

Polypropylene/Carbon Nanotube Composites Prepared with an Environmentally Benign Processes

Junsuk Kim, Yeonsu Jung, Young-Je Kwark, Youngjin Jeong

Department of Organic Materials and Fiber Engineering, Soongsil University, Seoul 156-743, South Korea

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ABSTRACT: Polypropylene (PP)/multiwalled carbon nanotube (MWNT) composites were prepared with an environmentally benign processes. The surface functionalization of the MWNTs was performed with water as a solvent, and the functionalized MWNTs were mixed with PP to form composites with a melt process. The effects of the MWNTs on the mechanical and thermal properties of the composites were studied. The tensile strength and modulus of the composites increased with the amount of MWNTs. The thermal stability was also improved by the

reinforced MWNTs. The MWNTs also improved the oxidative stability of the composite on UV irradiation. Although pure PP degraded almost completely after 12 h of irradiation, the composite reinforced with MWNTs retained some level of mechanical strength after UV irradiation. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 1335–1340, 2010

Key words: compounding; fibers; nanocomposites; processing

INTRODUCTION

Since the report on carbon nanotubes (CNTs) by Iijima,¹ CNTs have been studied extensively as a filler in polymer composites because of their high aspect ratio, nanosize, very low density, and more important, excellent physical properties, such as their extremely high mechanical strength and high electrical conductivity and thermal stability.^{2,3} However, the strong van der Waals interactions between CNTs makes them aggregate into bundles. Therefore, to use them as a reinforcing agent, it is essential to evenly disperse them in the polymer matrix by enhancing the interfacial bonding between the CNTs and the polymer.⁴

Introducing functional groups onto the surface of CNTs has been used most frequently for this purpose. One of the most commonly used methods is the refluxing of CNTs with concentrated nitric acid to create acidic sites on the CNTs, such as carboxylic acids and hydroxyl groups.^{5–8} These groups greatly enhance the interaction between the CNTs and the polymer matrix, which results in a huge improvement in the mechanical strength of the nanocomposites.⁹ However, because the method uses strong

acid, it is environmentally unfriendly and potentially dangerous. Recently, a more environmentally benign process was reported by Price and Tour.¹⁰ They functionalized single-walled carbon nanotubes (SWNTs) by reacting SWNTs with aromatic amines in the presence of an oxidizing agent. Because the process used water as a solvent, it was a safe and simple method for introducing functional groups onto the CNTs.

Generally, CNT/polymer composites have been prepared with solution mixing or *in situ* solution polymerization in the presence of CNTs. The solution-based processes are effective in dispersing CNTs into polymer matrix, mostly because of their low viscosity. However, the use of organic solvent makes them considered to be environmentally hazardous processes. Recently, there have been several attempts to mix CNTs with molten polymeric matrices at high temperatures.^{11–13} The melt process is preferred in industrial applications of polymer/CNT composites because it is environmentally benign and compatible with current industrial processes.^{14,15} However, the dispersion of CNTs in molten polymers is generally poor because of the high viscosity.

The aim of this study was to explore polypropylene (PP)/multiwalled carbon nanotube (MWNT) composites prepared with more environmentally friendly methods. PP was chosen because of its wide application in the composite industry.^{16,17} At the same time, it was challenging to use PP as a polymer matrix because the nonpolar nature of PP makes the incorporation of polar fillers and reinforcements very difficult.¹⁸ The effects of the functionalized

Correspondence to: Y. Jeong (yjeong@ssu.ac.kr).

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MWNTs on the mechanical and thermal properties of the PP/MWNT composites were studied. Also, the resistance of the PP/MWNT composites to UV oxidation was tested because the UV absorbing properties of the MWNTs was expected to enhance the oxidation resistance of the composites.¹⁹

EXPERIMENTAL

Materials and characterization

PP chips (purity = 99%) were supplied by Honam Petrochemical Co. in Yeosu, Korea (melt index = 3.5 g/10 min at 230°C). MWNTs prepared by the chemical vapor deposition method were purchased from Iljin Nanotech Co. in Korea. The MWNTs had a purity of 95% or greater, a diameter of approximately 10–20 nm, and a length of 10–50 μm. *N*-butylaniline and isoamyl nitrite were purchased from Aldrich and were used without further purification.

