

Morphology, Thermal Stability, and Dynamic Mechanical Properties of Atactic Polypropylene/Carbon Nanotube Composites

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ABSTRACT: Nanocomposites based on atactic polypropylene (aPP) and multiwall carbon nanotubes were prepared by melt blending at 80°C with a Barabender mixer. The morphology, thermal stability, and dynamic mechanical properties of the obtained composites were studied subsequently. SEM observations indicate that the nanotubes are well dispersed in the aPP matrix. Each nanotube is covered by a layer of aPP molecules. Thermal stability of the aPP in nitrogen is found to be enhanced significantly by the addition of nanotubes. Peak temperature of the DTG curve for the nanocomposite with 5 wt % nanotube loading shows

about 70°C higher than that of pure aPP. Dynamic mechanical properties of aPP are also influenced by nanotubes, as shown by the increase in the storage modulus as well as significantly broadened loss $\tan\delta$ peak. These effects of nanotubes on the thermal stability and mechanical properties of aPP are explained by the adsorption effect of the aPP molecules on the nanotube surfaces in this study. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1087–1091, 2005

Key words: nanocomposite; atactic polypropylene; carbon nanotube; thermal stability; morphology

INTRODUCTION

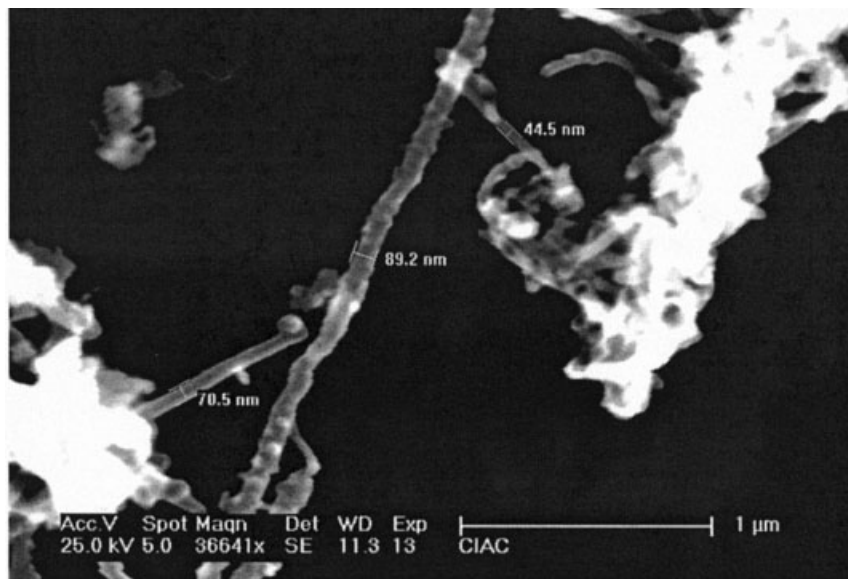
Nanocomposites are filled polymers with at least one dimension of the fillers on the nanometer scale. The addition of such nanoscale fillers as clay or talc into the polymeric matrix was found to enhance the thermal stability and mechanical properties efficiently. This enhancement was attributed to the unique characteristics of the nano-fillers.¹ One of the most frequently used nano-fillers recently is carbon nanotubes, either multiwall or single walled, as cost reduction and yield increase with technical progress. The higher surface area of the nanotubes ensures adhesion between the dispersed fillers and the matrix. Good adhesion is the key factor to obtain high performance for the resulting composites. The preparation of nanotube-filled composites and their mechanical, electrical, and optical properties are summarized in previous publications.^{2,3} It is realized that the dispersion and orientation of the carbon nanotubes in the matrix, as well as the interface tension between the nanotubes and the polymers, are important factors influencing the mechanical performance of the final materials.

