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Effect of crystalline structure on morphology and properties of MWCNT nanocomposites

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Abstract

We have studied the properties of MWCNT composites based on a polypropylene (semi-crystalline) and a polycarbonate (amorphous) matrix. Nanocomposites were prepared under different mixing conditions by diluting highly concentrated masterbatches. To promote nanotube dispersion in polypropylene nanocomposites and in order to investigate the effect of dispersion level on the properties of nanocomposites, different types of maleic anhydride grafted polypropylene were used including Polybond PB3150, Polybond PB3002 and Epolene E43. The state of dispersion was further analyzed by Scanning Electron Microscopy (SEM). The electrical percolation threshold of the PP/MWCNT composites is somehow less than of the PC composites; however, the percolation threshold and the conductivity level after threshold are completely dependent on nanotube dispersion in nanocomposite. Based on DSC results, the crystallinity of PP/MWCNT samples increased with the MWCNT content.

Introduction

Solid state nanomaterials such as carbon nanotubes (CNTs) are novel materials with extraordinary electrical, mechanical and thermal properties and represent an excellent potential as fillers for different composite materials. Particularly, polymer-based composites of CNT are suitable for the fabrication of microscale components where only grams of materials are necessary to manufacture high-valued products. However, the efficiency of nanotubes to live up to their theoretical potential depends on a good dispersion within the host material.

Carbon nanotubes are well dispersed in polar polymers such as poly (methyl methacrylate)(PMMA)[1] and polycarbonate (PC) [2]. However, in non-polar polymers such as polypropylene, CNT dispersion remains a big challenge. For instance high degrees of crystallinity, in polypropylene, result in a poor compatibility and

adhesion towards other materials and inorganic fillers. It has been found that in PP/clay nanocomposite, crystallization of the PP matrix, led to clay platelets expulsion from the crystalline phase by thermodynamic forces [3].

To improve dispersion and exfoliation of nanotubes in polymers, several techniques have been proposed [4, 5]. In polypropylene, compatibility can be improved by matrix modification using a suitable compatibilizer such as maleic anhydride grafted polypropylene (PP-g-MA). Strong hydrogen bonding between hydroxyl groups of the nanotubes and maleic anhydride groups of PP-g-MA may result in a nanoscale dispersion of the nanotubes in polypropylene [5, 6].

In the present study, we aim to investigate the effect of polarity and crystallinity of neat polymer on the CNT dispersion and nanocomposite properties. The attention was focused on two kinds of polymer: polycarbonate (PC) as a polar amorphous polymer and isotactic polypropylene (iPP) as a non-polar semi-crystalline polymer. We also used three types of compatibilizer to improve nanotube dispersion and to analyze the effect of compatibilization on the properties of polypropylene based nanocomposites.

A variety of characterization methods were then employed to examine the subsequent effects of nanotube loading on the crystallinity and electrical conductivity of polymer/CNT composites.

Experimental Procedure

The nanocomposites were prepared by diluting highly concentrated MWCNT masterbatches of 15 wt% and 20 wt% MWCNT in PC and PP respectively. The masterbatches were purchased from Hyperion Catalysis International, Cambridge, MA. The nanotubes are about 15-50 nm in diameter and 1-10 μm in length. PC/MWCNT masterbatch was diluted with PC (Calibre 1080) from DOW Chemical using a twin screw extruder operating at 100 rpm and 210 °C. Isotactic polypropylene (PP HD120) supplied by Borealis Co. was used to dilute PP/MWCNT masterbatch using twin screw extruder. The

