

# CONDUCTING PROPERTIES OF POLYPROPYLENE/ CARBON NANOFIBER COMPOSITES

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## **Abstract**

Effects of carbon nanofibers (CNFs) on the microstructure and properties of semi-crystalline polymers were studied based on preparation of polypropylene (PP) nanocomposites by a twin-screw extrusion. Crystallization behavior and morphology, as well as dielectric property, thermal and electrical conductivity of the CNF/PP nanocomposites were characterized. The degree of crystallinity of the PP exhibited an increased trend with addition of CNFs followed by moderate decreases at higher content. The PP nanocomposite containing 5wt% CNFs exhibited a surprisingly high dielectric constant under wide sweep frequencies attended by low dielectric loss. With the increasing of CNF content, electrical and thermal conductivities of nanocomposites were enhanced continuously.

## **1. Introduction**

As one of the most widely used plastics in large volume, polypropylene (PP) has a number of desirable properties, such as high chemical resistance, good mechanical properties, fine processability and low cost. To enhance low thermal stability and strength of PP, people have tried to apply novel additives and processing technology. Although numerous investigations were carried out on crystallization of PP composites [1-3], few studies have been reported related to overall influences of CNFs on the semi-crystalline polymers. In

particular, very few have reported work addressing the effects of CNFs on the final properties of the resulting nanocomposites through the crystallization behavior of the polymer matrix.

As an effective processing method, twin-screw extrusion can play an important role in preparing of nanocomposites to obtain nanocomposites with uniform microstructure [4-6].

This paper introduces the preparation carbon nanofiber/PP nanocomposites by a Micro-18mm twin-screw extruder which can provide the high shear compounding for polymer melts. After a great deal of exploring experiments, the optimal extruding procedures for carbon nanofiber/PP nanocomposites were established. The aim of the present work is to study the effects of carbon nanofiber content on crystallization behavior, mechanical properties, thermal conductivity, and electrical conductivity of the PP matrix.

## **2. Experimental**

### **2.1 Materials**

The PP was supplied by Formosa Plastics Corporation, USA under the trade name Formolene 5100H and had a density of 0.91kg/m<sup>3</sup>. CNFs used for nanocomposites preparation were supplied by Pyrograf Products, Inc., OH, USA under the trade name Pyrograf III<sup>®</sup> Carbon fiber. The average fiber diameter vary from 20nm to 200nm, and CNF content is >98%. The as-

received CNFs was dipped in hydrofluoric acid for 24h to get rid of impurities, and then CNFs was carefully washed and filtrated with deionized water until the pH level of the solution reached 6. Purified CNFs were dried prior to use for 24h in a vacuum oven to remove moisture. To avoid the effect of chemical reagent on the analyses results, only purified and dried CNFs were used and no other surface treatments were made in experiment.

## 2.2. Preparation of the CNF/PP composites

The CNFs up to 5wt% loading were melt-compounded with PP in a co-rotating Leistritz Micro-18/GL-40D twin-screw extruder manufactured by Brabender Technologie Inc, Germany. The screw rotation rate was set at 75 rpm, and the temperature profile from hopper to die was as follows: 182°C, 188°C, 193°C, 199°C, 204°C, 210°C, 210°C, 210°C. The extruded PP and composites were pelletized and then compression molded at 200°C to obtain test specimens.

## 2.3. Characterizations of the materials

Differential scanning calorimetry analysis was performed using TA Instruments DSC Q1000 in a nitrogen atmosphere. The specimens were heated at a rate of 10°C/min to 250°C. The morphology of the fracture interface of neat epoxy and composite specimens was observed by a JEOL JSM-6300 model scanning electron microscopy. The dielectric measurements of samples were carried out at room temperature using a Novocontrol Technologies Alpha-N high resolution Dielectric Analyzer made in Germany. Electrical conductivities of specimens were tested using a Keithley 6517A electrometer/high resistance meter at room temperature. A Keithley 8009 resistivity test fixture is connected. Thermal conductivity performances of samples were tested using a Mathis TC-30 Thermal Conductivity Instrument at room temperature.

## 3 Results and discussion

### 3.1. Morphological studies

The DSC thermogram of the neat PP and CNF/PP composite specimens is shown in Fig.1.