Isotactic polypropylene (iPP)/carbon nanotube composites have been studied extensively.^{4–9} The influences of nanotube-filling on the physical properties of iPP were concentrated on three aspects. First, the incorporation of carbon nanotubes, especially the single-walled ones, accelerates the nucleation and crystal growth mechanisms of iPP. This influence is weakened with the increase in the nanotube content. Second, the mechanical properties of iPP are reinforced as demonstrated from the dynamic mechanical analysis. Tensile strength and modulus of the melt-spun iPP fibrils with 1 wt % nanotubes was found to be increased by 40 and 55%, respectively. Third, nanotubes enhance the thermal stability and flammability of iPP. However, there are few open publications on atactic polypropylene (aPP)/nanotube composites.

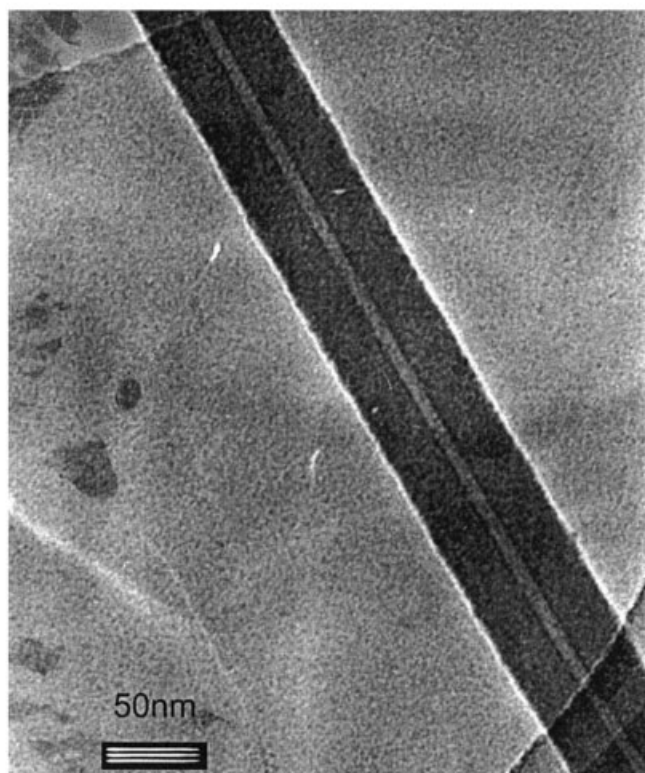
aPP is a general by-product of propylene polymerizing, which is often regarded as industry waste because of its broad molecular weight distribution. One major application is to disperse the functional groups grafted aPP into iPP-based composites as an interfacial modifier, since aPP is of easy chemical modification.^{10–12} aPP behaves like liquid oil, soft viscous solid, and elastomer, respectively, with increasing its molecular weight. The aPP synthesized with metallocene catalysts may have a weight-averaged molecular weight as high as 3.67×10^6 g/mol and narrow dis-

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(a)



(b)

Figure 1 Micrographs of carbon nanotubes: (a) ESEM and (b) TEM.

persion of 1.9, which exhibits good rheological properties.¹³

In this work, we investigated the morphology, thermal, and mechanical properties of aPP/carbon nanotube composites prepared by melt blending. The aim of this study is to obtain novel nanocomposites with desired properties, as well as to expand the applications of aPP.

EXPERIMENTAL

The aPP used in this work is a byproduct from a propylene polymerization reactor of Liaoyang Petrochemical Corp. (Liaoyang City, P.R. China). Its weight-averaged molecular weight (M_w) and number-averaged molecular weight (M_n) are 41,402 and 1481, respectively, as measured by GPC. The stereoregular-

ity is determined to be 42.9% (mm), 34.4% (mr), and 22.7% (rr) by ^{13}C -NMR. Multiwall carbon nanotubes (MWNTs) were supplied by the Institute of Metal Research Chinese Academy of Sciences. APP/carbon nanotube composites were prepared by mixing aPP melt with nanotubes on a Barabender mixer operating at 80°C and 50rpm for about 30min. The plain aPP was also processed under the same condition for comparison. aPP was dried in a vacuum oven for 48h at 50°C before blending. The obtained samples are marked as follows: aPP1 marks the composite of 1.0 wt % nanotube loading, and so on.

