Morphology and Tensile Properties of Polypropylene-Multiwalled Carbon Nanotubes Composite Fibers

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Received 5 November 2009; accepted 12 May 2010
DOI 10.1002/app.32794
Published online 29 July 2010 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: In this work, we analyzed tensile properties of polypropylene-multiwalled carbon nonotubes composite fibers. The multiwalled carbon nanotubes (MWCNTS) were used in different contents of 0, 1, 2, 3, 4, and 5 wt %. Dispersing agents were used to disperse MWCNTs in polypropylene matrix. After the dispersing agent was removed, the mixture was melt mixed. The fibers were spun by a home-made melt spinning equipment and stretching was done at a draw ratio of 7.5. By using 1–5 wt % of MWCNTs, the modulus of composite fibers increased by 69–84% and tensile strength increased about 39% when compared with the virgin polypropylene fibers. In addition, the MWCNTs dispersion in the matrix was monitored by scanning electron microscopy and transmission electron microscopy. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 962–967, 2011

Key words: polypropylene composite fibers; fiber spinning; multiwalled carbon nanotubes

INTRODUCTION

Polypropylene (PP) is a versatile thermoplastic that is used in many applications such as building materials, furniture, automobile, packaging, pipes, fittings, fibers, and toy industries because of its well balanced physical and tensile properties. It is a material that has good fatigue resistance, chemical resistance, and tensile properties with tensile strengths in the range of 30–38 MPa and tensile modulus ranging from 1.1 to 1.6 GPa and its easy processability at a relatively low cost.[1–5] It has been reported that fillers in PP produce the following improvements in properties such as increase in stiffness, modulus of elasticity, tensile stress at break and melt viscosity.[6,7] Polymeric composites based on the combination of polymers and mineral fillers, metals and fibers have investigated a wide range of applications over the past 40 years.[3,7,8] Recently, the tremendous potential for property enhancements when nanoscale particles and 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. Nanocomposites based on CNTs have received a tremendous amount of attention during the past few years.[3] The CNTs typically have diameters in the range of a few nanometers and the lengths of several hundred nanometers. They have a very high aspect ratio, Young's modulus and tensile strength of up to 1 TPa and 50 GPa, respectively.[5,2,9,10] In addition, they can exhibit electrical conductivity, ranging from metallic to semiconducting, depending on their structures. Potential applications of polymer/CNTs composites are in aerospace (high temperature and lightweight), automobile (bumpers, interior and exterior panels and gasoline tanks), electronics (printed circuits and electric components), packaging (films and containers), adhesives, and coatings. Furthermore, reinforcement of polymer with CNTs has been previously demonstrated to increase physical properties of the materials.[11,12]

Several researchers have used CNTs to enhance the strength of neat fibers. However, most of them used single walled carbon nanotubes (SWCNTs) because of their greater mechanical properties than those of MWCNTs. Jacob and Robert[4] used decalin to disperse SWCNTs. The mixture was sonicated and PP was added into the mixture. After mixing, the sample was heated in a vacuum oven to remove the solvent. The PP composite with 1 wt % SWCNTs loading was spun to fibers. The results of the tensile strength and modulus of fibers were increased by 40% and 55%, respectively. Chang et al.[11] dispersed

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Contract grant sponsors: NANOTEC, NSTDA, Ministry of Science and Technology, Thailand.

SWCNTs in the decahydronaphthalene with high power sonicator before mixing with PP at 140°C. The composite fibers with 1–5 wt % SWCNTs showed 45% increasing of tensile modulus. Bhattacharyya et al.[6] used melt blending to disperse SWCNTs in PP with 1 wt % loading and found a decrease of tensile properties. Moncy et al.[3] worked on aligning MWCNTs in PP composite fibers, the fibers were prepared by melt spinning. They found an increase of modulus by 25% with 1 wt % MWCNTs loading, and they stated that the increase of tensile properties was due to a good dispersion of CNTs in the polymer matrix. Kumar et al.[8] dispersed 5 wt % nano carbon fibers in PP fibers by using a twin screw extruder and found that the modulus was increased by 50%, and the SEM images showed a good dispersion of nano carbon fibers in PP matrix.