Fourier transform (FT)–Raman spectroscopy (Bruker Equinox 55 FT–Raman spectrometer) was used to characterize the chemical modification of the functionalized MWNTs with an Ar⁺ incident laser with a wavelength of 514.5 nm and a power of 36 μW. Fourier transform infrared (FTIR) spectra were obtained with a Jasco FTIR 6300 model in the range from 600 to 4000 cm⁻¹ with the KBr pellet technique. The morphology of the composites was examined with field emission scanning electron microscopy (FE–SEM). We prepared the samples for FE–SEM by fracturing the composites in liquid nitrogen. The thermal properties of the composites were determined with differential scanning calorimetry (DSC; PerkinElmer DSC-7). The temperature was scanned from 20 to 200°C at a rate of 10°C/min. Thermogravimetric analysis (TGA) was also carried out with a Seiko TGA 6200. Samples of about 3 mg were ramped at 10°C/min from room temperature to 600°C under an N₂ atmosphere. Tensile tests were carried out with a universal testing machine (Hounsfield H10K-S) at room temperature with a gauge length of 25 mm and a crosshead speed of 5 mm/min. The initial modulus was determined at 1% strain. The measurements were done in an air-conditioned laboratory at 20°C.

Preparation of the PP/MWNT composites

First, MWNTs were functionalized to help their dispersion in PP by an increase in the interfacial interaction with PP, according to the literature.¹⁰ 4-Butylphenyl groups were introduced onto the MWNTs in this study; we expected aliphatic interaction between the MWNTs and PP. Typically, MWNTs (50 mg) and deionized water (150 mL) were homogenized (IKA T25) in a round-bottom flask at the medium

setting for 30 min. Isoamyl nitrite (Aldrich, 0.975 g, 2 equiv per MWNT C) and 4-butylbenzene amine (Aldrich, 2.485 g, 4 equiv per carbon in MWNT) were added to the reaction flask, and the flask was heated at 80°C in oil bath for 12 h. The contents were cooled to room temperature and filtered on a Teflon filter (0.5 μm). The filter cake was washed repeatedly with deionized water and acetone and then sonicated (Sonics & Materials, Inc. (Yeosu, Korea), bath sonicator, 20 kHz, 150 W) for 10 min in *N,N*-dimethylformamide (100 mL). The final functionalized MWNTs were obtained by filtration and rinsed with acetone.

We created the nanocomposites by dry blending PP powder with a given ratio of the functionalized MWNTs (0.3, 0.5, 1, and 3 wt %). The preblends were mixed mechanically with a basic analytical mill (IKA A11) and were fed into a twin-screw extruder (Bautek BA11, Seoul, Korea) with a screw length-to-screw diameter of 40. A temperature profile, starting from the feeding zone to the die, of 120, 165, 168, 170, 173, and 175°C was used, and the screw speed was set to 150 rpm. The extrudates were spun into filaments with a single extruder (Ajin Machine Co., Korea) with a screw length-to-screw diameter of 26 and drawn to a 6 : 1 ratio in hot water (95°C). Finally, the drawn filaments were annealed at 110°C for 10 min.

UV irradiation

An accelerated UV-oxidation test was carried out with a UV irradiator (40 mW/cm², Korea Ultra-Violet Co., Incheon, Korea) with excitation wavelengths from 200 to 420 nm and a dominant wavelength of 340 nm. Pure PP and the prepared PP/MWNT composites were irradiated for various times up to 14 h.

