EFFECT OF CNT ON THE MECHANICAL PROPERTIES OF MELT SPUN PET/CNT NANOCOMPOSITE FIBERS

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Abstract
A co-rotating twin screw extruder with 3 zones of mixing elements was used to produce nanocomposite fibers of polyethylene terapthalate (PET) and carbon nanotubes. The PET and the CNT materials were fed using two separately controlled feeders. The polymer was fed at the first entrance to the extruder; whereas, the CNT was fed at three different positions located along the extruder barrel. The results showed that an addition of 1 wt% CNT enhanced the mechanical properties of PET/CNT nanocomposite fibers. The yield strength, tensile strength, and toughness were increased by 80%, 51%, and 134%, respectively, in contrast to the mechanical properties of pristine PET fibers. The scanning electron microscope (SEM) images showed that the feeding position with three mixing zones gives the most uniform distribution of CNT and the best spinnability of the PET/CNT fibers.

1 Introduction

Polymer composites are used in variety of industrial and household applications. Efforts are being made to increase the range of applications of polymer composites by modifying with organic and inorganic nanomaterials such as carbon nanotubes, carbon nanofiber, nanoclay, nanosilica and other nanomaterials. The blending of these organic and inorganic nanomaterials in polymeric matrix is not an easy task. The major hurdle in preparing these blends is the agglomeration of nanoparticles within the matrix [1-4]. It is very important to consider an effective mixing method to have a good dispersion of these nanomaterials within the polymer matrix. Several methods have been tried in literature to achieve effective mixing using different techniques. Some of the methods such as twin screw extrusion [4-9], melt compounding and kneading [5, 10, 11], ball milling or hand mixing [5], ultrasonic homogenizing [12] and rheomix mixer using roller type rotors [5] have been tried to obtain a good mixing of these organic/inorganic nanomaterials with the polymers.

In the present work PET/CNT nanocomposite fibers are produced using melt extrusion technique. The article includes the investigation of the effect of CNT feeding position on the on the quality of PET/CNT nanocomposite fibers. Further, the morphology and mechanical properties of these fibers are discussed.

2 Experimental

2.1 Extrusion and Melt Spinning Process

A Thermo Haake® twin screw extruder as shown in Figure 1 was used to produce the nanocomposite fibers. This extruder was designed with an L/D ratio of 40. All the heating zones and the screw speeds were externally controlled with a computer. The temperatures of the melt were measured using thermocouple sensors and the pressure at the extruder exit was measured with a pressure sensor. The torque required to turn the screw was electronically displayed and recorded on the computer. The pellets were fed into the extruder barrel through a metered feeder at a constant mass flow rate. A motor drove the extruder screws and its speed could be controlled as desired. The pellets melt in the extruder and then the melt was pushed through an adaptor die located at the exit of the extruder. The melt then was flown through a melt pump to the ten-hole spinneret (die) at a constant mass flow rate of 3.5 g/min. The hole diameter was 0.75 mm. The fibers were air cooled with the ambient air. The fibers were then spooled onto a drum using a motor winder. The twin screw extruder had seven controllable heating zones and three mixing zones with mixing elements. A temperature profile between 270°C - 290°C was selected by considering the processability, polymer degradation and the equipment limitations. The melt pump speed was set at 3 rpm and the temperature was set at 280 °C to pump the material to the spinneret die. An extruder screw speed of 20 rpm was used and a pressure of 14 to 46 bars was maintained at the extruder die exit.

For blending the CNT with PET, a separate feeder was used in addition to the pellet feeder as shown in Figure 1. The feeder was externally controlled using a computer. The PET pellets were fed through the first feeder. The CNTs were simultaneously fed into the extruder barrel from the second feeder. The feed rates were controlled and calibrated so as to obtain the CNT/PET blend ratios of 1wt%.