SWCNTs are expensive materials and may not be promising for preparation of their composites for commercial purpose. Therefore, in this work, the MWCNTs that are much more cheaper were used to strengthen PP composite fibers. A good dispersion of MWCNTs is a key to pull up the MWCNTs properties in their composites. Therefore, dispersing agents along with micronizing mill were utilized to disperse MWCNTs in PP matrix. In addition, the dispersion of MWCNTs in PP matrix has been investigated by scanning electron microscopy and transmission electron microscopy.

EXPERIMENTAL

The extrusion grade PP was supplied by IRPC Public Co., Thailand. It has a melt flow index of 11 g/10 min and $\overline{M_w}$ of 120,000 g/mol. MWCNTs used as reinforcement were purchased from Nanomaterials Research Unit of Chiang Mai University, Thailand. The nanotubes have a diameter in the range of 20 to 50 nm and a wall thickness of about 10 nm.[13] MWCNTs were calcinated at 480°C for 4 h to eliminate impurities prior use.

The 1 wt % MWCNTs samples were vibrated in a 20 mL solution of dispersing agent (composed of sodium lauryl sulfate, Triton X-100 and 2-propanol) using a McCrone micronizing mill for 1 h. PP powder was added to the solution and the mixture thus obtained was then mixed by mechanical stirring. Then, the composites were dried at 70°C in a vacuum oven and melt-blended using a two-roll mixer at 190°C for 20 min. After that the composite fibers were spun using a home-made melt spinning equipment with a die diameter of 1.0 mm at 190°C followed by a collection of the fibers on a speed take up device. The fibers were subsequently drawn at a draw ratio of 7.5 (the highest draw ration that could be obtained on continuous filaments on a hot plate at 130°C). It was found that the type of dispersing agent did not affect the composite tensile properties (Table I); therefore, for the ease of sample drying prior to fiber spinning, 2-propanol was selected to disperse MWCNTs at other concentrations. Because of its low boiling temperature, the drying step of composites was effectively performed. The composite fibers were prepared with different MWCNTs contents as 1, 2, 3, 4, and 5 wt % by using 2-propanol as a dispersing agent. The processes of mixing and fiber spinning were similar to the processes mentioned previously. As a control sample, as received PP without CNTs was also spun using the same equipment and processing conditions.

TABLE I
Effect of the Dispersing Agent Type on Tensile Properties of PP/MWCNTs 1% Fibers Stretched at a Draw Ratio of 7.5

Dispersing agent type	Secant modulus at 1% strain (MPa)	Tensile strength (MPa)	Strain at break (%)
Neat PP (control sample)	4272 ± 343	735 ± 40	40 ± 5
2-propanol	7243 ± 654	1024 ± 53	40 ± 5
SLS	6220 ± 606	949 ± 80	42 ± 4
Triton X-100	6971 ± 715	974 ± 60	41 ± 6

Fiber diameter was measured using a Mitutoyo micrometer (model ID-C112EBS) and was found to be in the range of 35–40 μm. Fiber tensile properties were determined using LRX tensile tester (LLOYD Instruments). The gauge length and crosshead speed for the tensile tests were 30 mm and 30 mm/min, respectively. For tensile tests, 25–30 filaments were tested for each sample, but the properties of only 15 filaments were used to get the average values after discarding those too far from the average. The data were analyzed using Duncan test of the analysis of variance (ANOVA). Mean values were considered at 95% significance level ($P < 0.05$). Secant modulus at 1% strain was reported. The morphology of the fibers was characterized by using scanning electron microscopy (SEM, JEOL JSM-6335F). The cross sections of the different samples were prepared by fixing the samples on the stub then dipping them in liquid nitrogen before cutting them. Transmission electron microscopy (TEM, JEOL JEM-2010) at an acceleration voltage of 85 KV was utilized to observe the axial sections of the samples. The samples were prepared by mounting the specimen by an epoxy resin and using a Riedhert microtome to cut the sample with a thickness of 100–120 nm.