RESULTS AND DISCUSSION

Functionalization of MWNTs

The functionalized MWNTs were characterized with Raman and FTIR spectroscopy. Figure 1 shows the Raman spectra of the pristine MWNTs and the functionalized MWNTs. Compared to the pristine MWNTs, the functionalized MWNTs showed increased intensity in the disorder mode (D-mode) at 1350 cm⁻¹. The increase in the D-mode was attributed to the sp³ carbons present in the MWNTs after functionalization.²⁰ The relative degree of functionalization was determined with a *D/G* ratio, the intensity of D-mode divided by the intensity of the tangential mode at 1580 cm⁻¹. The *D/G* ratio increased from 0.97 to 1.73 after functionalization. FTIR spectroscopy was also performed to characterize the MWNTs (Fig. 2). The FTIR spectra of the

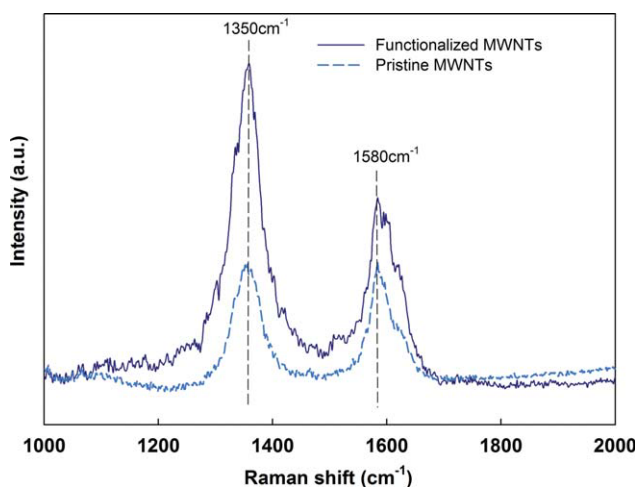


Figure 1 Raman spectra of the pristine (solid line) and functionalized (dashed line) MWNTs. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

functionalized MWNTs showed the sp^3 C–H stretching peak at 2950 cm^{-1} , which rarely appeared in the spectrum of the pristine MWNTs.

Morphological analysis

FE–SEM was used to investigate dispersion of the MWNTs in the PP matrix. Figure 3 shows the scanning electron microscopy (SEM) images of the fracture surfaces of the PP/MWNT composites containing pristine MWNTs [Fig. 3(a)] and the functionalized MWNTs [Fig. 3(b)]. It shows that the pristine MWNTs were aggregated into bundles, whereas the functionalized MWNTs were separated and well dispersed in the matrix. Also, the SEM micrograph in Figure 3(b) shows that the pullout nanotubes were shortly cut, which implied a strong

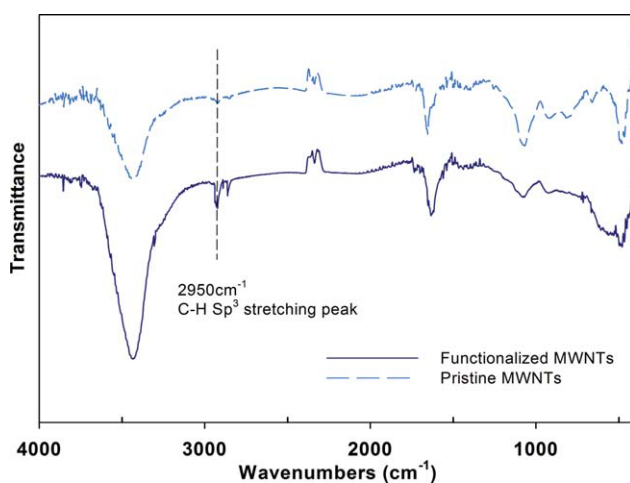


Figure 2 FTIR spectra of the pristine (solid line) and functionalized (dashed line) MWNTs. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