A Philips XL-30 environmental scanning electron microscope (ESEM) operated at 25kV was used to examine the fracture surfaces of the nanocomposites as well as the nanotubes. The composites were fractured at liquid nitrogen temperature to get the fresh surfaces gold coated before observation. In the case of the nanotubes, they were directly mounted onto a standard holder with conducting carbon tape for ESEM observation. A JEM-2010 TEM (Japan) was also employed to observe the microstructure of carbon nanotubes. In this case, a nanotube suspension after dispersing in chloroform with ultrasonication was prepared, and then it was dropped onto a copper grid for TEM observation. The thermogravimetric analysis (TGA) was carried out under nitrogen flow (20 mL/min) using a Perkin-Elmer TGA-7 thermoanalyzer. Samples about 5.0mg were heated from room temperature to 600°C with a heating rate of 20°C/min. DMA measurements were performed on a Netzsch DMA-242 dynamic mechanical analyzer at 3°C/min and 1.0Hz under tension.

RESULTS AND DISCUSSION

MWNTs are believed to have a structure assembled of concentric graphite tubes, where only weak van de Waal forces bond one tube to another. The nanotubes vary greatly in length and diameter, and it is impossible to find a pair of identical ones. Figure 1 shows the microstructures of the MWNTs used in this work. As shown in Figure 1(a), the nanotubes have a length larger than 2.0 μm and their diameters are not uniform, with an average of approximately 70nm. The surfaces of some nanotubes are of roughness with visible nodules that are impurities embedded during the preparation.¹⁴ One impurity proved to be the catalyst particles such as iron particles. These particles can be encapsulated anywhere inside the nanotubes and near the nanotube tips. Kinking of some nanotubes is also observed. The rib-like hollow structure with a diameter of about 10nm is clearly shown in Figure 1(b).

Figure 2 shows the typical ESEM micrograph of the fracture surfaces of aPP/carbon nanotube composites. The main feature on the micrograph is the mountains-

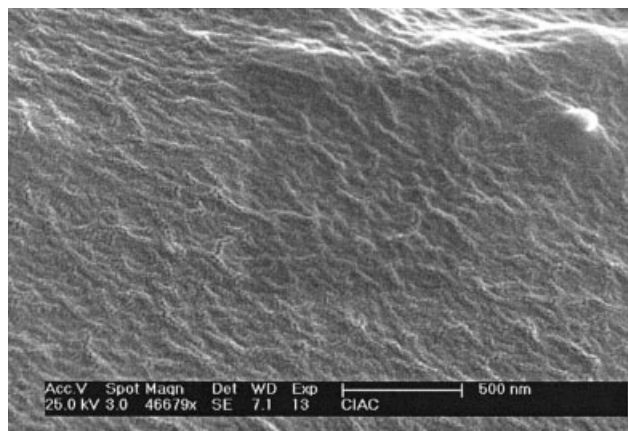


Figure 2 ESEM micrograph of the fracture surface of aPP1.

like prominences with a network of fine cracks. The width of the crazes is of the same magnitude as the inner diameter of the nanotubes as shown in Figure 1(b), that is, about 10.0nm. This means that the composite breaks through the splitting of the nanotubes. The fine crack network presents the residues of the breaking nanotubes and is also evidence of good dispersion of the nanotubes in the aPP matrix. And there are no pulling-out nanotubes observed in the fracture surface, which means nanotubes are well wetted by the aPP molecules. Hollow structure induced holes into the polymers. These holes act as stress concentrators and initiate premature cracking when the temperature is lower than the glass transition temperature.¹⁵ The stress concentration may be attributed to the difference in thermal expansion coefficients between the matrix and the air trapped within the nanotubes, especially as the composites were quenched at liquid nitrogen temperature. Therefore, carbon nanotubes can only be used as reinforcement fillers instead of toughening agents. In contrast, solid nano-fillers are believed to increase both the strength and toughness of the matrix so long as even and isolated dispersion is satisfied.¹