2.2 Materials

A Commercial grade Poly (ethylene terephthalate) (PET) material (grade: BC-112) supplied by SABIC was used for fiber production. The properties of PET as indicated by the supplier are intrinsic viscosity 0.84 dl/g and bulk density 838 kg/m3. High aspect ratio Multi-wall Carbon nanotubes (MWCNTs) shown in Figure 2, were produced using chemical vapour deposition (CVD) process. The CNT materials were heat treated in the Lindberg/Blue furnace at 375 °C for the duration of 24 hours. Further, the moisture was removed from the PET pellets and the CNTs by keeping them in the vicinity of temperature of 120 °C for the minimum duration of 10 hours under vacuum before the run.

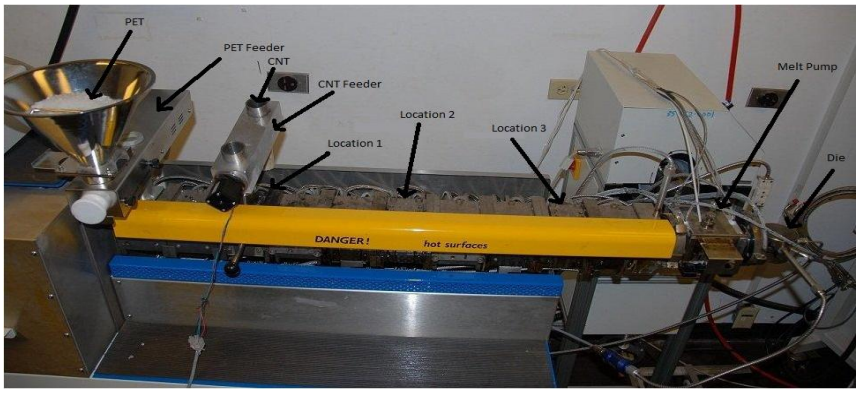

Figure 1. Positioning of the feeders on the extruder.

2.3 Scanning Electron Microscopy

JEOL® 6400 Scanning Electron Microscope was used to study the size and quality of the CNT produced in the laboratory. It was also used to observe the distribution and alignment of CNT on the fracture surface of PET/CNT nanocomposite fibers. Samples were gold coated using a sputtering instrument.

2.4 Tensile Test

Lloyds® tensile testing machine was used for testing PET/CNT nanocomposite fibers in tension. Specimens of nanocomposite fibers were cut to a gauge length of 25 mm and their diameters were measured using the optical microscope. These specimens were then placed on a paper window frame. The fibers were stretched at a controlled rate of 50 mm/min. A load cell of 100 N was used for the tensile tests. The tensile properties such as the yield stress, ultimate tensile strength, modulus, strain and toughness were determined from the tensile test plots. Modulus was obtained by determining the slope of initial curve of the Stress-strain plot. The toughness was calculated as the area under stress-strain curve. Five samples were tested at each condition and the average values of the properties were reported.

3 Results and Discussion

In order for the composite fibers to have better mechanical properties the high aspect ratio CNT needs to be properly distributed and aligned along the fiber axis. A good distribution of CNT within the PET matrix was achieved by incorporating mixing elements along the extruder screw. A constant concentration of 1wt% CNT was considered for observing the effect of mixing elements on the CNT distribution in the nanocomposite fibers.

The PET polymer and CNT are fed in to the extruder by two separately controlled feeders. The PET pellets are fed at the entrance, whereas the CNT is fed at three different positions on the extruder barrel where the mixing zones are located (Figure 1). The addition of CNT was found to increase the diameter of nanocomposite fibers. The extruded fiber diameters are plotted as a function of CNT feeding positions and shown in Figure 3. It was also observed that the diameters for extruded fibers decreased with CNT feeding position from 1 to 3. The average diameter of pure PET fibers was 256 µm. The average diameters of PET/CNT nanocomposite fibers were 535, 505, and 430µm at positions 1, 2, and 3, respectively.

