

Polypropylene/Carbon Nanotube Nanocomposite Fibers: Process–Morphology–Property Relationships

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ABSTRACT: This study is focused on aligning carbon nanotubes in polypropylene matrix by melt spinning. Two different weight percentages (0.5% and 1.0%) of nanotubes were used for the synthesis of the nanocomposite fibers. The effect of the nanotubes on the crystallization and mechanical behavior of polypropylene as well as the effect of draw ratio on the nanocomposite morphology and properties is also discussed. Correlation of fiber morphology and nanotube alignment was done using differential scanning

calorimetry, wide-angle X-ray diffraction, and transmission electron microscopy. Significant improvement in tensile modulus and tensile strength were observed, which is characteristic of a highly aligned nanotube system. A substantial increase in the onset of decomposition was observed. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 3844–3850, 2007

Key words: polypropylene; multiwalled nanotube; morphology; WAXD; thermal stability

INTRODUCTION

Polymeric composites based on the combination of polymers (both thermoplastic and thermoset) and mineral fillers, metals, and fibers have found a wide range of applications over the past 40 years. Recently, the tremendous potential for property enhancements when nanoscale particles, such as layered silicates or carbon nanotubes (CNTs), are incorporated into polymers has led to an explosion of research activity in polymer-based nanocomposites. These property enhancements are due to the high aspect ratio, strength, and modulus of the nanoparticles.^{1,2} Properties that have been shown to undergo substantial improvements in nanocomposites include mechanical properties, decreased permeability to gases, water and hydrocarbons, thermal stability and heat distortion temperature, flame retardancy and reduced smoke emissions, chemical resistance, electrical conductivity, and optical clarity.³

Nanocomposites based on CNTs have received a tremendous amount of attention during the past 5 years. CNTs typically have diameters in the range of a few

nanometers and lengths of several hundred nanometers resulting in a very high aspect ratio, typically in the range of several thousand. Typically nanotubes have an extremely high elastic modulus of 1 TPa, comparable to that of diamond (1.2 TPa) and reported strengths of 10–100 times that of the strongest steel at a fraction of the weight.^{4–7} In addition, they can exhibit electrical conductivity, ranging from metallic to semi conducting, depending on their structure.⁸ Potential applications of polymer/CNT composites are in aerospace (high temperature, light weight), automobile (bumpers, interior and exterior panels, gasoline tanks), electronics (printed circuits, electric component), packaging (films, containers), adhesives, and coatings.

The keys to maximizing nanocomposite property enhancements are to obtain a uniform distribution of nanoparticles within the polymer matrix, and to achieve nanoparticle–polymer adhesion, which is critical for load transfer from the matrix to the particle. The nanotubes can be dispersed in the polymer matrices using techniques such as melt processing, solution processing, or *in situ* polymerization. While a number of studies have reported on polymer/CNT nanocomposites in which the tubes are randomly dispersed in the matrix, controlled spatial distribution of the CNTs provides more control over properties and opens the door to an even wider range of applications, including electrically and thermally conductive polymer composites, actuators, sensors, and ultrastrong fibers. Uniaxial alignment of CNTs using magnetic^{9,10} and shear fields^{11–17} has been the focus of several recent studies.

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Thostenson and Chou¹¹ studied the alignment of multiwalled nanotubes (MWNT) in a polystyrene matrix. They produced aligned nanocomposite films by shear mixing of the nanotubes in a microscale twin-screw extruder. The mechanical properties were studied using a DMA. A fivefold increase in storage modulus was found in the aligned system compared with the randomly oriented system. Haggemueller et al.¹³ studied the alignment of single-walled nanotube (SWNT) in poly(methyl methacrylate) (PMMA) via melt spinning, which resulted in a composite with enhanced mechanical and electrical properties. The electrical conductivity increased from 0.118 to 11.5 S/m as the composition increased from 1.3 to 6.6 wt % of the tubes. The elastic modulus of the fibers also increased with the increase in tube compositions. The effect of shear process parameters on the alignment of nanotubes both SWNT and MWNT, in polycarbonate (PC) matrix was studied by Sennett et al.¹⁴ The CNTs were mixed with PC in a co-rotating intermeshing conical twin screw micro-compounder. Transmission electron micrographs showed that with increase in extruder residence time and drawing speed the nanotubes were aligned in the drawing direction. For polymeric fibers used in structural applications, the compressive property is just as important as the strength and modulus, because while the polymers are very stiff and strong when the chains are aligned along the fiber axis, they are very weak perpendicular to this axis. As a result, compressive load causes fibers to fail by buckling and subsequent defibrillation. Kumar et al.¹⁵ investigated the effect of carbon nanotubes on the compressive properties of a rigid-rod poly (*p*-phenylene benzobisoxazole) (PBO)/SWNT composites. The modulus increased by 13% and tensile strength increased by 88% with the addition of 5% SWNT. The modulus and strength further increased to 21% and 61%, respectively, from the pure polymer as the nanotube loading reached 10%.

