the shear stress exceeds a critical value that could separate the agglomerates in a short time [7,8]. However, the critical shear stress needed for rupture by the onion peeling mechanism is lower and requires a longer time [9]. Both of these two mechanisms are dependent on the stress transmitted from the polymer matrix to CNT agglomerates, which is strongly influenced by the polymer wetting on the CNT surface and polymer infiltration into the agglomerates. CNT is typically incompatible with polymers, especially non-polar polymers, such as PP and polyethylene. That would affect the wetting and infiltration process resulting in an incomplete dispersion. In order to achieve a better interaction between the host polymer and CNT, a widely known method of using a graft or a copolymer as a coupling agent was established. Zhou et al. [10] studied the effect of maleic anhydride grafted SEBS (MA-g-SEBS) in the PP/CNT composites, and found an improvement in the thermal, mechanical and anti-static properties. However, Lee et al. [11] reported that MA-g-SEBS slightly increased the electrical conductivity but almost did not make any change in rheological properties. Another way to increase the interfacial force is to modify the CNT surface by a chemical functionalization that induces groups or long chains to the surface in order to reduce the polarity of CNT and improve the compatibility of CNT and polymer

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http://dx.doi.org/10.1016/j.polymer.2014.02.014
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[12]. Lee et al. [11] used three methods (acid, amine and heat treatments) to pretreat CNT. They found that the heat treatment of CNT increased the storage modulus and complex viscosity of PP/CNT melt significantly. Yang et al. [13] grafted PP on the CNT surface and blended it with PP. The modified CNT showed a much better dispersion in PP and dramatically increased mechanical properties in comparison with the untreated one. Specifically, the tensile strength and Young's modulus were improved by 141% and 108%, respectively.

In contrast with the sophisticated chemical modification of polymer or CNT, a two-step processing can be used. In particular, a polymer/CNT masterbatch can be prepared first and then diluted with the polymer to increase the CNT dispersion. Although there is no thorough study on the mechanism of dispersion using the polymer/CNT masterbatch, it is generally accepted that a better dispersion is due to the high shear stress acting on the agglomerates during the second dilution step. There are two reasons for the better dispersion: (i) the high concentration of CNT in the masterbatch (usually higher than 10 wt%) leading to high viscosity [14]; (ii) the longer residence time due to the second processing step. On the other hand, this technique may induce some negative effects such as CNT shortening. Potschke et al. [15–17] used the masterbatch technique to process polycarbonate (PC)/CNT composites. They found masterbatch method is quite helpful to get a uniform dispersion of CNT in PC. They also showed that increasing mixing time could change the nonpercolated system into a percolated one near the percolation threshold, and the mixing devices chosen also affect the electrical percolation threshold.

The dispersion of CNT in different polymers shows different behaviors. For non-polar polymers, such as LDPE, high agglomerates area ratio with moderate nanotube shortening was observed [18]. However, for polymers exhibiting more polarity than polyolefins, such as in case of PC, much better macrodispersion was achieved with intensive nanotube shortening [18]. Even for a specific polymer, the dispersion cannot be generalized easily. The higher viscosity usually leads to a better dispersion, but the length shortening is also higher. PP is a non-polar polymer incompatible with CNT, therefore it is almost impossible to get a uniform dispersion and distribution of CNT in PP, and huge amounts of agglomerates always exist in the matrix [19].