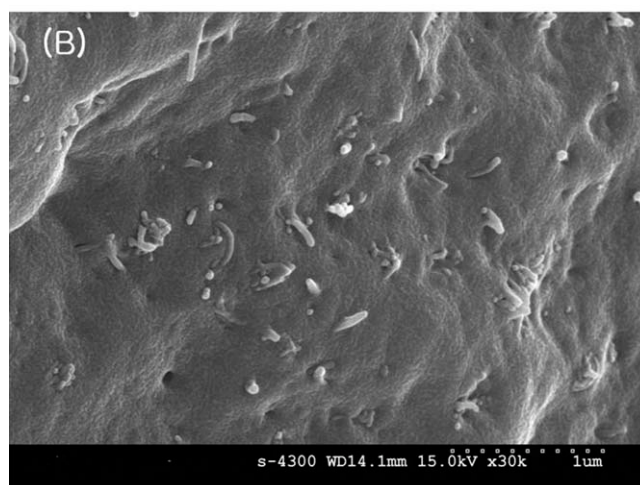
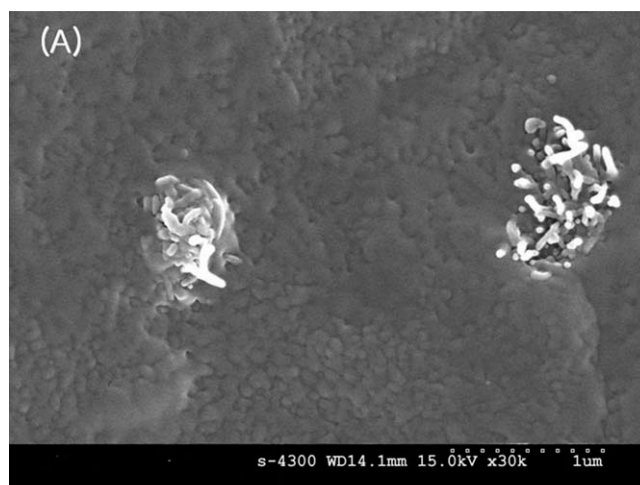


Figure 3 FE–SEM images of the PP/MWNT composites containing 1 wt % of (A) pristine and (B) functionalized MWNTs.

interfacial strength between the matrix and the MWNTs. The enhanced interaction appeared to be due to the better interaction between 4-butylphenyl groups on the MWNTs and the PP matrix.

Thermal properties

DSC measurements were carried out to check the thermal properties of the PP/MWNT composites. The results are shown in Table I and Figure 4. The crystallization temperature increased with the content of MWNTs, indicating that the MWNTs facilitated the crystallization of PP. Some inorganic fillers, such as glass fiber, clay, or carbon black, incorporated in a polymer matrix acted as nucleation agents to accelerate crystallization. The change in crystallinity with the incorporation of MWNTs (Table I) also supported this explanation. The crystallinity of the composites was calculated from Eq. (1) with a ΔH_f^0 value of 207.1 J/g for 100% crystalline PP²¹ (where ΔH_f is the enthalpy change during crystallization

TABLE I
Thermal Properties of the PP/MWNT Composites with Different Contents of MWNTs

Sample	Crystallinity (%)	Crystalline temperature (°C)	Melting temperature (°C)	Decomposition temperature (°C)
Pure PP	41.3	108.21	160.4	389.6
PP/MWNT (0.3%)	43.07	118.8	160.2	390.2
PP/MWNT (0.5%)	43.37	120.14	160.7	396.4
PP/MWNT (1%)	43.45	120.2	159.9	408.1
PP/MWNT (3%)	44.2	121.0	160.4	415.8

measured for the composites). Table I shows that the crystallinity of the composites increased with the content of the MWNTs. For instance, pure PP had a degree of crystallinity of 41.3%, whereas the composite with 3 wt % MWNTs showed a value of 44.2%. Similar results were reported by Haggemueller et al.²² for polyethylene/SWNT composites. They suggested that SWNTs could act as nucleating agents for the crystallization of polyethylene. On the other hand, the melting temperature of the PP/MWNT composite was not affected by the incorporation of the MWNTs:

$$\text{Crystallinity}(\%) = \frac{\Delta H_f}{\Delta H_f^0} \times 100 \quad (1)$$