TGA results of aPP, aPP1, and aPP5 in nitrogen and a heating rate of 20°C/min are shown in Figure 3. Both aPP and its nanocomposites decompose in a single step beginning at 200°C, but TGA curves of the nanocomposites shift toward higher temperatures compared with those of aPP. The end temperature of decomposition is retarded with increasing nanotube content. The masses remaining at 500°C are almost entirely due to the remaining nanotubes, and are consistent with initial nanotube loading. The peak temperature (T_p) on one DTG curve represents the temperature at which the maximum weight loss rate is reached, as shown in Figure 3(b). T_p appears at about 360°C for aPP, and it is significantly increased by about 40°C and 70°C for aPP1 and aPP5, respectively, in the experimental conditions of this work. The re-

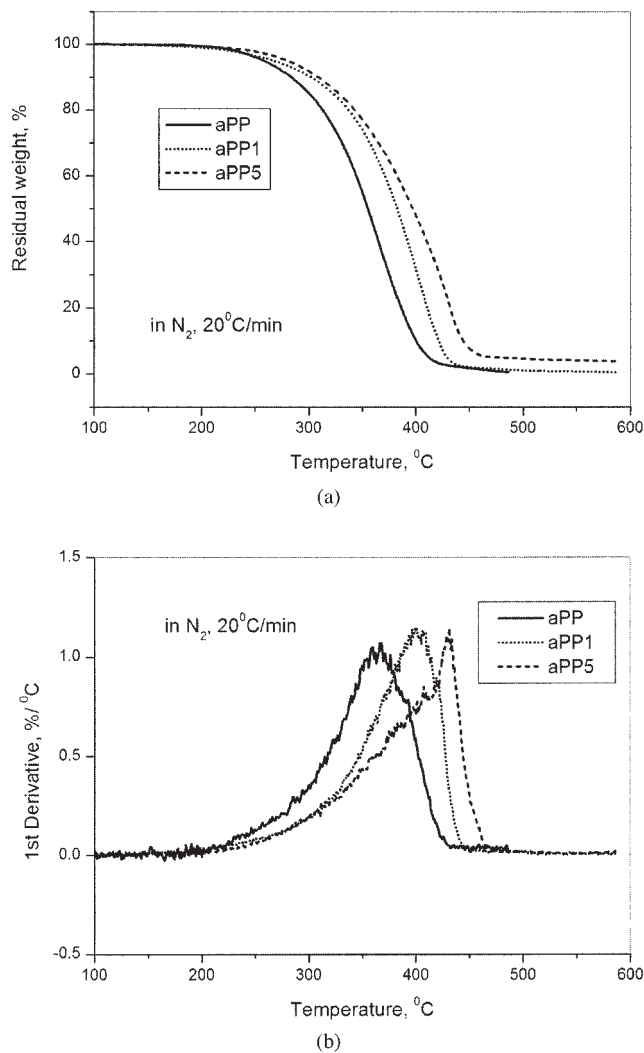


Figure 3 TGA curves (a) and the corresponding DTG ones (b) of aPP, aPP1, and aPP5 in a nitrogen atmosphere.

sults indicate that the addition of nanotubes significantly enhanced the thermal stability of aPP in nitrogen.

The increase in peak temperature is also found in the iPP/MWNTs system, where a 12°C increase is reached with 2 vol % nanotube loading.⁴ The authors concluded that the temperature increase could arise from the barrier effect of the well-dispersed nanotubes, which hindered the transport of degradation products. This labyrinth effect was employed originally to explain the onset temperature increase for an iPP/silicate system, of which the onset temperature is increased by 50°C whereas the peak temperature is only increased by 17°C. Another mechanism due to physical-chemical adsorption of the decomposed products was presented simultaneously.¹⁶ Here, we suggest that the significant enhancement in thermal stability of aPP by carbon nanotube addition is mainly attributed to the strong physical adsorption of aPP

molecules on the nanotube surfaces. If the labyrinth effect were the main cause, the onset temperature of aPP/nanotube composites would have been increased as in the iPP/silicate system. The layered structure of silicate favors the intercalation of degraded low molecular weight hydrocarbons, which remarkably delay the release. For nanotube fibrils, the intercalation does not exist. Each nanotube is covered with a layer of aPP molecules through physical adsorption since no chemical modification was made for both nanotubes and the matrix. The adsorbed molecules are much less active than those far from the nanotube surfaces, and thus their volatilization is delayed evidenced by the peak temperature increase.