Mičušík et al. [20] studied the effect of PP viscosity in diluting masterbatch. The best dispersion is obtained using the lowest viscosity PP. This indicates that chains of the lower molecular weight could easier penetrate into agglomerates of the masterbatch resulting in a better dispersion compared with the longer chains. Ganß et al. [21] prepared PP/CNT composites by premixing a PP powder with CNT (Nanocyl NC7000), and then adding the mixture into a twin screw extruder at a rotation speed of 300 rpm. The tensile stress and Young's modulus in the injection molding direction were increased by 20% and 30% without a decrease of the elongation at break as compared with pure PP. In all the other studies of PP/CNT, the elongation at break is usually decreased by more than 50% at high concentration of CNT (over 3 wt%) [22–27]. Lee et al. [28] studied the effect of PP-g-MAH compatibilizer on the rheological and electrical properties of PP/CNT composites. They claimed that there is no effect of the compatibilizer on these properties, because the compatibilizer could not provide sufficient wrapping of CNT. However, a contrary observation was reported by Prashantha et al. [23] indicating that PP-g-MA increased the storage modulus and viscosity, electrical and mechanical properties. Unlike the above literature which used the commercial concentrated masterbatch, Pascual et al. [27] prepared their own PP/CNT masterbatch and found that the tensile strength, Young's modulus and Vicat softening temperature are increased, but the elongation at break was substantially dropped.

CNTs are generally used in polymers to obtain conductive properties. Accordingly, a lot of research was done on the electrical properties of PP/CNT composites. The lowest percolation threshold of 0.22 vol% was reported by Tjong et al. [29] on a composite prepared in Haake mixer by intensive shearing at 200 rpm for 15 min. The electrical percolation threshold is influenced by many factors, including the length, diameter and packing density of CNT [21], the shortening of length in melt mixing [30], the dispersion of CNT in polymers [11], the extent of secondary agglomeration [31] and polymer viscosity [32]. The composites containing loosely packed CNTs, such as Nanocyl NC7000, achieve lower percolation threshold than those with densely packed CNTs, such as Baytubes C150P [33].

Although a lot of studies have been carried out on PP/CNT composites using masterbatch technique, the detailed and systematic investigations were limited. Therefore, in the present study, the PP/CNT masterbatch is first prepared, then the rheological, electrical, mechanical and morphological properties of composites prepared using masterbatch dilution (MD) method are compared with those prepared using direct compounding (DC) method. It is known that high power ultrasound is quite a useful tool to separate filler agglomerates in melt state during compounding [34,35]. To the best of our knowledge, this is the first study to use the ultrasonic treatment during compounding of CNTs in polymer melt using the masterbatch method. The processing-structure-properties of composites treated without and with application of high power ultrasonic treatment during melt extrusion were also studied in details.

2. Experimental

2.1. Materials

The PP used for preparing PP/CNT composites is metallocene i-PP (Achieve grade 3825) supplied by Exxon Chemical Company. Its melt flow rate is 32 g/10 min (230°C/2.16 kg, ASTM D1238). CNTs of Baytubes C150P (carbon purity ≥95 wt%, diameter 4–13 nm, length >1 μm) made by chemical vapor deposition (CVD) were purchased from the Bayer Material Science AG.

2.2. Preparation of PP/CNT composites

The PP/CNT composites are prepared using a co-rotating twin-screw micro-extruder (Prism USALAB 16, Thermo Electron Co., UK) modified by installing an ultrasonic treatment section in the barrel close to the exit of the extruder, as shown in Fig. 1. The diameter of the screws is 16 mm and L/D is 25. The ultrasonic power supply (Branson Ultrasonics Corp., CT) which consists of a converter (Branson Ultrasonics Corp., CT), booster and water cooled titanium horn generates ultrasound at a frequency of 40 kHz. The ultrasonic

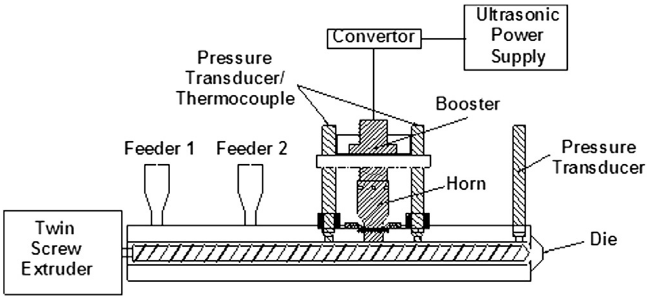

Fig. 1. Schematic of the ultrasonic twin-screw extruder.