best and the worst mixing conditions were found through a set of controlled experiments by changing mixing temperature and screw speed. Nanocomposites with different nanotube loadings were then prepared at 250 rpm and 190°C as the best mixing condition and at 100 rpm and 250°C as the worst conditions. In an attempt to promote better dispersion in polypropylene nanocomposites samples to be investigated, we also tried to improve the quality of dispersion in the original PP/MWCNT masterbatch by extruding it alone at 250rpm and 250°C. Another set of nanocomposites samples with various nanotube loadings were then prepared by diluting of this extruded masterbatch at the best mixing conditions (250rpm and 190°C). Furthermore, to critically compare the performance of the various compatibilizers, nanocomposites with 3 wt% MWCNT were prepared using 3 wt % of different maleic anhydride grafted polypropylenes including Polybond PB3150 with 0.5 wt% MA, Polybond PB3002 with 0.2 wt% MA and Epolene E43 with 2.9 wt% MA. All compatibilizers were dried at 70°C for a minimum of 4 h under vacuum.

The morphology of nanocomposites was then studied to investigate the effects of nanotube concentration, mixing conditions and compatibilization on the final properties. For the morphology and the dispersion degree, we used scanning electron microscopy (SEM). High resolution Hitachi S-4700 microscope was used in this study. For PC nanocomposites, SEM was done on ultramicrotomed surfaces of samples cut with a diamond knife at room temperature. However, in the case of PP nanocomposites the samples surfaces were chemically etched. by acid treatment. Employing this method, the amorphous phase of polypropylene is eliminated from the surface by chemical treatment at the surface of the samples and only crytalline phase remains which support the nanotubes. Therefore we could see the quality of dispersion much better in this method rather than using ultramicrotomed surface of samples. SEM samples were coated with a vapor deposit of Pt for 25 s.

The volume resistivity was determined using two types of Keithley electrometer: model 6517 for resistive samples, before percolation, and Keithley 6220 for more conductive samples after percolation. For each sample the I-V curve was obtained and the sample resistance was determined from the slope of the curve. The resistance was then converted to volume resistivity, ρ_v , using the formula

$$\rho_v = AR_v / L \quad (1)$$

where A is the surface area, L is the thickness of the sample, and R_v is the measured resistance.

The thermal behavior of PP/MWCNT nanocomposites was characterized using TA instrument Q-100 differential scanning calorimetry (DSC). Samples were heated at 10°C/min to 260°C then cooled to 25 °C before starting a second heating at the same rate to the same final temperature.

Results and Discussions

In this study, we first investigated composites of PP/3 wt% MWCNT prepared in the twin screw extruder, to find suitable mixing conditions. Figures 1(a) and 1(b) show SEM photomicrographs of melt-mixed nanocomposites prepared at the best and the worst mixing conditions respectively. Big white spots in these figures are representative of nanotube aggregates within the PP matrix as figure 1(d) shows clearly. Even though the quality of dispersion is relatively better in figure 1(a), the presence of large aggregates of nanotube even at the best mixing condition indicates that polypropylene is a difficult host in the sense that the carbon nanotubes were not fully dispersed as individual entities. Improving the mixing conditions resulted in significantly smaller aggregates with uniform distribution within the matrix; however, the nanotubes were not dispersed in nanocomposites at nano or even microscale in this case.

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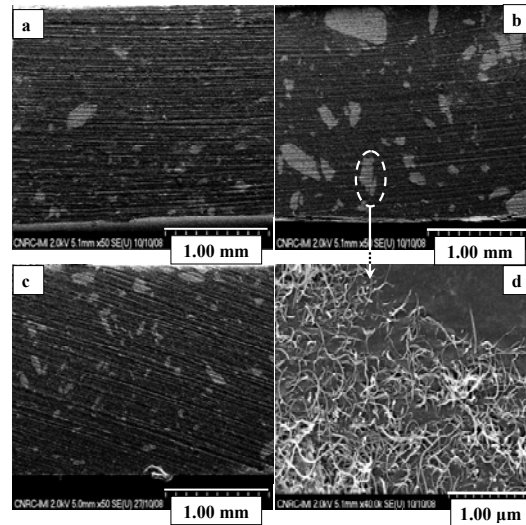


Figure 1. SEM micrographs of etched surfaces of PP / 3wt% MWCNT nanocomposites extruded at (a) 190 °C and 250 rpm and (b) 250 °C and 100 rpm (c) 190 °C and 250 rpm using extruded masterbatch. (d) an aggregate of nanotubes at high magnification).