A comparative TGA of pure PP and the composites with various MWNT contents is shown in Figure 5. The TGA curves showed no significant weight loss until 300°C. However, the onset of degradation was delayed by an increase in the content of the loaded MWNTs. This indicated that the addition of MWNT improved the decomposition stability of the

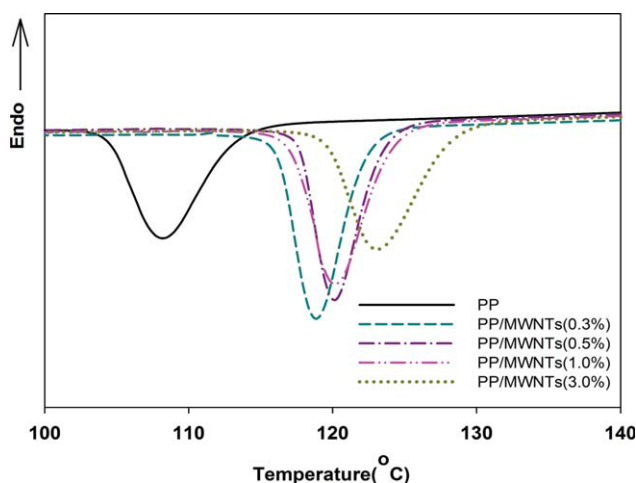


Figure 4 DSC thermograms for pure PP and the PP/MWNT composites on the first cooling: (a) pure PP, (b) PP/MWNT (0.3 wt %), (c) PP/MWNT (0.5 wt %), (d) PP/MWNT (1 wt %), and (e) PP/MWNT (3 wt %). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

PP matrix. The improved thermal stability of the PP/MWNT composites appeared to be due to the high thermal conductivity of the MWNTs²³ and the improved interaction between the MWNTs and PP.²⁴ Marosfői et al.²⁴ reported that improved interfacial interaction increased the activation energy for degradation at interfaces between the MWNTs and PP and retarded the thermal degradation at the surface of the composite because of the superior thermal conductivity of the MWNTs.

Mechanical properties

Tensile tests for the composite filaments were performed with a universal testing machine. Figure 6 shows a representative set of stress–strain curves for the PP/MWNT composite filaments with different MWNT contents. It clearly shows that the tensile strength and initial modulus of the composite filaments increased with the content of the MWNTs. On the other hand, the breaking elongation decreased with the addition of the MWNTs. The tensile strength increased by approximately 49.2% with 1 wt % MWNTs, which supported both homogeneous dispersion of the MWNTs into the polymer matrix and the effective load transfer from the polymer matrix to the MWNTs. These results were also in line

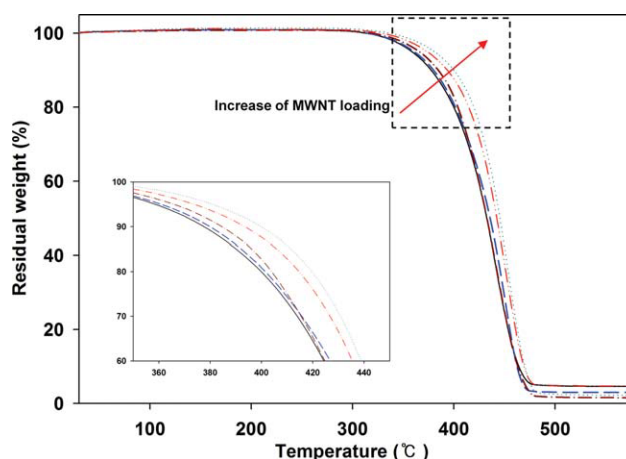


Figure 5 TGA curves for the pure PP and PP/MWNT composites with different contents of MWNTs. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