Polypropylene (PP) is a commodity polymer, with a wide range of commercial uses, in a variety of forms, including fibers. Thus, enhancing of PP properties through the dispersal and alignment of multiwalled carbon nanotubes (MWNTs) should be of significant interest. The research discussed herein focuses on the alignment of multiwall carbon nanotubes in a PP matrix using mechanical shear mixing. The effect of different weight percent loadings of nanotubes on the morphology, thermal, and mechanical properties of the nanocomposites is also presented.

EXPERIMENTAL

PP was obtained in the pellet form from Volt Industrial Plastics (Flippin, AK) under the trade name Rexene[®]. PP is a semicrystalline polymer and has

three different crystal phases α , β , and γ . It has a tensile modulus of about 1 GPa and a tensile strength of about 24 MPa. The MWNT used was commercially obtained from MER Corp. (Tucson, AZ). It was produced by arc discharge method and had a purity of >95%. The MWNTs have a diameter in the range of 50–100 nm. A ThermoHaake[™] Minilab co-rotating twin-screw extruder was used for the fiber synthesis. PP/MWNT nanocomposite was prepared with two different weight percentages of MWNTs (0.5 and 1.0). The operating temperature of the extruder was selected after conducting differential scanning calorimetric (DSC) scan and thermogravimetric analysis (TGA) on the pure polymer. The screw speed was set at 60 rpm and the polymer and MWNT were allowed to mix for 60 min. The composite fiber was then extruded from a die of 0.5 mm diameter and spun onto a take up spool using a fiber spinning apparatus. The take up speed was maintained constant to obtain a uniform diameter fiber. The fibers had an average diameter of 50 μ m. Further studies to determine the effect of high draw ratio (DR) on the fiber mechanical properties were also conducted. For drawing the fiber a known load (2.5 g) was attached to one end of the fiber and allowed to hang in a furnace, which was maintained at 90°C.

DSC of the fibers was conducted on a TA Instrument DSC Q1000. The sample was ramped at 10°C/min from room temperature to 250°C. A Rigaku RU200 rotating anode generator equipped with a Statton camera was used to acquire 2-D wide-angle X-ray diffraction (WAXD) patterns. Nickel-filtered CuK α radiation was used at an accelerating voltage of 50 kV/170 mA. The data were collected on phosphor image plates and digitized using a Molecular Dynamics scanner. Transmission electron microscopy (TEM) studies were conducted using a Hitachi H700 TEM, at an acceleration voltage of 75 kV. Axial and cross sections of the samples were prepared by mounting the specimen in an epoxy resin and microtoming was done using a Riechert ultramicrotome to yield samples with a thickness of 70–100 nm. Tensile property studies were conducted using a Rheometrics Minimat mechanical tester. The gauge length was 50 mm and the test was conducted with a cross-head speed of 0.1 mm/min at ambient temperature. A minimum of five samples were tested. Thermal stability was studied using TA Instruments TGA 2950 and the scans were conducted in air at a scan rate of 10°C/min.