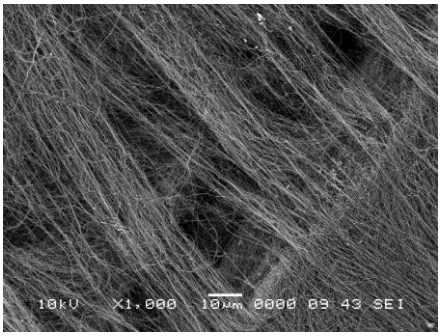

Figure 2. SEM micrographs of aligned MWCNT

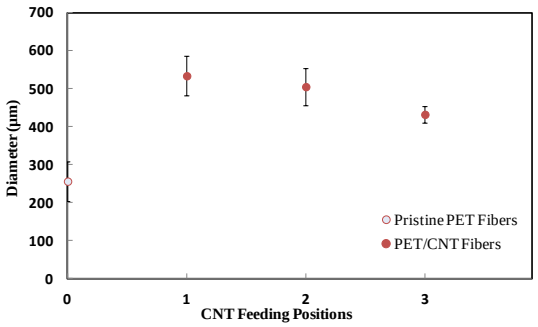

Figure 3. Fiber diameter from CNT feeder positions

Figure 4 to Figure 6 shows the SEM micrographs of PET/CNT nanocomposite fibers using different CNT feeding positions i.e. position 1, position 2 and position 3, respectively. It can be observed that the fibers produced using CNT feeding position 1 (Figure 4) and 2 (Figure 5) have good distribution of CNT and the CNT are aligned along the length of the fibers. However, fibers produced from CNT feeding position 3 (Figure 6) have poor distribution of

CNT in the PET matrix and show clear agglomeration of CNT on one side and no CNT on other side.

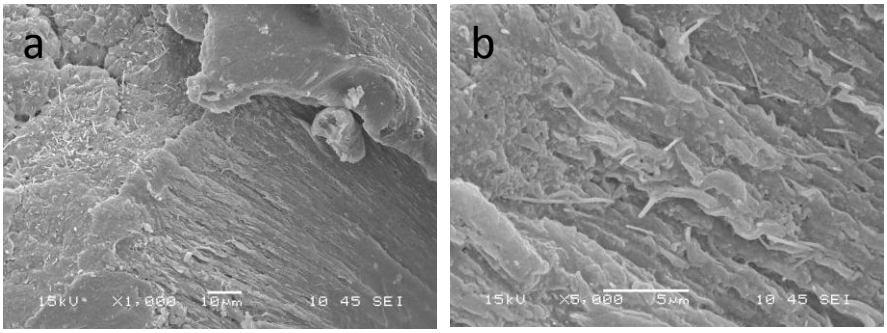

Figure 4. Fracture surface of extruded PET/CNT nanocomposite fibers produced with CNT feeder at Position 1 (a) Lower magnification and (b) Higher magnification

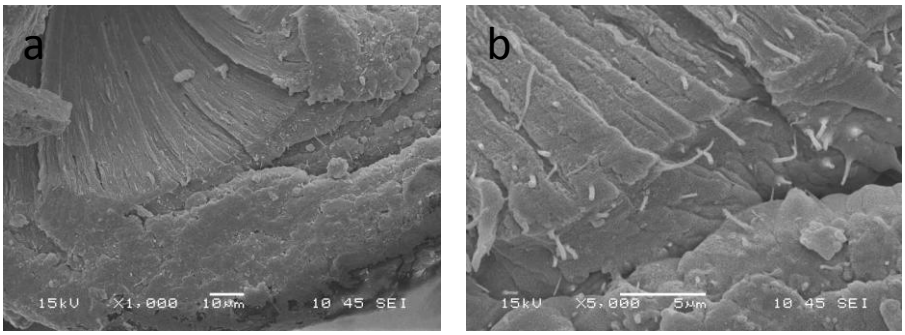

Figure 5. Fracture surface of extruded PET/CNT nanocomposite fibers produced with CNT feeder at Position 2 (a) Lower magnification and (b) Higher magnification

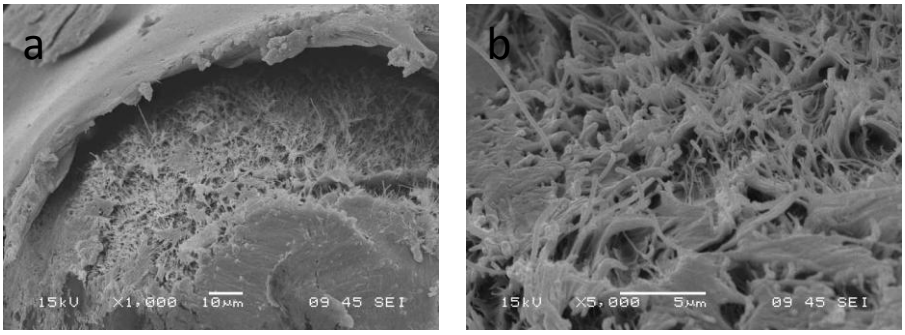

Figure 6. Fracture surface of extruded PET/CNT nanocomposite fibers produced with CNT feeder at Position 3 (a) Lower magnification and (b) Higher magnification

