Influence of twin screw extrusion processing condition on the properties of polypropylene/multi-walled carbon nanotube nanocomposites

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Abstract

Polypropylene/multi-walled carbon nanotube (PP/MWNT) nanocomposites were prepared in a twin screw extruder using masterbatch dilution technique. The nano-dispersion state of the nanotube in polymer matrix was estimated using rheological measurement, SEM and TEM. The effects of melt viscosity of PP and processing conditions such as screw speed and screw L/D ratio on the dispersion state and electrical property of the PP/MWNT nanocomposite were investigated. According to rheological and electrical properties, nanocomposite based on lower viscosity polypropylene has better performance compared to that based on the higher viscosity PP. As the screw speed increased the viscosity of PP/MWVT composite was increased but further increase in screw speed resulted in the decreased viscosity, which may be due to possible defects in MWNT. The mechanical properties of nanocomposites as increasing contents of MWNT were also investigated with the processing conditions.

Keywords: polypropylene, multi-walled carbon nanotube, nanocomposite, masterbatch dilution, melt-compounding, twin screw extrusion

1. Introduction

Carbon nanotubes (CNTs) are cylindrical graphitic structures characterized by a diameter of 10–40 nm and a length up to millimeters. CNTs play a crucial role in current material science due to superb mechanical strength (Ajayan et al., 1996; Baughman et al., 2002), high thermal and chemical stability, excellent electric and heat conduction (Collins and Avouris, 2002; Frank et al., 1998). The remarkable physical and electrical properties of CNTs result from the chemical nature of the sp²-bonded carbon, and their nanometric diameter combined with their length. Due to these CNT properties, one of important applications of CNT is as reinforced fibers in polymer composites. CNT diameter size not only play an important role for producing proximity to the molecular interactions, the small diameter with long extensions also result in high aspect ratios in nanotubes, which is an important requirement in reinforcing composites (Baštík and Baštík, 2008). Another important characteristic of CNTs has been shown when these nanoscale materials are stressed, and when the stress is released, CNT can recover their original forms. This flexibility is yet another indication that these materials may serve as possible reinforcements in composites, given that neither carbon fibers nor other known reinforcements present this property (Harris, 2004).

The addition of CNT can cause significant change in viscoelasticity for the nanocomposites. Some researchers reported a transition to solid-like response at low oscillation frequencies in polymer nanocomposites containing carbon nanotubes (Zhang et al., 2006; Xiao et al., 2007; Ganß et al., 2008). This solid-like rheological behavior is attributed to a filler network in the nanocomposites. The formation of the network structure strongly depends on the concentration and dispersion states of nanotubes in polymer matrix. But carbon nanotubes have a tendency to form agglomerates during synthesis because of van der Waals' attraction between nanotubes. In the composites, these agglomerations decrease the surface area and disturb the formation network structure which is essential to improve mechanical and electrical properties.

Polypropylene (PP) is one of those most versatile polymers available with applications in virtually all of the plastics end-use markets because of its well balanced physical and mechanical properties and easy processability at a relatively low cost (Mihaela and Olaru, 1993). Specifically, isotactic PP is a commodity thermoplastic with a high consumption and its impact on industry is significant. Conventional method to improve its mechanical properties has been incorporation of micro-fillers including mica, tale, glass fiber, carbon black, etc. with typical micro-filler contents of 20–30 wt%. With these contents, the resulting composites may have decrease in properties such as light-
weightness, toughness, thermoform ability. However, only very small amounts of CNT are required to improve the mechanical and electrical properties.