In an attempt to improve the situation we used a two steps procedure to prepare the nanocomposites. First the masterbatch of 20 wt% MWCNT in polypropylene was extruded at 250 rpm and 250°C. The high mixing temperature was required because the masterbatch viscosity was too large to obtain an easy flowing melt in the twin screw extruder.. The extruded masterbatch was then diluted to various loading levels, at the best

conditions established previously. Figure 1(c) shows the SEM micrograph of nanocomposite prepared with this new procedure. The quality of dispersion improved slightly but, nanotube aggregate are still found in the nanocomposites.

The effect of the maleic anhydride compatibilizer on the nanotubes state of dispersion is examined next using three types of PP-g-MAH. Figure 2 shows the SEM micrographs of compatibilized samples using (a) Epolene-E43, (b) Polybond 3002 and (c) Polybond 3150. It seems that Polybond 3150 (figure 2(c)) gives rise to the smallest aggregates and the highest degree of dispersion with the presence of some individual ropes of MWCNTs as can be observed in figure 1(d), at higher magnification. This was the only case where we could observe nanotube dispersion at micro scale so clearly. The lowest dispersion is achieved when using Epolene-E43 which had the lowest molecular weight and the highest maleic content. Obviously, Polybond 3002 results in an intermediary degree of dispersion.

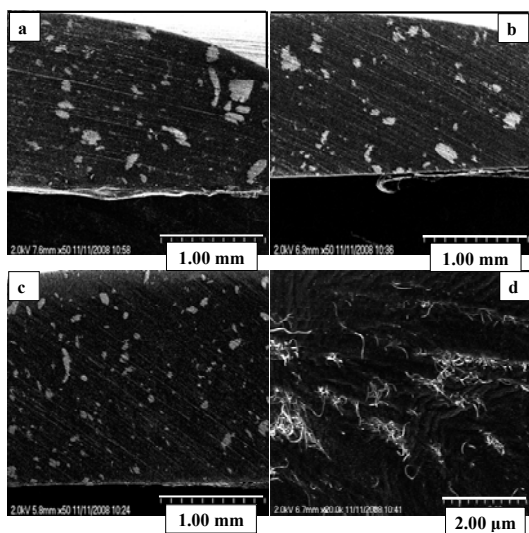


Figure 2. SEM micrographs of etched surfaces of PP / 3wt% MWCNT / MA-g-PP nanocomposites (a) Epolene E43 (b) Polybond 3002 (c) Polybond 3150 and (d) Polybond 3150 at higher magnification.

SEM micrographs of PC/MWCNT nanocomposites are shown in figure 3. It is observed that the nanotubes are dispersed almost individually in the matrix and not many nanotube bundles can be seen; even though, the distribution at the microlevel is not uniform there is no big aggregates of nanotubes like those observed in the PP/MWCNT system. These results reveal clearly the big difference between compatibility of MWCNT with polycarbonate as a polar and amorphous polymer and with polypropylene as a non-polar polymer with high

degree of crystallinity. Due to formation of strong polar-polar bonds, nanotubes are better dispersed in polycarbonate without formation of considerable aggregates; however, at polypropylene the lack of such polar bonds results in a poor dispersion of the nanotubes. In addition, the growth of the crystalline phase in the later case may have resulted in the expulsion the nanotubes towards the amorphous phase and led to formation of big aggregates in the PP-based nanocomposites [7].

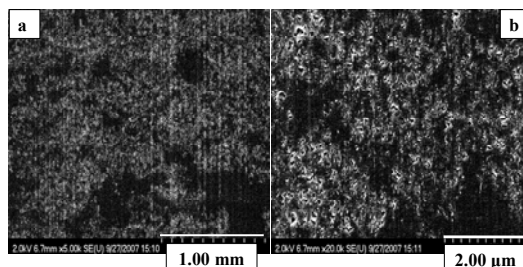


Figure 3. SEM micrographs of crayon surfaces of PC / 5wt% MWCNT nanocomposites.