RESULTS AND DISCUSSION

Effect of MWNTs on the PP/MWNT fiber crystallinity and orientation

DSC thermographs (first scans) of extruded pure PP fibers and PP/MWNT fibers with different MWNT

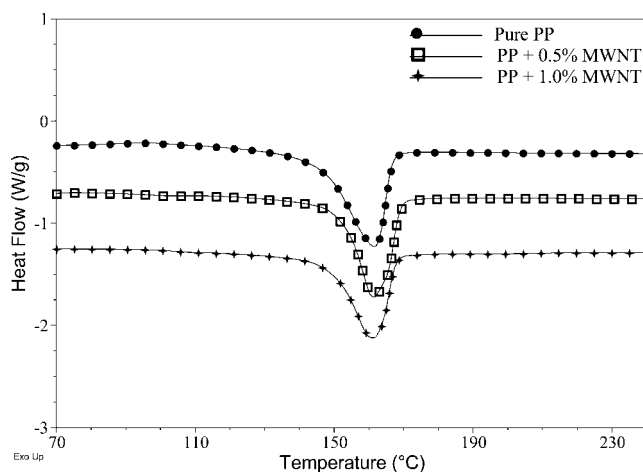


Figure 1 DSC thermographs for different weight percentages of nanotube loadings in PP fibers.

weight loadings are shown in Figure 1. The heat of fusion, melting point, and degree of crystallinity of the composites were obtained from the thermographs and are included in Table I and presented graphically in Figure 2. Crystallinity has a major effect on the mechanical properties of polymers and hence the effect of nanoparticles on nucleation and crystallinity development is of interest. The main stable crystal form is the α -form, which has a monoclinic structure and is obtained from melted PP without any special treatment.^{16,17} The melting range of α -PP is 160–165°C, which is similar to the melting temperature obtained in our study. This suggests that the pure PP and the nanocomposites are in the stable α -crystalline form.¹⁸ The heat of fusion obtained was used to calculate the percent crystallinity. As the MWNT loadings increased, the percent crystallinity decreased slightly, with no observable change in the melting temperature. The decrease in the ΔH_f with increasing nanotubes concentration may be attributed to the proportional reduction of the PP concentration in the composite,¹⁹ or nucleation of the PP crystallites, caused by the nanotubes.¹⁷

WAXD on PP and PP/MWNT fibers

Two-dimensional WAXD patterns were used to analyze the fiber morphology and are shown in Figure 3. The WAXD patterns of pure PP show diffuse

TABLE I
Heat of Fusion, Melting Point, and Percent Crystallinity for As-Spun (DR = 1) PP and PP/MWNT Fibers

Sample	ΔH_f (J/g)	T_m (°C)	% Crystallinity
PURE PP	94	161	44
PP + 0.5 wt % MWNT	81	161	38
PP + 1.0 wt % MWNT	79	160	37

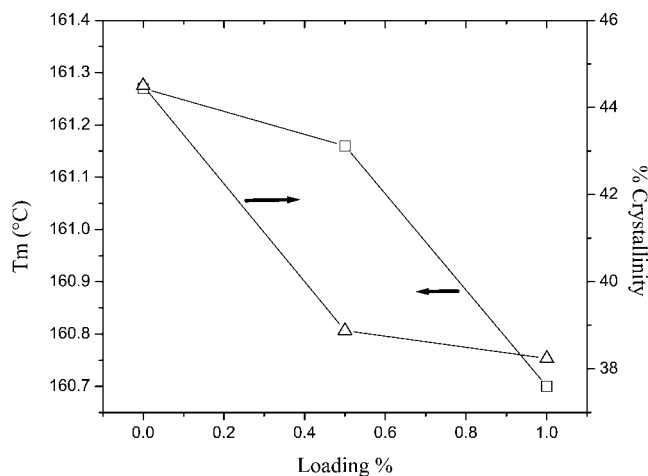


Figure 2 Effect of different weight loadings of MWNT on melting point and percent crystallinity of PP. Squares denote T_m and triangles denote crystallinity.

equatorial reflections with d -spacings of 6.12, 5.18, 4.68, and 3.48 Å, and one diffuse meridional reflection, for the pure PP. These reflections are all typical of the α -crystalline form, which correlates with the DSC data discussed earlier. Both 0.5 and 1.0 wt % samples, which are shown in Figure 3(b,c), exhibit more arced reflections, with d -spacings of 6.19, 5.14, 4.70, 3.42, 3.10 Å, respectively. The arced reflections are indicative of a decrease in the orientation and crystallinity. This correlates with the decrease in crystallinity with nanotube addition that was shown in our DSC data, as well as optical microscopy and isothermal crystallization studies reported by Bhattacharyya et al.¹⁷ Their studies suggested that the CNTs have a nucleating effect on the PP, resulting in smaller crystallites, and hence, lower crystallinity. A reflection due to the 002 diffracting planes which appears at $26.5^\circ 2\theta$, and corresponds to a d -spacing of 0.336 nm can often be observed.²⁰ However, it is not visible in our patterns and this is presumably due to the relative concentration of MWNTs used in our study. Further drawing of the pure PP fibers (DR \sim 4.0), resulted in significant improvement in the orientation, as observed in the WAXD patterns in Figure 4, which exhibit more distinct equatorial and meridional reflections. This is also corroborated by a distinct decrease in the azimuthal breadth of the 110 reflection, which is plotted in Figure 5.