General methods for the preparation of CNT filled polymer composites include in situ filling polymerization, solution mixing and melt blending. Unlike the other methods, melt processing of nanocomposites provides the cost effectiveness, fast production rate and environmental benefits (Abdel-Goad et al., 2007). The melt processing is a more practical method of producing CNT-polymer composites and is particularly interesting for industrial scale processes. Among available melt processing techniques twin screw extrusion may provide some advantages over other techniques due to its effective dispersion performance. In twin screw extrusion, several factors determining the state of dispersion have been reported, such as the properties of the polymer matrix (Hotta and Paul, 2004), and the type and concentration of compatibilizer used (Lertwimolnum and Vergnes, 2005). Electrical percolation threshold also seems to be dependent on the matrix material or process used (Bauhofer and Kovacs, 2009). However, the effect of these parameters is not fully explained and related to the dispersion results.

The purpose of this paper was to examine the effect of processing condition and viscosity of matrix polymer on the dispersion of PP/MWNT nanocomposites by melt processing. Rheological properties were reported for composites based on the different processing condition, such as screw speed, feeding rate. These materials were characterized on rheological, mechanical and electrical properties, and morphology of nanocomposites also investigated by transmission electron microscopy.

2. Experimental

2.1. Materials

Two kinds of isotactic PP were used as the base polymer resin: MOPLENE HP522H (MI=2 g/10 min, ASTM D1238, Polymirae), YUHWA POLYPRO 4017 (MI=8.5 g/10 min, ASTM D1238, KOREA PETROCHEMICAL), it termed high viscous polypropylene (HVPP) and low viscous polypropylene (LVPP) respectively. MWNT were produced by CVD process and obtained from Nanocyl (NC7000). The purity of the MWNTs was 90%. The diameter of carbon nanotubes was 9.5 nm the length was 1.5 μm. MWNT was heated at 80°C under vacuum for 12hr to eliminate any volatile substances. Antioxidant (Igafos 1010, Ciba Special chemical) were also used to reduce thermal and mechanical oxidation.

2.2. Preparation of PP/MWNT composites

The PP/MWNT nanocomposite was prepared by diluting highly concentrated MWNT masterbatch chips. One of the most general processing methods is the masterbatch process which is one of the simplest method in processing. In this study, we investigated the characteristics of PP/MWNT nanocomposites on masterbatch base twin screw extrusion system. Masterbatch was prepared using co-rotating twin screw extruder (SM Platek, TEK-25, L/D=41). MWNT was contained 15 wt% in HVPP.

The dilution was done for two kinds of polypropylene in a co-rotating twin screw extruder (Technovel Corporation, KZW 15TW, L/D=105) at barrel temperature of 160–200°C. High L/D ratio may promote good dispersion of clay platelets in a much longer residence time (Dong and Bhattacharya, 2008). The screw of this extruder could be divided into L/D 50 conditions to confirm the effect of large L/D ratio for dispersion of nanocomposites. Fig. 1 shows the configuration of twin screw extruder (KZW 15TW) for L/D 105 and L/D 50. It was composed of screw conveying elements, left hand screw, kneading and mixing element to promote dispersive and distributive mixing. The operating temperature profile for extruder varied from 130°C at the feed section to 200°C at the die. We investigated the effect of processing condition such as screw speed, feeding rate, L/D ratio for PP/MWNT nanocomposites.

Fig. 1. Schematic representation of screw configurations for L/D=105 and L/D=50 in twin screw extruder.
2.3. Characterization

An ARES rotational rheometer (Rheometric Scientific) was used to measure the complex viscosity and modulus. Parallel-plate fixture, diameter 25 mm, with a gap size of 1.0 mm was used. The frequency range was 0.03–400 rad/sec and strain amplitude was kept enough value (10%) to ensure a linear viscoelastic response of the polymers. The measurements were performed at 200°C. All samples were compression molded into a disk of 25 mm diameter and 2 mm thickness by using a hot press at the same temperature as the barrel temperature of the extruder.