The mechanical properties of pristine PET, and PET/CNT (1wt %) nanocomposite fibers obtained with three different CNT feeding positions. The modulus was obtained from the slope of the stress-strain curve in the linear region and the toughness was determined by computing the area under the stress-strain curve.

The polymer PET and CNT are fed by two separate feeders. The PET pellets are fed at the entrance, whereas the CNT is fed at three different positions on the extruder barrel where the mixing zones are located. The parameter feeding position of CNT was studied to investigate the quality of PET/CNT nanocomposite fibers. A constant CNT concentration of 1wt% was considered for the present study. The average modulus of PET/CNT nanocomposite fibers showed small increase from 1.62 GPa (pristine PET) to 1.82, 1.95, and 1.76 GPa from

position 1, 2 and 3, respectively. Similar effect was observed in the work of Mezghani et al. [13] that is the modulus obtained for the LLDPE/CNT nanocomposite fiber was twice stiffer than the pure LLDPE fibers by addition of just 1 wt% CNT in LLDPE matrix. In the present study, the modulus PET/CNT nanocomposite fiber was found to have about 20% increment. The improvement in this property was due to good distribution and alignment of CNT in polymer matrix shown in SEM micrographs of Figure 4 and Figure 5. It shows better distribution of CNT in PET matrix of nanocomposite fibers obtained with the CNT feeding positions 1 and 2 when compared to that of position 3 (Figure 6). The CNT distribution is the main reason for the difference in the modulus improvement with respect to the feeding position. Moreover, the CNT are stiffer than pure PET, hence addition of CNT enhanced the stiffness of final nanocomposite fibers, the same was evident from Mun et al. [14] work. In addition, well distributed CNT has an impact on mechanical properties of nanocomposite fibers such as yield strength, tensile strength, strain at break and toughness.

The average yield strength of PET/CNT nanocomposite fibers produced using different CNT feeder positions are shown Figure 7. The addition of CNT via position 1 enhanced the average yield strength of pure PET fiber from 35 to 49MPa i.e about 40% increment. Similarly, addition of CNT through position 2 and 3 enhanced the average yield strength of the nanocomposite fibers by about 31 and 14 % increment, respectively as compared to the pure PET fiber. Tensile strength of PET/CNT nanocomposite fibers with respect to CNT feeder positions are shown in Figure 8. The average tensile strength of nanocomposite fiber increased to 77MPa, compared to pure PET fiber of 51MPa. This was observed for both the CNT feeding position 1 and 2. Whereas addition of CNT through position 3, showed marginal difference in tensile strength of 52 MPa, compared to pure PET fibers. A 24% increment in tensile strength was possible due to addition of 1wt% CNT in pure PET fibers.

The increment in tensile strength and yield strength was due to good distribution of 1 wt % CNT in PET/CNT nanocomposite fibers. SEM micrograph (Figure 4 and Figure 5) shows the well distributed CNT in PET matrix of nanocomposite fibers obtained with CNT feeding position 1 and 2. The well distributed CNT has good adhesion to the polymer matrix as observed from pulled out fibers. On the other hand, agglomeration of CNT in PET matrix was observed for the PET/CNT nanocomposite fibers produced with CNT feeder at position 3 as shown in SEM micrograph (Figure 6). Hence, 51 and 40% increments in yield and tensile strength was observed for the PET/CNT nanocomposite fibers obtained with CNT feeder position 1 as shown in Figure 7 and Figure 8, respectively. Similar effect of increase in tensile strength have been shown for the addition of CNT into polymer matrix by Kim et al. [15]. It was reported that the tensile strength of PET/MWCNT nanocomposite increased by about 29% (77.8MPa). Mun et al. [14] reported that adding low content of 0.5wt% Ph3P-MWNT has the highest tensile strength of 64 MPa of PET/modified CNT nanocomposite fibers, which is about 40% higher than that of pure PET fibers (46 MPa). Similarly, Mezghani et al. [13] reported that 1wt% CNT content in LLDPE matrix enhanced the tensile strength by 40%. This increment in the tensile strength was attributed to the good distribution and enhanced interfacial adhesion between CNT and polymer matrix which makes the composite more favourable for effective load transfer from the polymer matrix to the nanotubes.