Figure 4 shows the effect of nanotube dispersion on the electrical resistivity of PP nanocomposites.

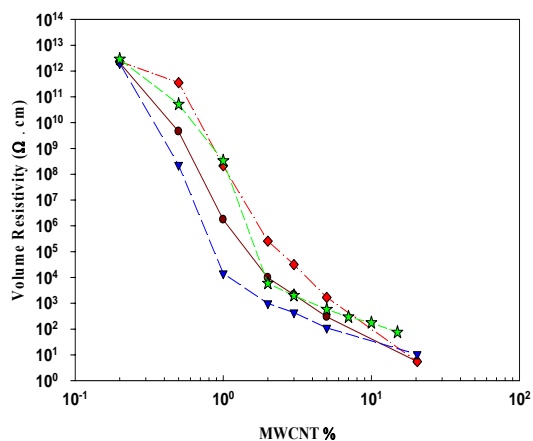


Figure 4. Electrical resistivity of PC (green marks) and PP/MWCNT nanocomposites with different level of dispersion. (samples prepared by dilution of extruded masterbatch, samples prepared at the best mixing condition using original (non-extruded masterbatch) and samples prepared at the worst mixing condition using original masterbatch are denoted with blue, brown and red marks respectively).

As it is observed, better quality of dispersion, or alternatively smaller aggregates, result in a lower percolation threshold. The conductivity level is also

altered significantly by the dispersion level. The resistivity of samples with the highest degree of dispersion (according to the SEM results) is nearly two orders of magnitude lower than the samples with large aggregates of nanotube in them. Figure 4 also compares the electrical resistivity of PP and PC nanocomposites. The electrical resistivity of PP nanocomposites, in the case of good dispersion of nanotubes, is relatively lower than PC nanocomposites with much better dispersion. Obviously the presence of a crystalline phase in the polypropylene nanocomposites facilitates the formation of electrical conductive networks and therefore the percolation threshold and the electrical resistivity of the corresponding samples are moderately lower.

Interestingly, the effect of nanotube dispersion on the electrical conductivity has not always the same trend. Figure 5 shows the volume resistivity of PP/3 wt% MWCNT at various dispersion levels. This figure reveals that there is an optimum level of nanotube dispersion or aggregate size in which the electrical conductivity is at the maximum level. In this case, improving the dispersion by adding PP-g-MAH led to less conductivity of nanocomposites.

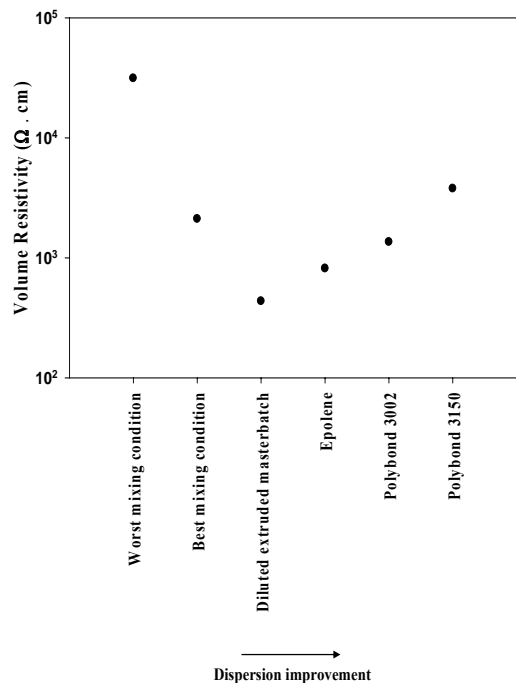


Figure 5. Effect of nanotube dispersion on electrical resistivity of PP/3 wt% MWCNT nanocomposite.