In order to assure the dispersion states in nanocomposites, morphology of nanocomposites was confirmed with a scanning electron microscope (SEM, Hitachi S-2500, 25 kV). Cryo-fractured PP/MWNT nanocomposites were mounted on a standard scanning electron microscopy. We also checked the state of nanotube in matrix polymers by transmission electron microscope (TEM, JEOL 2010F) operating under an accelerating voltage of 120 kV. Ultrathin sections of approximately 50 nm thickness were cryogenically cut with a diamond knife while cooled using liquid nitrogen at temperature of −60°C using an RMC PowerTome XL microtome.

Electrical properties were evaluated using surface resistivity measurement (SRM-110, WOLFGANG). Samples were molded using hot press (CARVER laboratory press) with rectangular size (3 mm × 13.5 mm × 65 mm) to check surface resistance. Because the surface resistivity is very sensitive to temperature and humidity, all measurements were conducted at 23°C, 50% RH according to ASTM D257.

Tensile test of nanocomposites was investigated using a universal testing machine (UTM, LR-5K from Lloyd Co.). The crosshead speed was fixed at 5 mm/min for all of the specimens and measurements for each case were performed more than at least 5 times. The geometry of specimen corresponds to ASTM D638.

3. Results and Discussion

3.1. Rheological properties

3.1.1. Effect of screw L/D ratio and PP melt viscosity

Screw L/D ratio is expected to influence the properties of nanocomposites in twin screw extrusion system. Fig. 2 shows complex viscosities of HVPP/3 wt% MWNT and LVPP/3 wt% MWNT nanocomposites processed in the twin screw extruder with different L/D ratios. The extrusion at screw speed was 200 rpm and feeding rate was 0.4 kg/hr. In low frequency region, from Fig. 2(a), the complex viscosity of HVPP/MWNT nanocomposite prepared with the L/D 105 extruder is higher than that of the nanocomposite with L/D 50. This indicates that high L/D ratio with long residence time is effective in dispersing nanotubes in high viscosity polypropylene matrix. But in Fig. 2(b) for the LVPP matrix, opposite result was obtained. The complex viscosity of LVPP/MWNT nanocomposite prepared with the screw L/D 105 extruder is lower than that of the nanocomposite with L/D 50. It seems that with long L/D the dispersion state of the LVPP/MWNT composite is reduced compared with that with shorter L/D.

Comparing the shapes of complex viscosity curves of HVPP and LVPP nanocomposites (Fig. 2 (a) and (b)), LVPP-MWNT nanocomposites clearly show more shear thinning behavior at low frequencies. Wagener and Reisinger (2003) proposed the value of shear thinning exponent at low shear rate range as a semi-qualitative measure of nanodispersion of the nanocomposites. The increase of shear thinning of LVPP-MWNT nanocomposite can be interpreted as the enhancement of the dispersion of...
MWNT in LVPP. High melt viscosity of HVPP could increase the shear stress in melt blending (Ganß et al., 2008; Lertwimolnum and Vergnes, 2005), thus it could easily depart the individual nanotubes. But, long PP chain with high viscosity characteristics appears to be not effective in penetrating into agglomerate of MWNT. For the dispersion in LVPP/MWNT nanocomposites, penetration into agglomerated MWNT by low viscosity of PP is more effective. It seems that the effective penetration of LVPP into the nanotube agglomerates is more important than the higher load transfer capability of HVPP into the agglomerates in overall dispersion of nanotubes in the matrix.