The strain at break for the fibers is shown in Figure 7. A 21% increase in strain at break of the fibers was observed with CNT addition via position 1 compared to position 3. Furthermore, compared to pure PET fibers, 97, 92 and 63% enhancement of strain at break of PET/CNT nanocomposite fibers was achieved due to addition of 1wt % CNT through position 1, 2 and 3, respectively. The toughness of the as extruded and drawn fibers was determined for the

three feeding positions studied as shown in Figure 8. The average toughness of the extruded fibers decreased from 369 to 246 MPa for position 1 to position 3, respectively. An increment of 50% was observed in the toughness of PET/CNT nanocomposite fibers produced with position 1 compared to position 3. A very marginal difference in average toughness was observed for extruded PET/CNT nanocomposite fibers with CNT feeding positions 1 and 2. However, significant improvement in the toughness was observed in nanocomposite fibers compared to pristine PET fibers. Among all the feeding positions studied, position 1 had the highest average toughness of PET/CNT nanocomposite fibers with an increase of 135%, compared to pristine PET fibers of 157MPa as shown in Figure 8. Likewise, compared to toughness of pristine PET drawn fibers, nanocomposite fibers achieved 122 and 57 % improvement due to addition of CNT through position 2 and 3, respectively. This improvement is due to the good distribution of CNT in the polymer matrix achieved from the feeder position 1.

Similar effect has been shown by some researchers [4, 13] that the improvement in the strain at break and toughness is due to good distribution of CNT in polymer matrix. Initially, in the nanocomposite fibers, the CNT are randomly oriented however, during tensile test the CNT try to orient itself with molecular chain towards the tensile direction. Thus, the strain at break and toughness of PET/CNT nanocomposite fibers increased compared to pristine PET fibers.

In general, the addition of 1 wt% CNT through position 1 of the twin screw extruder produced nanocomposite fibers with good mechanical properties. A good mixing of CNT with PET was achieved due to the presence of several mixing elements in the twin screw extruder. This resulted in a uniform CNT distribution in the PET matrix which in turn improved the tensile strength, yield strength, strain at break and toughness of the nanocomposite fibers. Furthermore, when the PET/CNT nanocomposite fibers were melt spun it was observed that the minimum reachable diameter was obtained with CNT feeder position 1 compared to position 2 and 3 as shown in Table 1. Thus, nanocomposite fibers produced using CNT feeder position 1 not only had good mechanical properties but also exhibited good spinnablity compared to other CNT feeder positions. Other studies [4] show that the melt spinning has an effect on the alignment of CNT in PET matrix that in return improves the mechanical properties.

Position	**Minimum Reachable Diameter –[µm]**
1	39
2	131
3	171

Table 1. Influence of CNT feeding position on the diameters of PET/CNT nanocomposite fibers.

4 Conclusion

The PET/CNT nanocomposite fibers containing 1 wt% CNT was produced using melt spinning process. Good distribution of CNT was achieved by using an extruder with good mixing capability. In this study, a co-rotating twin screw extruder with 3 zones of mixing elements was used to produce PET/CNT nanocomposite fibers. The CNT is fed at three different positions on the extruder barrel where the mixing zones are located. The parameter CNT feeding position was studied to investigate the quality and mechanical properties of PET/CNT nanocomposite fibers. It was observed that the addition of 1 wt% CNT through position 1 significantly enhanced the mechanical properties of extruded PET/CNT