Dynamic mechanical properties of aPP, aPP1, and aPP5 are shown in Figure 4. Storage modulus of aPP is increased with increasing the nanotube content, and the glass transition temperature as corresponding to

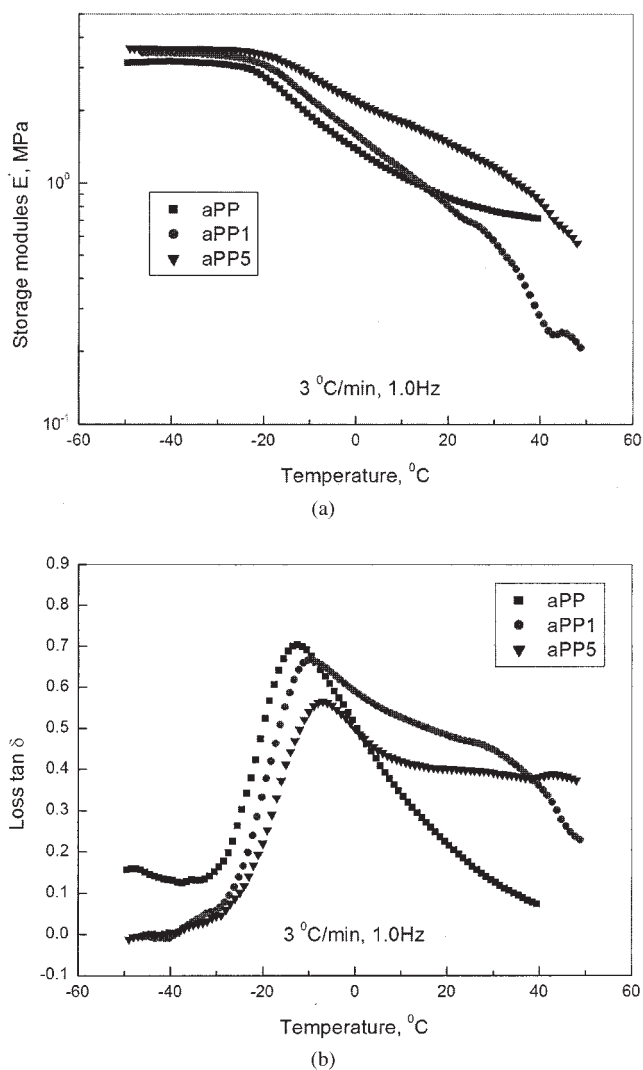


Figure 4 Dynamic mechanical analysis of aPP, aPP1, and aPP5: (a) storage modulus versus temperature, and (b) $\tan \delta$ versus temperature.

the peak $\tan\delta$ of aPP is slightly affected by the filled nanotubes. The biggest difference is that the $\tan\delta$ peak is significantly broadened at higher temperatures. This might be attributed to the less mobile of the adsorbed aPP molecules on nanotube surfaces. Similar effects have been observed in poly(vinyl alcohol)/carbon nanotube systems¹⁷ as well as a carbon black-filled styrene-butadiene rubber system.¹⁸ It is indicated that the enhancement effect of loss $\tan\delta$ after the glass transition temperature is more prominent in nanotube reinforced polymer composites than in carbon black ones. It is also noticed that the addition of single wall nanotubes (SWNTs) into iPP has little effect on the loss $\tan\delta$ peak.⁸ This may due to the preferential aggregation of SWNTs into bundles, which weakens the adhesion of iPP molecules on nanotube surfaces.

CONCLUSION

Atactic polypropylene and multiwall carbon nanotube (MWNTs) composites have been prepared by melt blending, and their morphology and physical properties have been investigated to obtain novel nanocomposites with balanced properties. It is found that the nanotubes disperse well in the aPP matrix. The thermal stability of aPP is significantly enhanced by the addition of nanotubes, and the mechanical properties are reinforced simultaneously. The results indicate that MWNTs are good fillers for improving the thermal and mechanical properties of aPP.

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