3.1.2. Effect of MWNT concentration

Fig. 3 (a) and (b) show the complex viscosity and storage modulus of HVPP/MWNT nanocomposites with varying MWNT contents processed at screw speed of 200 rpm, feeding rate of 0.40 kg/hr and L/D ratio of 105. In Fig. 3 (a), the complex viscosity of the pure PP shows Newtonian behavior at low frequency range. As the MWNT content is increased the filled samples exhibit an increase in melt complex viscosity. At 3 wt% MWNT concentration, the complex viscosity in low frequency range is significantly increased and the curve shape is different from those for lower MWNT concentrations. The complex viscosity at 3 wt% MWNT concentration tends to diverge as the frequency is decreased. The change in the shape of the curve indicates that a transition from liquid-like to solid-like behavior has occurred and the 3 wt% MWNT concentration can be regarded as rheological percolation threshold. In nanocomposites, a steep increase in complex viscosity at low shear rate region is attributed to an indication of yielding phenomena resulting from network structure of highly delaminated or disordered system. The storage modulus curves for filled and unfilled MWNT composites shown in Fig. 3 (b). The neat PP and the PP/MWNT composites with the concentration up to 2 wt% show fully relaxed and terminal behavior with scaling property, approximately by \( G' \propto \omega^2 \), but as the MWNT concentration increases the storage modulus is increased and becomes independent of frequency at the low frequency range indicating non-terminal behavior. The non-terminal behaviors can be attributed to a percolated network structure (Galgali et al., 2001; Solomon et al., 2001; Ren et al., 2000).

Fig. 4 (a) shows the Van Gurp Palman plot for HVPP/MWNT nanocomposites at screw speed 200rpm, feeding rate 0.4 kg/hr and L/D ratio 105. In this plot, PP/MWNT nanocomposites indicates that a transition from the liquid-like to solid like behavior has taken place and the system with 3 wt% MWNT can be regarded as rheologically percolated. Below 3 wt% of MWNT, the curves approach a phase angle of 90 degree indicating a viscous behavior, but at 3 wt% of MWNT the rheological behavior changes from a viscous fluid to an elastic solid indicating a percolation threshold (Abdel-Goad et al., 2007).

3.1.3. Effect of screw rotational speed

The complex viscosity of 3 wt% HVPP/MWNT nanocomposite with changing screw rotational speed is shown in Fig. 5. At low screw rotational speed (100 rpm), the complex viscosity of nanocomposite is low because of the agglomerates of MWNT in matrix polymer. As the screw rotational speed is increased to 200 rpm the complex viscosity jumped to higher value but further increase in the screw rotational speed results in the decrease in the complex viscosity of the nanocomposite. The deterioration is probably due to structural change of MWNT by high shear stress. The fact that the complex viscosity of the composite is highest at the screw rotational speed of 200 rpm indicates that the nanocomposite has reached the highest dispersion state at 200 rpm.
3.2. Electrical properties

Fig. 6 shows the electrical properties of LVPP/MWNT and HVPP/MWNT nanocomposites at the screw rotational speed of 200 rpm, the feeding rate of 0.4 kg/hr and L/D of 105. For both PP/MWNT nanocomposites, surface resistance was dramatically reduced at the MWNT concentration between 2 wt% and 3 wt%. This decrease in the surface resistance suggests the formation of a conductive network formed through hopping and tunneling processes in the PP-MWNT nanocomposite (Wang and Dang, 2005). Therefore, the electrical percolation threshold of the PP/MWNT composites could be located at the MWNT concentration between 2 wt% and 3 wt%, which is similar to the rheological percolation threshold as previously shown. Moreover, above the electrical threshold the surface resistance of the LVPP/MWNT nanocomposite is lower than that of the HVPP/MWNT nanocomposite. The difference in electrical properties of both composites is related to the difference in the degree of dispersion for MWNT in matrix polymer for both composites. Because of the enhanced penetration of low viscosity matrix polymer into the MWNT agglomerates, the nanotubes in LVPP/MWNT nanocomposites were effectively dispersed, as can be seen in Van Gurp Palman plot, Fig. 4. It seems that the more enhanced dispersion state of LVPP/MWNT nanocomposite caused the lower surface resistance of the composite.

Fig. 7 shows the effect of screw speed in electrical properties of 3 wt% PP/MWNT nanocomposites. The screw speeds seem to have influence on the state of MWNT in nanocomposites. At the screw rotational speed of 200 rpm, PP/MWNT nanocomposite has the lowest resistance. This result is caused by the highest dispersion state without any defect of nanotubes at screw rotational speed 200 rpm. At 100 rpm screw speed, MWNT seems to agglomerate, but
as increase of screw speed, 400 and 600 rpm, MWNT may defected by high shear stress. This result is in good agreement with the complex viscosity result shown Fig. 5.