Transmission electron microscopy

TEM micrographs of the nanocomposite fibers were used to study the extent of CNT dispersion and alignment. Images taken along the fiber axial direction for the 1.0 wt % are shown in Figure 6 and are representative of the 0.1% sample. The images show very good exfoliation of the nanotubes within the PP

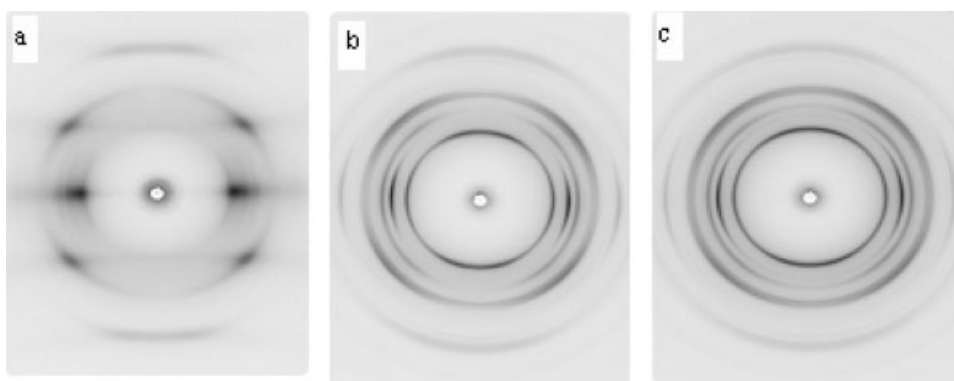


Figure 3 2-D WAXD on as-spun PP fibers (DR = 1) with different MWNT weight loadings: (a) pure polypropylene, (b) PP/0.5 wt % MWNT, and (c) PP/1.0 wt % MWNT.

matrix. In this context, exfoliation refers to how well the nanotubes are deaggregated. There are, however, some regions in which the tubes show a small degree of aggregation, which is to be expected, since these tubes are not modified. The images also show excellent alignment along the fiber axis, which is denoted by the arrows. This alignment, along with the alignment of the polymer chains, leads to the enhanced mechanical properties. Thus, the mechanical shearing provided by the extruder was very effective in dispersing and aligning the nanotubes. Cross-sectional images shown in Figure 7 also suggest that the nanotubes are well dispersed within the matrix of the PP; however, regions of aggregated tubes can also be observed from this perspective. The presence of black spots suggests that the tubes are aligned parallel to the long axis of the fibers (i.e., the chain axis). These observations were used to develop a model of the state of nanotube alignment and dispersion, which is shown in Figure 8. The model depicts the longitudinal and cross-sectional view for the ideal case in which the nanotubes are well oriented with respect to the axial direction of the fiber as well as a small number of the fibers arranged at

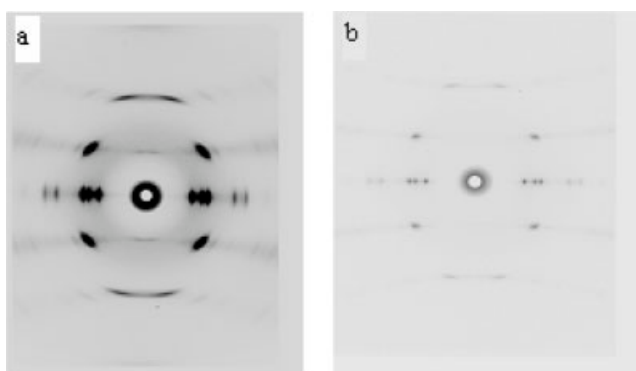


Figure 4 2-D WAXD on (a) pure PP and (b) PP/1.0 wt % MWNT with a draw ratio of 4.0.