RESULTS AND DISCUSSION

SEM image of the MWCNTs before calcination is shown in Figure 1(a). It could be seen that there

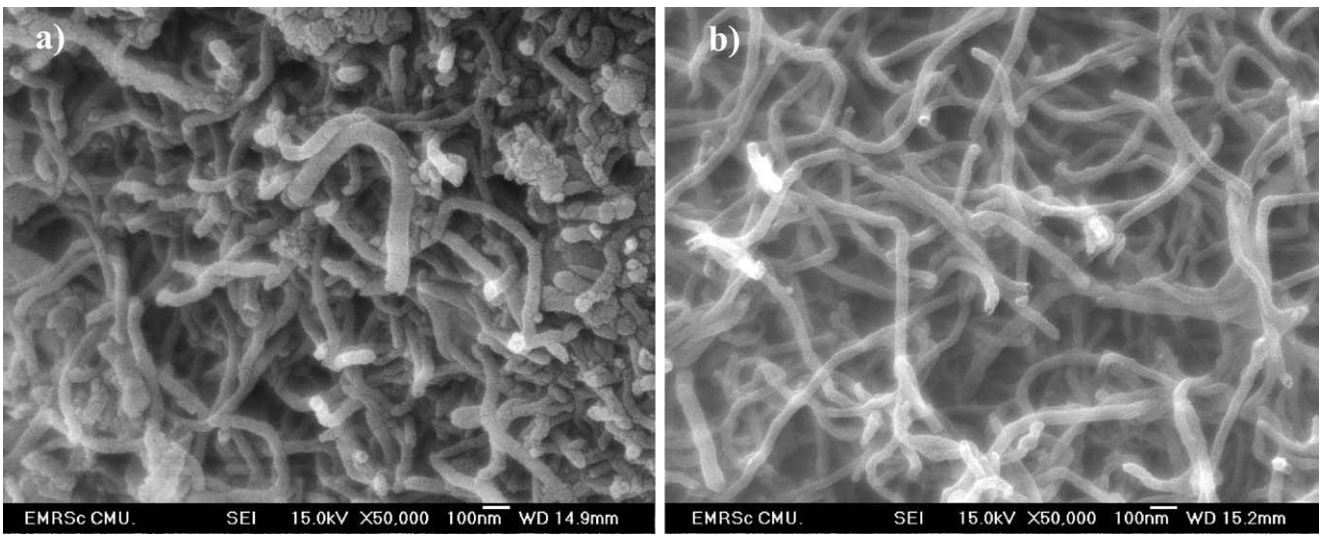

Figure 1 SEM images of MWCNTs (a) before calcination (b) after calcination.

were crumbs of impurities between tubes, which could be amorphous carbon from the MWCNTs production. Figure 1(b) showed the MWCNTs after calcination, the images revealed that the impurities were removed. TEM image of the MWCNTs is shown in Figure 2. It shows that the tube diameter are in the range of 20–50 nm with the average size of $\sim$ 27 nm and the length is greater than 10 μm (data from the producer[13]).

The MWCNTs exhibit to bundle together because of intrinsic Van Der Waals attraction between the individual tubes in combination with high aspect ratios and large surface area.[12] It is known that for effective reinforcement, a good CNTs dispersion is necessary. Tensile properties of neat PP fiber and PP composite fibers containing 1 wt % MWCNTs and stretched at a draw ration of 7.5 with different dispersing agents are given in Table I. Based on this data, it is clear that the composite fibers have higher modulus and higher tensile strength when compared with neat PP fiber. Strain at break remained unchanged as a result of filling with the MWCNTs. For different dispersing agents, the modulus and tensile strength of fibers were not significantly affected. For the ease of sample drying purpose, 2-propanol was selected to use as a dispersing agent.