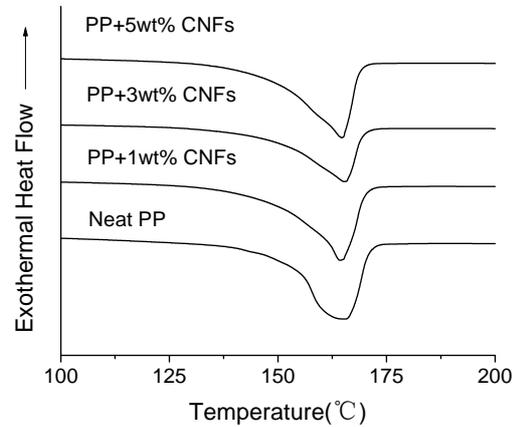


Fig.1 DSC curves of neat PP and CNF/PP composites

The  $T_m$  (peak temperature of crystallization melting), and  $\Delta H_m$  (melting heat of crystallization) are listed in Table 1. The degree of crystallinity of a specimen can be calculated from the melting heat of crystallization according to the following equation:

$$X_c = \frac{\Delta H_m}{\Delta H_0}$$

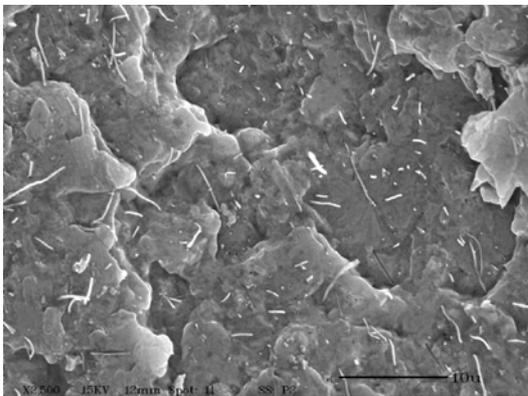
Where  $\Delta H_0 = 207.1\text{J/g}$  is the melting heat of 100% crystalline PP [7]. When increasing the loading of the CNFs, the peak temperature of crystallization melting of specimens was almost independent of CNF loading. The calculated degree of crystallinity of the specimens exhibited an increased trend with increasing CNF load, followed by a moderate decrease at 5wt% content of CNFs. It was implied that as the CNFs were added into the PP matrix, the lower loading of nanofibers could facilitate the mobility of the PP macromolecular chains. Nanofibers brought heterogeneous nucleation effects simultaneously, thus the degree of crystallinity of specimens increased. As the content of nanofibers increased, the nanofibers started to obstruct the mobilization of the macromolecular chains

and prevented macromolecular segments from obtaining ordered alignment of the crystal lattice. The degree of crystallinity of specimens decreased accordingly.

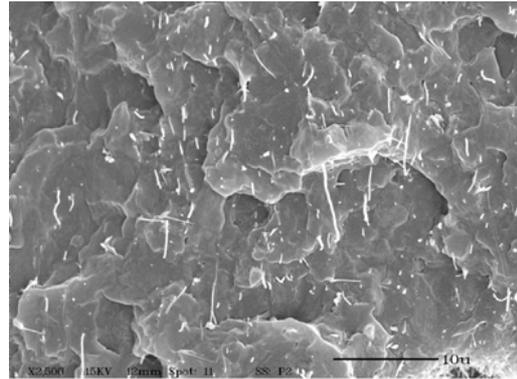
Table 1 Crystallization parameters of neat PP and CNF/PP composites

	$T_m(^{\circ}C)$	$\Delta H_m(J/g)$	$X_c(\%)$
PP+5wt% CNFs	164.68	91.11	43.99
PP+3wt% CNFs	165.25	96.78	46.73
PP+1wt% CNFs	164.29	93.08	44.94
Neat PP	165.39	87.46	42.23

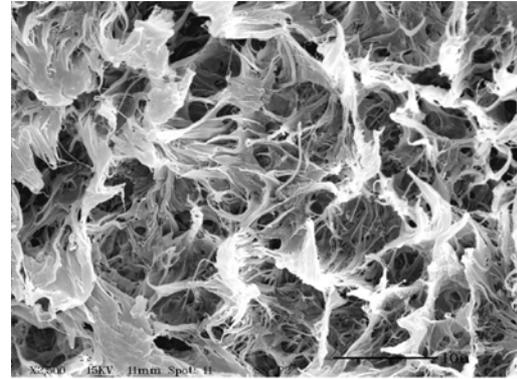
Fig.2 shows the micro-morphology of the CNF/PP composites prepared in experiments. Generally, nanofillers with high aspect ratios, such as nanofibers, are difficult to uniformly disperse within polymer matrices due to their high surface areas. The CNF/PP nanocomposites prepared for this study showed no obvious agglomerations however, suggesting that the nanofibers were dispersed uniformly in the PP matrix by means of the twin-screw extrusion. The micro-morphology of the nanocomposites containing 5wt% CNFs presented different features from other specimens. It can be observed that plastic deformation was prevalent in this nanocomposite, which is thought to be the result of both a stronger reinforcing effect from the high concentration of CNFs and higher amorphous portions of the PP inside this nanocomposite.