varying angles to the fiber axis. Bhattacharyya et al.¹⁷ studied the orientation of PP fibers containing SWNTs using a combination of X-ray diffraction and Raman spectroscopy. Comparison of Herman's orientation parameters of the PP fiber (determined from the X-ray data) and that for the SWNTs (determined by Raman data) showed that the SWNTs were more oriented than the PP. This difference was attributed to the higher stiffness of the nanotubes relative to that of the PP. A similar finding has also been reported for PP/carbon nanofiber composite fibers.^{21,22}

In some areas CNTs can be observed parallel to the plane of the cross section, which is due to artifacts of the microtoming process. Their presence, however, permits comparison of diameters with those which are oriented perpendicularly. The diameter in both cases is about 50 nm, which agrees well with the measurement from the TEM measurements of pure nanotubes as well as the values supplied by the manufacturer. The good dispersion and align-

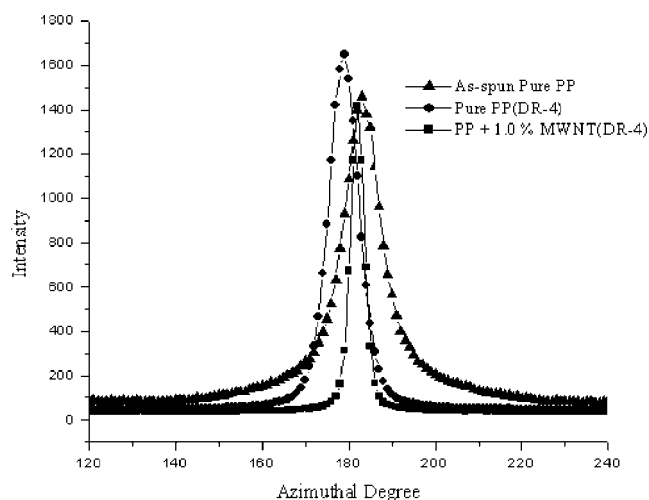


Figure 5 Azimuthal scans of as-spun pure PP fiber and fibers with a draw ratio of 4.0.

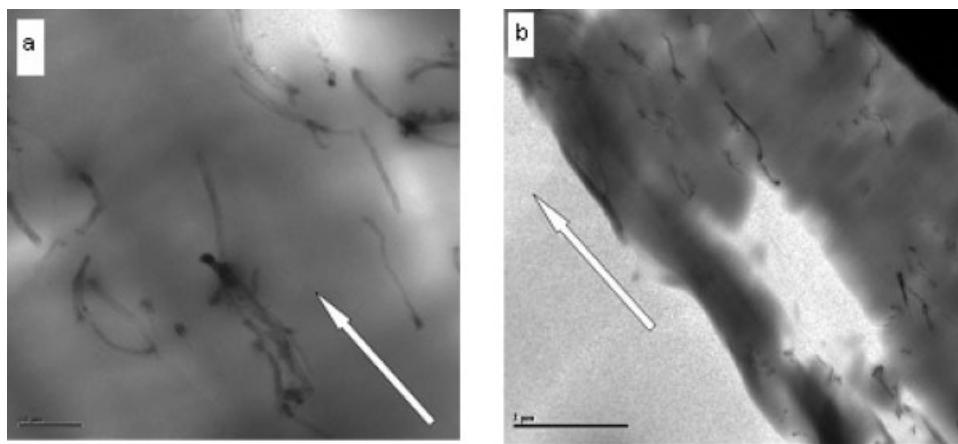


Figure 6 Longitudinal TEM images of PP/1.0 wt % MWNT sample. The arrows denote orientation of MWNTs along the fiber axis.

ment of the nanotubes along with good polymer-fiber adhesion are key requirements for significant mechanical property enhancements.

Tensile properties of PP and PP/MWNT fibers

Tensile strength and modulus values for as-spun and drawn fibers are listed in Table II. For a nanotube loading of 0.5 wt % the tensile properties showed more than a threefold increase in the tensile modulus and strength when compared with pure PP fibers. With a nanotube loading of 1.0 wt % the modulus increased 3.7 fold and strength increased fivefold compared with pure PP. Similar trends have been reported for PP/SWNT nanocomposites as well as PMMA/carbon nanofiber composites, respectively.^{23,24}

Correlation of the tensile properties with the TEM data suggests that the significant property enhancements that we have obtained at the relatively low

DR are due to highly dispersed and well aligned CNTs, and/or good adhesion between the nanotubes and the polymer matrix. This results in good load transfer from the polymer matrix to the nanotubes. The degree of exfoliation is very critical for obtaining enhanced properties. It has been shown that poorly dispersed SWNTs have no effect in reinforcing the fibers even though the fibers were drawn at a very high DR of 4.0.¹⁷ The ineffectiveness of nanotubes was presumed to be due to poor dispersion. Aggregations of the nanotubes essentially nullify their reinforcement effect.