The effect of the MWCNTs content on tensile properties of the composite fibers stretched at a draw ratio of 7.5 were investigated, and the tensile stress–strain behavior of neat PP fiber and composite fibers containing different MWCNTs concentrations with 2-propanol dispersing agent are shown in Figure 3. The diameter of the drawn fibers were 35–40 μm. The tensile strength and modulus values for the fibers are listed in Table II. Tensile strength increased about 33–45% when concentration of MWCNTs increased from 1 to 5 wt %, respectively. Secant modulus (defined as the stress–strain ratio at 1% strain) is presented in

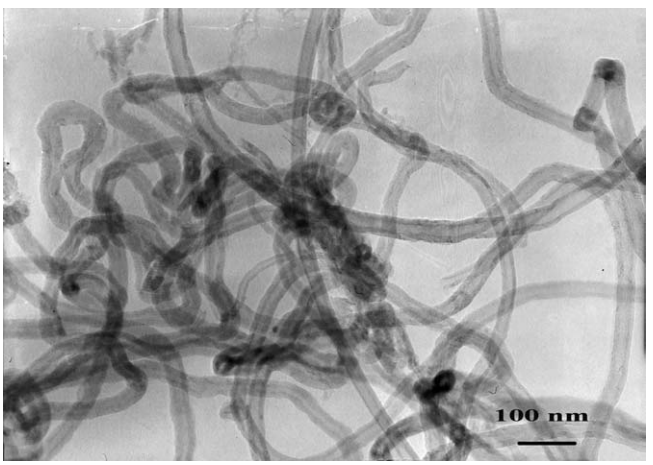

Figure 2 TEM image of MWCNTs after calcination.

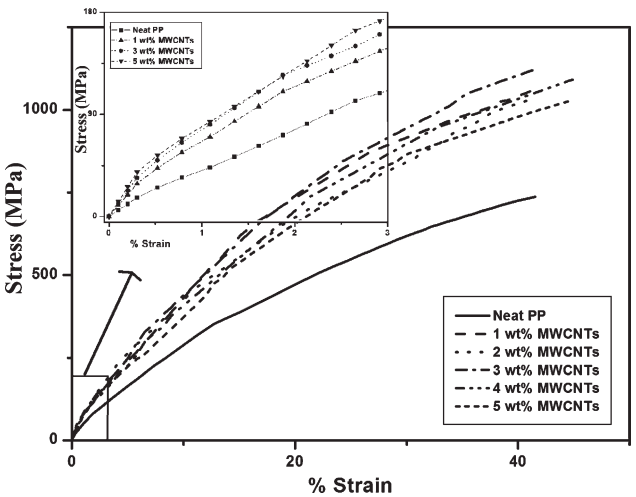

Figure 3 Stress–strain curves of neat PP and PP composite fibers with different contents of MWCNTs.

TABLE II
Effect of MWCNTs Content on Tensile Properties of PP/MWCNTs Fibers Stretched at a Draw Ratio of 7.5

MWCNTs content (wt %)	Secant modulus at 1% strain (MPa)	Tensile strength (MPa)	Strain at break (%)
0 (Neat PP, control sample)	4272 ± 343	735 ± 40	40 ± 5
1	7243 ± 654	1024 ± 53	40 ± 5
2	7347 ± 465	1019 ± 47	41 ± 2
3	7772 ± 762	1071 ± 80	40 ± 3
4	8119 ± 764	1042 ± 70	39 ± 3
5	7875 ± 612	984 ± 77	40 ± 4

Figure 4 as a function of the MWCNTs concentration. The modulus of the fibers increased sharply by 69% with the addition of 1 wt % of MWCNTs in PP matrix. The high modulus is attributed to the homogeneous dispersion of MWCNTs in PP matrix as it can be observed in Figure 5(a) from the SEM image of a