nanocomposite fibers compared to other position 2 and 3. A good mixing of CNT with PET was achieved due to the presence of several mixing elements in the twin screw extruder. This resulted in a uniform CNT distribution in the PET matrix which in turn improved the tensile strength, yield strength, strain at break and toughness of the nanocomposite fibers. The toughness increased by 135% compared to the pristine PET polymeric fiber. The strain at break (ductility) increased by 97%, the yield strength by 40% and the tensile strength by 51% in contrast to the mechanical properties of pristine PET fiber. This huge increase in mechanical properties of PET/CNT nanocomposite fibers is attributed to the presence of CNT, and its distribution and alignment in the PET matrix. SEM showed a good distribution of CNT in PET matrix. Furthermore, when the PET/CNT nanocomposite fibers were melt spun it was observed that the minimum reachable diameter was obtained with CNT feeder position 1 compared to position 2 and 3 as shown in Table 3. Thus, nanocomposite fibers produced using CNT feeder position 1 not only had good mechanical properties but also exhibited good spinnablity compared to other CNT feeder positions.

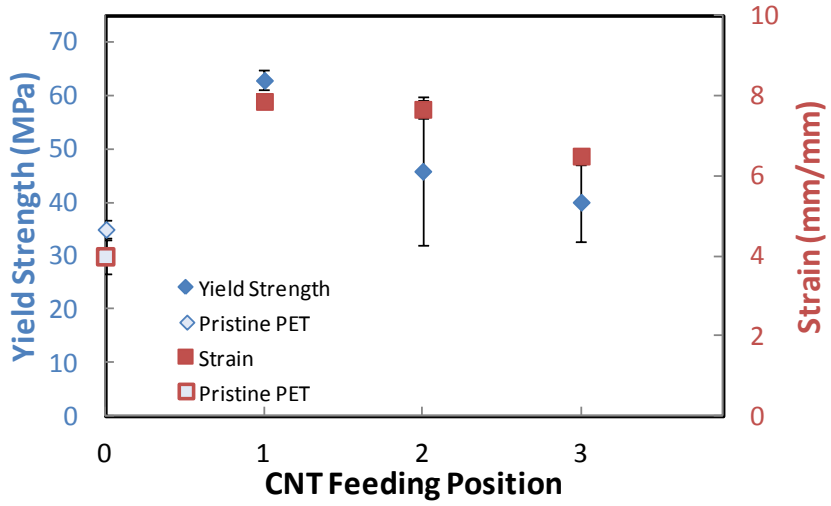

Figure 7. Yield strength and strain at break for nanocomposite fibers produced from different CNT feeding positions.

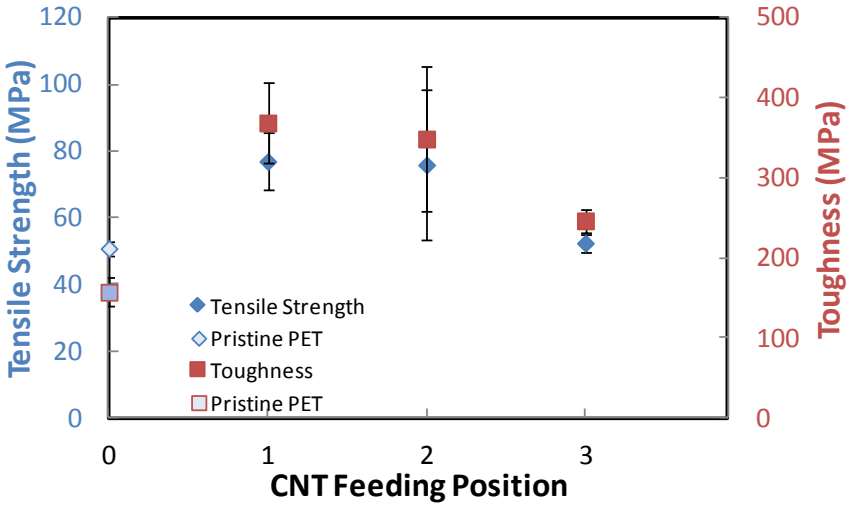

Figure 8. Tensile strength and toughness for nanocomposite fibers produced from different CNT feeding positions.

5 Acknowledgement

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