Drawing the fiber further resulted in significant improvement in the mechanical properties, as shown in Table II. A DR of 4.0 gives a fourfold increase in the strength of the PP/1.0 wt % MWNT nanocomposite fibers compared with the nondrawn nanocomposite fibers, suggesting high orientation of the polymer chains as well as further alignment of the nanotubes. Presumably, with increasing DR, the

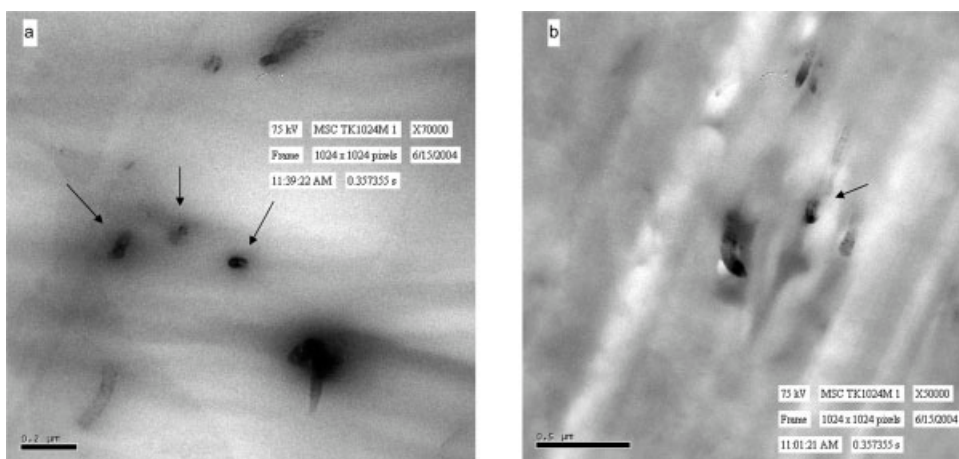


Figure 7 Cross-sectional TEM images of PP/MWNT fibers; arrows in (a) and (b) denote MWNTs.

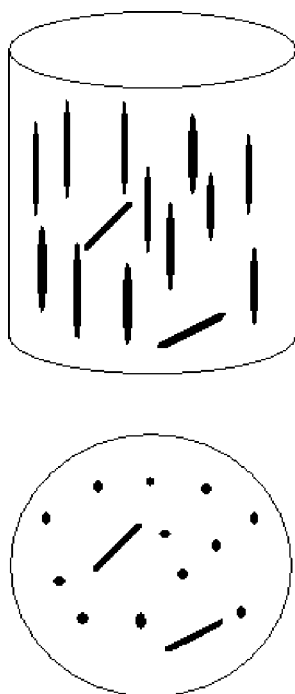


Figure 8 Model of fiber showing nanotubes along (a) the fiber axis and (b) the cross section. The black spots represent nanotubes viewed parallel to their long axis.

MWNTs orient parallel to the fiber axis,⁴ further contributing to the increase in strength. Comparison of the drawn nanocomposite properties with that of the drawn pure fiber allows us to delineate the contributions of the MWNTs to the property enhancements. The drawn pure fiber has a strength of 330 MPa and a modulus of 1.67 GPa, compared with strength and modulus of 25 MPa and 1 GPa, respectively, for the pure, undrawn PP. The strength of the drawn nanocomposite fibers increased by a factor of 1.3, indicative of the contribution of the nanotubes. The modulus values for the two samples are similar, which is to be expected, since the strength is dependent on the morphology to a higher degree than the modulus.