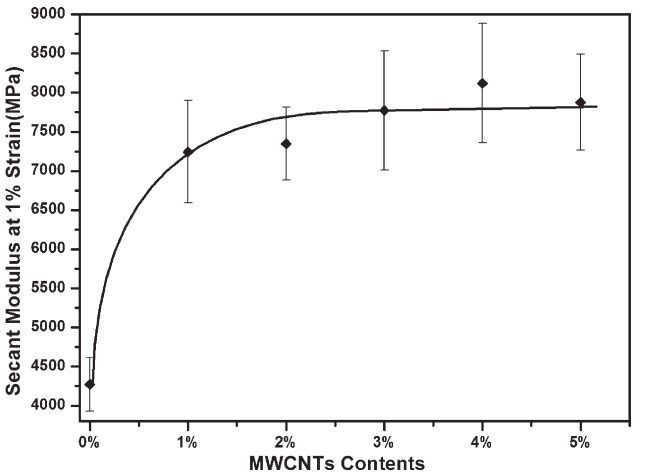

Figure 4 Variation of secant modulus of neat PP and PP/MWCNTs composite fibers as a function MWCNTs content.

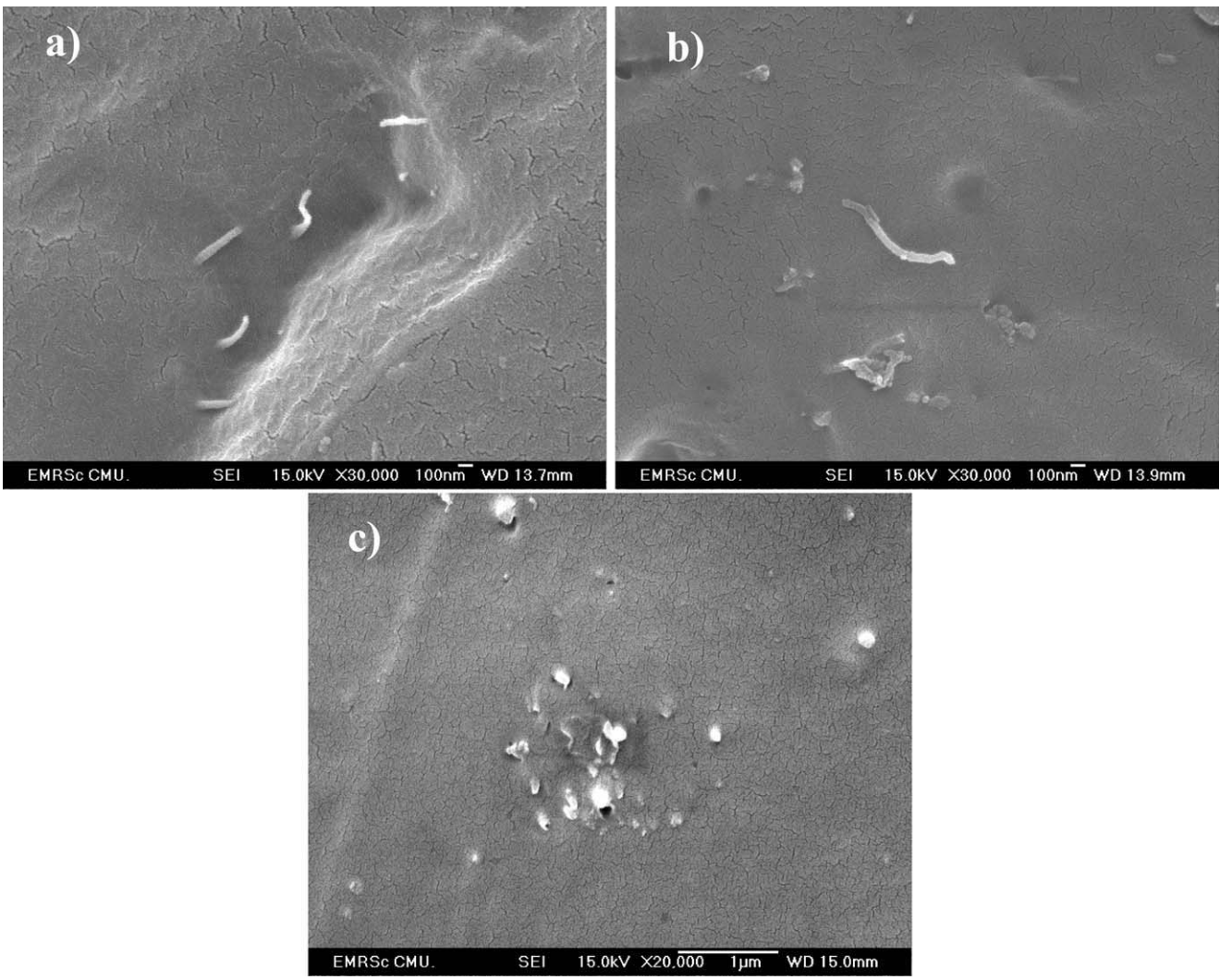

Figure 5 SEM images of PP composite fibers with (a) 1% MWCNTs, (b) 3% MWCNTs, and (c) 5% MWCNTs.