DSC crystallization and melting peaks from first cooling and second heating cycles for neat polypropylene and PP/ MWCNT nanocomposites are given at figure 6. It

shows that the maximum temperature of crystallization peak increases and the onset of melting point decreases with nanotube loading suggesting that nanotubes act as nucleating agent in nanocomposites. The melting peak is also broadening due to the formation of crystals of various sizes. The enthalpy of fusion slightly increases with nanotube loading which indicates minor increases in crystallinity percentage.

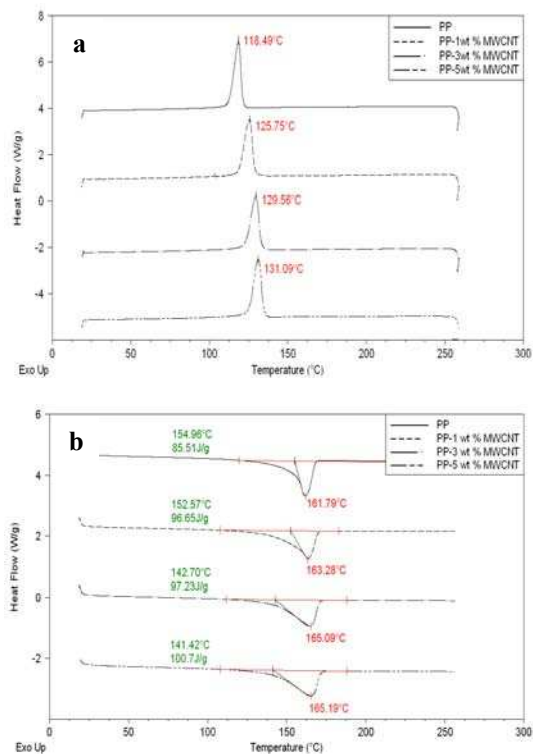


Figure 6. DSC crystallization plots for neat PP and PP/MWCNT with various nanotube loading. (a) first cooling cycle (b) second heating cycle.

The crystallization and melting data have been summarized in table 1. The percent of crystallinity is calculated assuming the enthalpy of melting of 207J/g for 100% crystalline polypropylene [6].

Table 1. Non-isothermal crystallization and melting parameters for nanocomposites with various MWCNT loading.

NT %	T _C (°C)	T _M (°C)	Enthalpy (J/g)	Crystallinity (%)
0	118.49	161.79	85.51	41.3
0.2	123.81	162.70	87.32	42.2
0.5	124.10	163.18	91.23	44.1
1	125.75	163.28	96.65	46.7
2	127.51	163.82	96.95	46.8
3	129.56	165.09	97.23	47.0
5	131.09	165.19	100.70	48.7

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Key Words: Multiwalled carbon nanotubes, Nanocomposites, Polycarbonate, Polypropylene, Morphology, Electrical resistivity, Differential scanning calorimetry

Conclusions

PC/MWCNT and PP/ MWCNT nanocomposites were prepared by diluting masterbatches containing 15 and 20 wt% MWCNT respectively. Different mixing conditions and various PP-g-MAH type compatibilizers were used to investigate the effect of processing conditions on nanotubes dispersion. The microscopic analysis reveals that in comparison to polycarbonate, the compatibility of polypropylene with carbon nanotubes is much less and even in presence of PP-g-MAH as a compatibilizer, big aggregates are found in this system. Measurements of the electrical resistivity show that the electrical percolation threshold and the conductivity level depend on the nanotube dispersion and aggregate size within the matrix. Our conductivity results indicate that there is an optimum level of dispersion and aggregate size at which nanocomposites electrical conductivity is highest. The crystalline structure can also affect the electrical resistivity and can lead to more conductivity and a lower percolation threshold. It is also found that the addition of nanotubes to polypropylene increases the percent of crystallinity suggesting that nanotubes act as nucleation agents in nanocomposites.

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