Thermal stability characterization using thermogravimetric analyzer

A comparative TGA of pure PP and the nanocomposites with MWNTs loadings of 0.5 and 1.0 wt % is

TABLE II
Effect of MWNT on the Tensile Properties of PP and PP/MWNT Fibers

Sample	Strength (MPa)	Modulus (GPa)
Pure PP	25	1.0
PP + 0.5 wt % MWNT	80	3.1
PP + 1.0 wt % MWNT	125	3.7
Pure PP (DR ~ 4)	330	1.67
PP + 1.0 wt % MWNT (DR ~ 4)	420	3.5

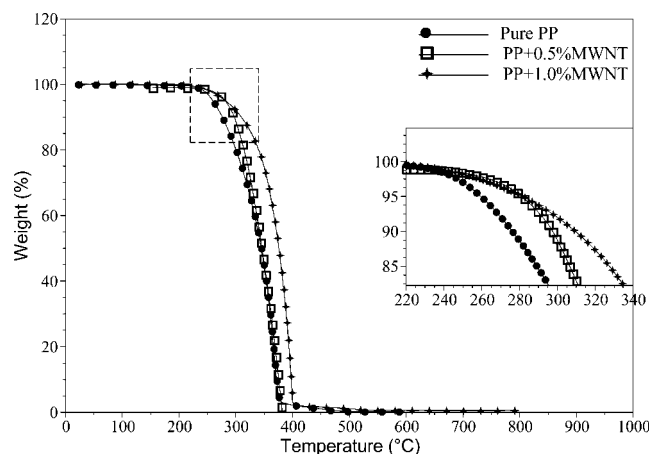


Figure 9 TGA thermographs of pure PP and PP/MWNT fibers (inset shows the variation in onset temperature).

shown in Figure 9 and the corresponding data are given in Table III. It is clear that PP degrades in a single step. The step initiates at 220°C and ends at 410°C. The TGA curves show no significant weight loss till 250°C. However beyond this temperature the onset of degradation was notably influenced by the nanotube loading within the polymer. The onset of thermal decomposition values increased with nanotube loading and the nanocomposite attained a maximum onset of 354°C. Compared with the pure PP, the nanocomposites showed an increase of 16°C with the addition of 0.5 wt % MWNT and 34°C with the addition of 1.0 wt % in the onset of thermal degradation. The improvement in thermal stability can be attributed to good matrix–nanotube interaction and also due to the thermal conductivity of the nanotubes. As the nanotubes are good thermal conductors the tubes easily take up the heat that is applied to the nanocomposite fibers. The good dispersion of the nanotubes in the polymer matrix allows the spreading of heat uniformly along the fiber.

Another factor that can potentially contribute to the thermal stability is the formation of a relatively uniform network-structured layer which covers the entire sample surface without any cracks or gaps forming during heating.²⁵ This layer re-emits much of the incident radiation back from its hot surface, thereby reducing the heat transmitted to the PP layers below.²⁵ This increased thermal stability is dependent

TABLE III
Effect of MWNT on Decomposition of PP

Sample name	Onset temperature (°C)	Temperature at maximum decomposition (°C)
Pure PP	320	366
PP + 0.5 wt % MWNT	336	375
PP + 1.0 wt % MWNT	354	395

on the size and shape of the filler particles.²⁶ Also this is an expected result since TGA studies conducted on MWNTs showed an onset of decomposition at 630°C, showing clearly that the nanotubes have no part in the initiation of degradation of PP.

CONCLUSIONS

PP/MWNT nanocomposite fibers were synthesized using melt extrusion. Two different weight loadings of 0.5 and 1.0 wt % were used for the synthesis. Morphological characterization was done using DSC and WAXD. The DSC and WAXD characterization showed a decrease in crystallinity with the increase in nanotube loading, suggestive of a nucleation effect provided by the nanotubes. Mechanical characterization was done and the tensile tests showed a three-fold increase in the modulus and a fivefold increase in the tensile strength versus the pure PP fibers. Similarly as the nanotube loading increased from 0 to 1.0 wt % a 25% increase in the modulus and a 17% increase in the strength were observed. The increase in mechanical properties is due to good dispersion of the nanotubes and good wetting of the nanotubes by the polymer matrix, resulting in good load transfer from the polymer matrix. Further increase in the strength was observed when the fibers were drawn, suggesting further alignment of the nanotubes. The study shows the significant mechanical property enhancements that can be realized by the alignment of CNTs. Thermal characterization was done using a TGA, which showed an increase in the onset of decomposition temperature of 34°C for PP/1.0 wt % MWNT versus pure PP fiber.

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