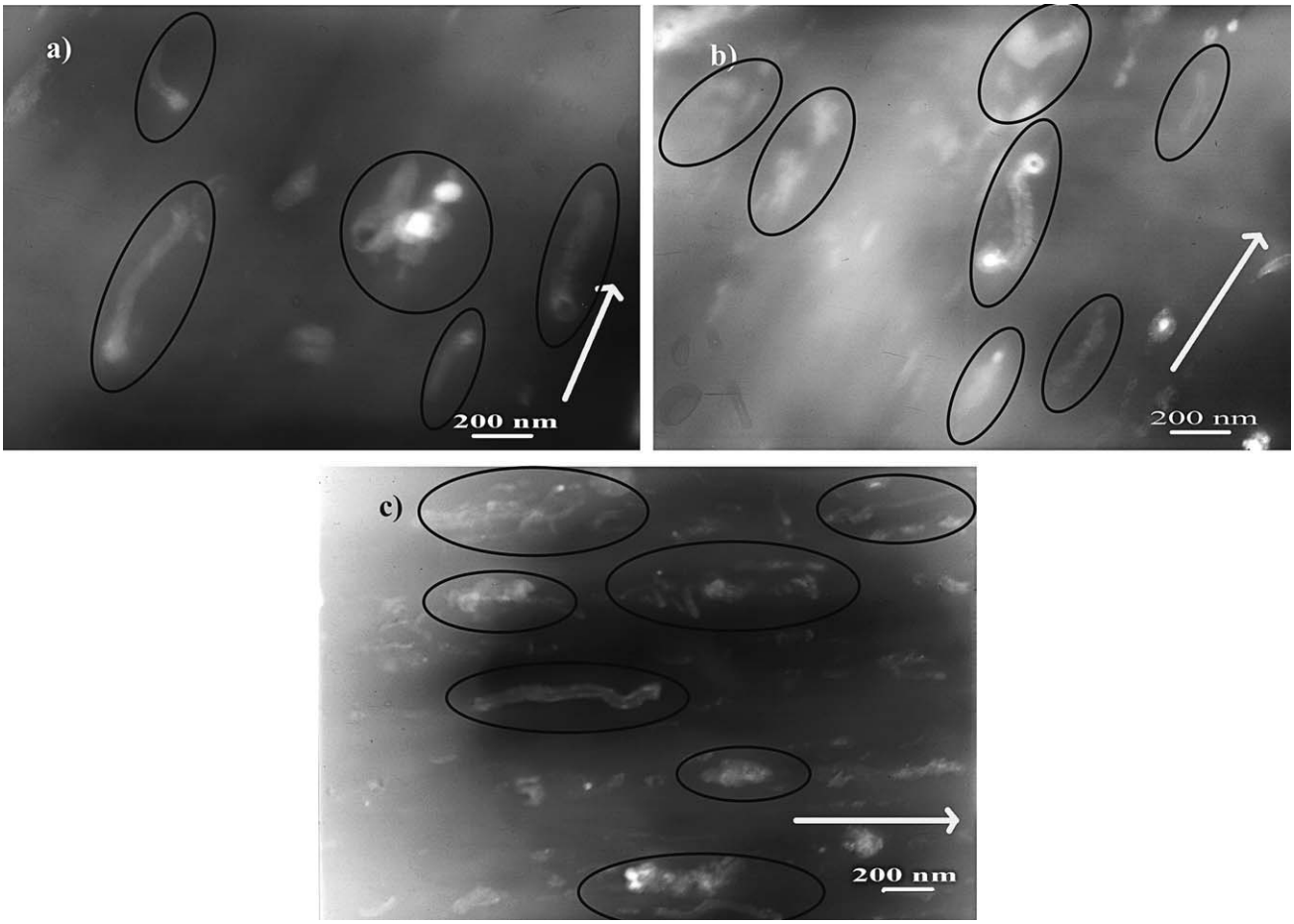

Figure 6 TEM images of PP composite fibers with (a) 1% MWCNTs, (b) 3% MWCNTs, and (c) 5% MWCNTs.

cross section of the fiber and Figure 6(a) from the TEM image of a longitudinal of fiber. The isolated tubes from MWCNTs bundles are observed. However, the modulus exhibited a very slight increase with further addition of MWCNTs. Figure 5(b) shows the SEM image of 3 wt % MWCNTs composite fiber. The globally dispersion is good; however, small bundles of MWCNTs are observed locally. This is why a slight increase of modulus was found. However, at 5 wt % of MWCNTs, the tensile properties of composite fibers decreased. This should be a result of nanotubes aggregation as showed in Figures 5(c) and 6(c). Similar trends have been reported by Chang et al.[11] for PP/SWCNTs nanocomposites. They found an increase of Young's modulus of composite fibers when 1 wt % SWCNTs was used, but when the content of SWCNTs was increased further to 2–5 wt %, the modulus stayed stable. In addition, Wang et al.[14] studied the effect of MWCNTs content on tensile properties of ultra-high molecular weight polyethylene fibers: the modulus of fibers increased with addition of MWCNTs at 1 wt % and decreased when the content of MWCNTs exceeded 2 wt % (effect caused by the agglomeration of MWCNTs).

TEM micrographs of the nanocomposite fibers were used to reveal the MWCNTs dispersion and alignment. Images were taken along the fiber axial direction for the 1, 3, and 5 wt % MWCNTs composite fibers as shown in Figure 6. The images show a good dispersion of the nanotubes in the PP matrix. However, for 5 wt % MWCNTs composite fiber, some aggregations were observed. The images also show the alignment along the fibers axis (see arrow directions). These alignments lead to the enhancement of tensile properties.

CONCLUSIONS

1. The type of dispersing agents did not affect the composite fibers tensile properties.
2. The composite fibers with 1 wt % MWCNTs showed a significant increase of tensile properties; 39% and 69% for tensile strength and secant modulus at 1% strain, respectively. The SEM and TEM images of this composite revealed a good dispersion of MWCNTs.

3. The addition of 2–4 wt % MWCNTs into PP matrix could not enhance the tensile properties further. SEM image of these composites showed the globally dispersed but locally aggregated MWCNTs.
4. SEM and TEM images showed the agglomeration of MWCNTs in 5 wt % MWCNTs composite fibers.

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