3.3. Morphology

The dispersion states of nanocomposites with different processing conditions were observed by scanning electron microscope images of cryo-fractured surfaces of 3 wt% HVPP/MWNT nanocomposites as shown in Fig. 8. From Fig. 8(a) and (b), it is observed that as screw rotational speed is increased from 100 rpm to 200 rpm the agglomerates size is reduced. The high shear stress at high screw rotational speed obviously enhances the dispersion of HVPP/MWNT nanocomposites. Without high shear stress, Fig. 8(a), MWNT agglomerated due to the strong attractive force originating from high van der Waal’s force and entanglements between individual MWNT fibers. Fig. 8(b) and (c) explain the effect of L/D ratio of the extrusion system for 3 wt% HVPP/MWNT nanocomposites. The bigger agglomerates size is evident for the composite processed in smaller L/D ratio (50 L/D). This result is in agreement with the complex viscosity result shown in Fig. 5.

Fig. 9 shows TEM images of MWNT dispersed within the HVPP matrix with increasing the screw rotational speed. From Fig. 9(a) and (b), in low shear (100, 200 rpm) operating condition MWNT agglomeration is detected, but in high shear operating condition (400, 600 rpm), agglomerates size of the MWNT is decreased. But note that the length scales of nanotubes for the screw speed of 400 and 600 rpm are significantly reduced compared with those for the screw speed of 100 and 200 rpm. It seems that the carbon nanotubes are defected by high shear. Remember that the rheological property and electric conductivity deteriorated with the screw speed above 200 rpm as seen in Figs. 5 and 7, respectively. It seems that the main factor which determines the deterioration is the MWNT deflection by high shear.
3.4. Mechanical properties

The mechanical properties of HVPP/MWNT nanocomposites prepared in feeding rate 0.4 kg/hr, L/D 105 ratio with different contents of MWNT and different screw rotational speed are shown in Fig. 10. In Fig. 10(a) the tensile strength of the iPP/3 wt% MWNT nanocomposites extruded with 200 rpm shows the highest value among other screw rotational speeds. This enhancement of the mechanical properties was attributed to the better dispersion of MWNT in the PP matrix as seen in previous results(Figs 5 and 7). In comparison with neat HVPP, the HVPP/MWNT nanocomposites exhibited higher Young’s modulus and tensile strength, and this enhancement was more pronounced in the case of the optimum processing condition of the current system (3% MWNT and 200 rpm). On the incorporation of 3 wt% MWNT, the Young’s modulus of PP/MWNT nanocomposites was improved by 57% and the tensile strength was improved by 20% relative to neat PP.

4. Conclusions

PP/MWNT nanocomposites were prepared with co-rotating twin screw extruder. The effect of processing conditions and extruder characteristic on the dispersibility of nanocomposites are investigated. Rheological results show that storage modulus and complex viscosity were increased with the enhancement in MWNT dispersion. The large L/D ratio of extruder is effective for HVPP/MWNT nanocomposites. But in LVPP/MWNT nanocomposites reaggregation may occur. Screw speed is a strong factor to improve dispersion of MWNT in polypropylene. High screw speed enhanced the dispersion of nanocomposites by imposing high shear during processing, but too high speed also may generate mechanical degradation of nanocomposites. Well dispersion of MWNT in polypropylene matrix could more effectively transfer stress and also build up the electron pathway than aggregated MWNT. Thus mechanical and electrical properties of HVPP/MWNT nanocomposites mixed with 200 rpm and large ratio extruder length of diameter are more improved than nanocomposites mixed with the other conditions. Morphology of nanocomposites also confirmed the dispersion states of MWNT in polymer matrix.

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