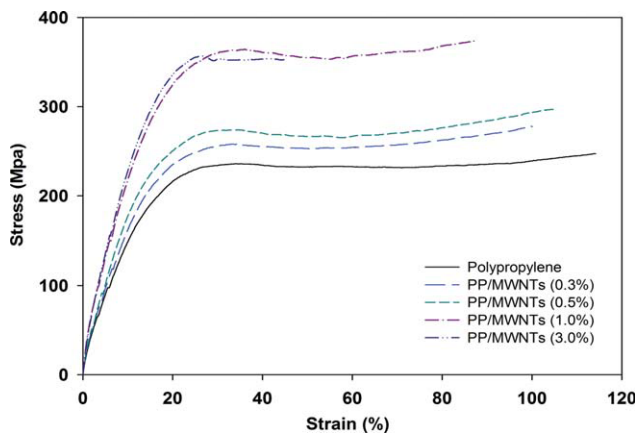


Figure 6 Stress–strain curves for the pristine PP and PP/MWNT composite filaments: (a) pure PP, (b) PP/MWNT (0.3 wt %), (c) PP/MWNT (0.5 wt %), (d) PP/MWNT (1 wt %), and (e) PP/MWNT (3 wt %). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

with the increased crystallinity of the PP/MWNT composites. However, the strength did not increase further with higher loadings of MWNTs.

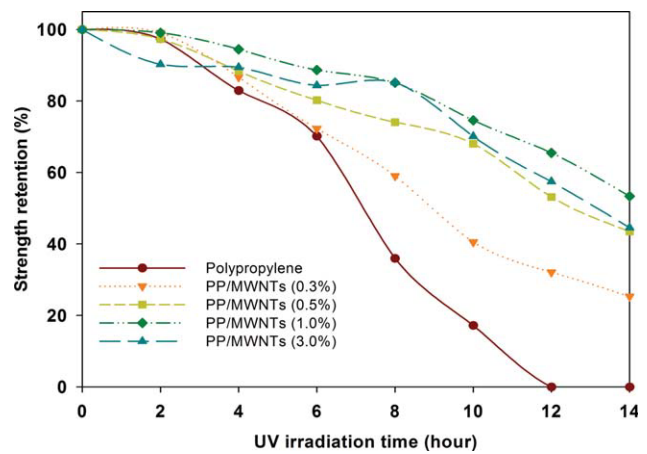


Figure 7 Strength retention of PP and the PP/MWNT composite filaments after UV irradiation. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

UV irradiation

UV irradiation experiments were carried out on the composite filaments. It is well known that PP is liable to be degraded by UV, and antioxidants