(a) PP + 1wt% CNFs



(b) PP + 3wt% CNFs



(c) PP + 5wt% CNFs

Fig.2 Micro-morphology of CNF/PP composites

This is consistent with the DSC test results which showed the crystallization degree to be lower with the addition of 5wt% of CNFs.

### 3.2. Dielectric properties

Dielectric constant showed the ability of a material to store electric potential energy under the influence of an electric field. In Fig.3 the effects of CNF loading on the dielectric constant under various applied sweep frequencies is shown. The dielectric constant of the neat polymer exhibited low frequency dependence, but with the addition of CNFs, the frequency dependence was gradually increased. Compared to neat PP, the addition of CNFs initially caused a decrease in the overall level of the dielectric constant. However, further loading to 5wt% CNFs saw the dielectric constant increase to a level much greater than that of the neat polymer.

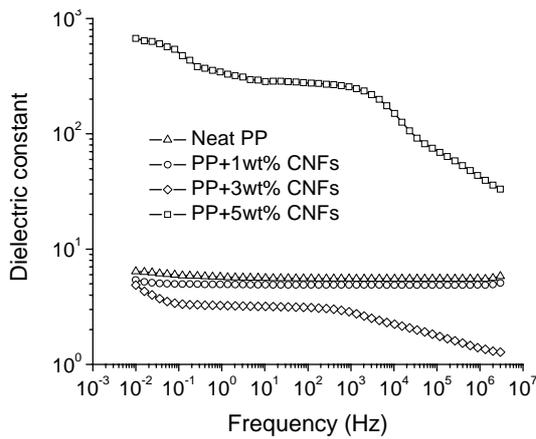


Fig.3 Dielectric constants vs. frequency

The experimental declines seen for PP composites with 1wt% and 3wt% CNF loading were suspected to be result of both an improvement in conductivity of the composite (which will be shown in the next section), and the increased degree of crystallinity in the specimens, which affected the dipole polarization of the groups and segments. From this study, it is reasonable to consider that the crystal characteristic of polymer matrix is also an important factor influencing the dielectric property of composite. However, the PP matrix containing 5wt% CNFs exhibited a surprisingly high dielectric constant under wide sweep frequencies, being more than 600 under low frequency and greater than 200 through to 4000Hz. This is considered to be a result of space charge polarization, structural defects in the matrix, and electrode effects [8]. The number of polarizable groups in the PP composites increased with the addition of CNF, which can cause extra polarization under an electrical field. The lower crystallization degree of the PP filled with 5wt% CNTs facilitated all kinds of polarization of the groups and segments in CNF/PP composites. Moreover, the electrical conductivity of the PP with 5wt% loading of CNTs exhibited no obvious increase compared to the 3wt% CNTs-filled PP composites (shown in the next section). All of the above factors brought about the outstanding dielectric properties of PP containing 5wt% CNTs. Meanwhile, the

variation of dielectric constant with frequency indicates the presence of an interfacial polarization in PP matrix. This gradually decreasing dielectric constant with increased frequency is thought to be caused by the slow dielectric relaxation of the matrix resin and the interface of the composite. The value scale and stabilization of dielectric constant obtained in this work is comparable with other reported dielectric materials, even is more remarkable and practical [9-12].

The loss factor of the dielectric constant of neat PP and the CNF/PP composites under various applied sweep frequencies is shown in Fig.4. Except for the PP matrix containing 5wt% CNFs, the loss factor of the samples all exhibited initial decreases with increased frequency, followed by an increase to a certain frequency. However, for the PP nanocomposites containing 5wt% CNFs, the loss factor increased with frequency at low frequency, and a peak of loss factor appeared around 3Hz. The first increase of loss factor at low frequency can be attributed to dipole polarization [8]. As the frequency further increased, the dipole polarization effects reduced and the value of the loss factor declined accordingly. More significantly, the values of loss factor of all samples are quite small compared to other related reports [9-11]. The PP nanocomposites containing CNFs studied in this work may find promising applications in dielectrics for advanced electronic devices.

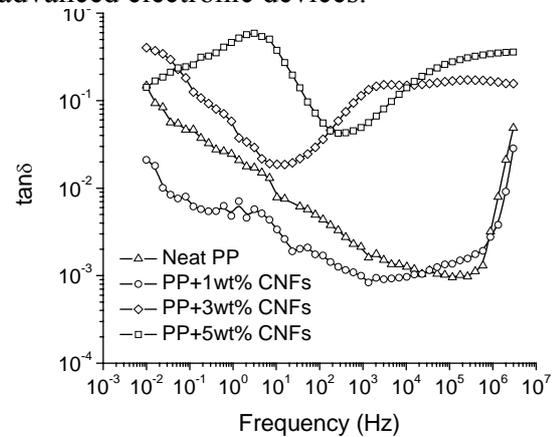


Fig.4 Dielectric loss factor,  $\tan \delta$ , vs frequency

### 3.3. Electrical and Thermal conductivities

The electrical conductivities of neat PP and CNF/PP composites were tested and the results are shown in Fig.5. The resistivity of the neat PP is larger than  $10^{13}$  ohm-m, consistent with the magnitude of an insulator. With the increasing of CNF loading, electrical resistivity of the PP nanocomposite was seen to decrease, which is attributed to the high electrical conductivity and good dispersion of the CNFs. At 3wt% CNF loading, a sharp decrease in the resistivity of the material was seen, decreasing roughly  $10^8$  times that of neat PP. In terms of electrical conductivity, 3wt% also marked what appeared to be the critical percolation threshold of CNFs in the PP matrix. The nanocomposites exhibited a visible transition from an insulator to a semiconductor, arising from the formation of a conductive network which conforms to the percolation theory of electrical conductivity.

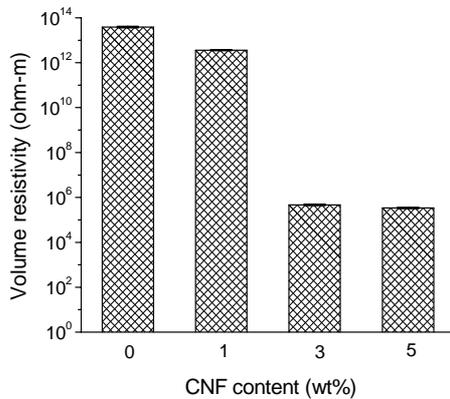


Fig.5 Electrical conductivity of neat PP and CNF/PP composites

Table 2 shows thermal conductivity and thermal effusivity values of the PP and CNF/PP nanocomposites. Unlike electrical conductivity, which exhibits a sharp percolation effect, the value of thermal conductivity increases linearly with an increase in CNF concentration. There is generally no percolation threshold value, because although the thermal conductivities of the CNFs and the polymer matrix differ, their ratio is less than  $10^4$ , while the electrical conductivity of the CNFs are  $10^{15}$  times

greater than that of the polymer resin. Scattering of phonons by interaction with surround materials also causes the loss of thermal conduction. From the data in Table 3, it can be seen that thermal conductivity and thermal effusivity of the PP matrix gradually increased with increasing contents of the CNFs. At 5wt% loading of CNF, the thermal conductivity and thermal effusivity of the PP matrix increased 38% and 54%, respectively, over that of the neat PP. This show that overall, the interfaces and additive characteristics do have an impact on the thermal conductivity of the polymer composites.

Table 2 Thermal conductivity and effusivity of neat PP and CNF/PP composites

	Thermal conductivity ( $w/m\cdot k$ )	Thermal effusivity ( $w\sqrt{s}/m^2k$ )
Neat PP	$0.225\pm 0.015$	$502.3\pm 13.9$
PP+1wt%CNFs	$0.231\pm 0.020$	$527.1\pm 15.7$
PP+3wt%CNFs	$0.258\pm 0.014$	$625.6\pm 13.5$
PP+5wt%CNFs	$0.311\pm 0.024$	$772.7\pm 20.2$

### 4. Conclusions

CNFs were dispersed uniformly throughout the PP matrix by means of melt blending with a twin-screw extrusion. The degree of crystallinity of the PP matrix within the nanocomposites exhibited an increasing trend with CNF loading up to 3wt%, followed by a moderate decrease at 5wt% loading. The PP nanocomposite containing 5wt% CNFs exhibited a high dielectric constant, which was more than 600 under lower frequency, and remains higher than 200 at a frequency of 4000Hz. With the increasing of CNF content, thermal conductivity and electrical conductivity of the nanocomposites increased continuously, but the enhanced extent was diminishing.

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