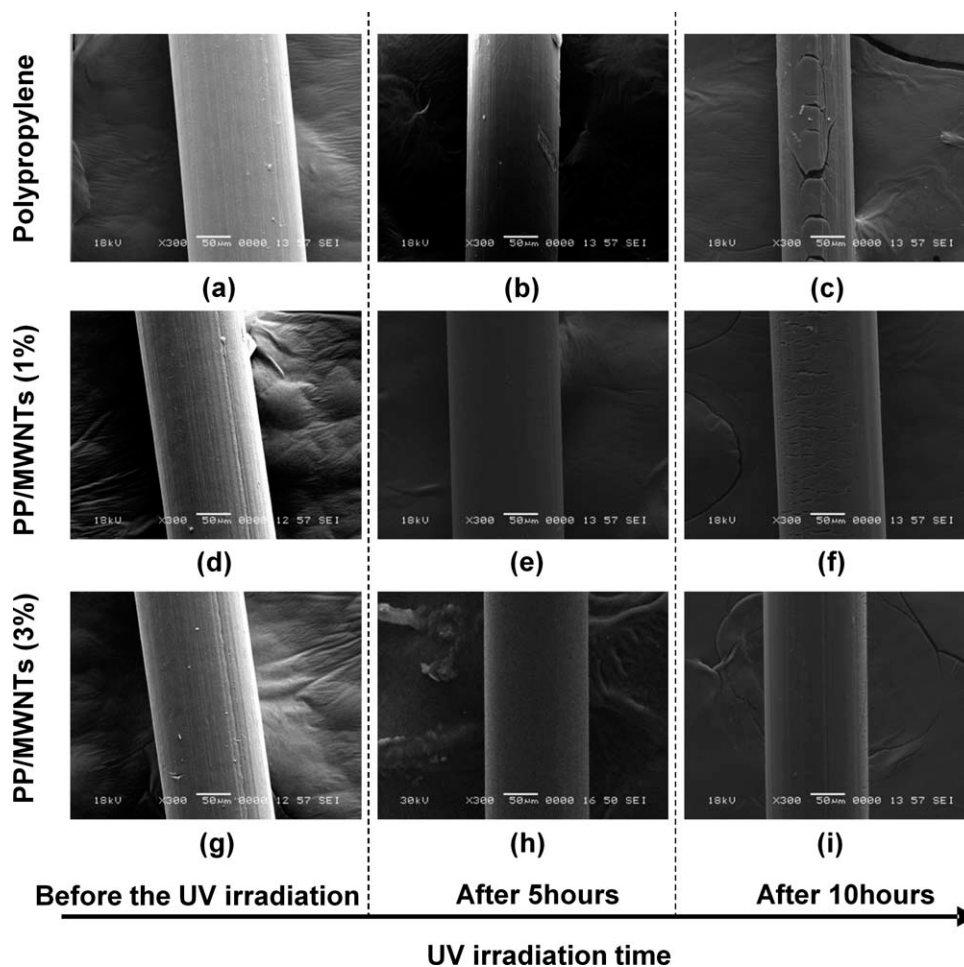


Figure 8 Morphological changes of the pristine PP and PP/MWNT composite filaments with UV irradiation time.

should be added for outdoor applications.¹⁹ In this study, the resistance to UV oxidation of PP reinforced with the MWNTs was tested with various irradiation times and contents of the MWNTs. Figure 7 shows that the tensile strength of the composites changed with the irradiation time and the content of the MWNTs. Pure PP lost its original strength almost completely after 12 h of irradiation, whereas the PP/MWNT composite (1.0 wt %) retained more than 65.5% of its original strength. Although it was not easy to draw a clear relationship between the strength retention and the amount of MWNT loading, we could see that the strength retention increased generally with the content of MWNTs. Figure 8 shows the effect of the UV irradiation on the morphologies of the PP and PP/MWNT composites. Pure PP had a serious crack on the surface after 10 h of UV radiation, whereas the PP/MWNT (3 wt %) composite did not show any noticeable change. From these results, we concluded that MWNTs could protect PP by absorbing UV light. This was due to the unique properties of CNTs of absorbing UV light. CNTs 10–50 nm in diameter had a large band gap. When light was irradiated, the light with less energy than the band gap passed through the CNTs. However, the light with higher energy than the band gap was absorbed.²⁵ Because of the mechanism, photooxidation of the PP/MWNT composite filaments became slower than in the pristine PP filament.²⁵

CONCLUSIONS

PP/MWNT composites were prepared by an environmentally benign processes. The FE-SEM results indicated that the MWNTs functionalized with the “green” method were well dispersed into the PP matrix through melt mixing. Because of the enhanced dispersion and interfacial bonding, the tensile strength and modulus increased with the content of MWNTs. Also, the functionalized MWNTs increased the thermal stability, crystallinity, and crystallization temperature of the composites. Melt-mixing processes have been not considered as effective to prepare CNT composites. However, our results indicate that the proper functionalization of the CNTs could make the processes valuable.

The effect of UV irradiation on the PP/MWNT filaments was also studied. The selective absorption of

UV light by the MWNTs prevented oxidative degradation of the PP matrix. Therefore, the incorporation of the properly functionalized MWNTs not only increased the mechanical properties of the PP matrix but also would improve the lifetime of the composites in outdoor applications.

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