

# Thermal and Electrical Characterization of Polypropylene/Carbon Nanotube Nanocomposites

Ch. Pandis<sup>\*</sup>, E. Logakis<sup>\*</sup>, M. Chorianopoulos<sup>\*</sup>, A. Spanoudaki<sup>\*</sup>, A. Kyritsis<sup>\*</sup>, V. Peoglos<sup>\*</sup>, P. Pissis<sup>\*</sup>,  
M. Mičušík<sup>\*\*</sup>, I. Krupa<sup>\*\*</sup>, M. Omastová<sup>\*\*</sup>, J. Pionteck<sup>\*\*\*</sup>, and P. Pötschke<sup>\*\*\*</sup>

<sup>\*</sup>National Technical University of Athens, Zografou Campus 15780, Athens, Greece

<sup>\*\*</sup>Polymer Institute, Slovak Academy of Sciences, 842 36 Bratislava, Slovakia

<sup>\*\*\*</sup>Leibniz Institute of Polymer Research Dresden, 01069 Dresden, Germany

## ABSTRACT

The influence of multi-walled carbon nanotubes (MWCNT) on electric/dielectric and thermal properties of CNT-reinforced polypropylene (PP) nanocomposites is studied. The investigation is focused on electrical and dielectric properties in relation to percolation: ac and dc conductivity,  $\sigma_{ac}$  and  $\sigma_{dc}$ , respectively, above the percolation threshold  $p_c$  and dielectric permittivity,  $\epsilon'$ , below  $p_c$ . To that aim, broadband dielectric relaxation spectroscopy (DRS) was used. In addition, the effect of MWCNT on the thermal transitions (glass transition, crystallization, melting) of the nanocomposites was examined by differential scanning calorimetry (DSC) measurements.

**Keywords:** polypropylene, maleic anhydride, carbon nanotubes, dielectric properties, thermal transitions

## 1 INTRODUCTION

The reinforcement of polymers with nano-scaled fillers developed a new class of advanced multifunctional materials with improved properties, used in many fields ranging from microelectronics to aerospace [1, 2]. Among nanofillers, carbon nanotubes (CNT) are an especially attractive class of inclusions because of their exceptional mechanical, thermal, and electrical properties. Apart from mechanical reinforcement, one key interest is the development of conductive polymer composites, preferably at low concentration of CNT taking advantage of their high aspect ratio (~1000) for numerous applications, which include antistatic devices, capacitors, materials for electromagnetic interference (EMI) shielding, and sensors.

A homogeneous dispersion and good interfacial adhesion are crucial for the successful preparation of nanocomposites [3, 4]. This is a rather difficult task, since CNTs tend to stay aggregated due to strong inter-tube van der Waals interaction. The uniform dispersion could be promoted either by functionalization of carbon nanotubes, but in the expense of reduced conductivity, or by the modification of the polymer matrix in order to improve the

wetting of the filler with the polymer used, and thus promote the incorporation of the CNT into the matrix.

Among the most versatile polymer matrices are polyolefins, such as polypropylene, because of their good balance between properties and cost, as well as their ease of processibility and low density. Polypropylene grafted with maleic anhydride (MA-PP) [5, 6] has been extensively used for compatibilization of immiscible polypropylene-polyamide and polypropylene-polyester blends, as well as to improve the interfacial adhesion of PP with glass and carbon fibers. Therefore, the investigation of the incorporation of CNT into a MA-PP matrix is a matter of special interest.

The purpose of this work is to examine the influence of carbon nanotube addition on both non-modified and maleic anhydride grafted isotactic polypropylene. Non-isothermal DSC measurements were carried out in order to study thermal transitions of the nanocomposites. Quantitative analysis was performed for the determination of the subsequent changes in heat capacity and enthalpy in order to extract as much information of CNT behavior in the nanoscale. Furthermore, dielectric relaxation spectroscopy was used in order to examine percolation aspects by measuring the real part of complex permittivity for the insulating samples below the percolation threshold.

## 2 EXPERIMENTAL

### 2.1 Materials and Sample Preparation

Masterbatch granules of polypropylene containing 20 wt. % of MWCNT, obtained from Hyperion Catalysis International (USA), were used as components for the preparation of the thermoplastic composites with lower CNT contents with maleic anhydride modified polypropylene (MA-PP). The nanotubes are produced from high purity, low molecular weight hydrocarbons in a proprietary, continuous, catalyzed gas phase reaction. The outside diameter ( $D$ ) of the tube is approximately 10 nanometers and the length ( $L$ ) is over 10 microns giving a high aspect ratio ( $L/D$ ) of  $> 1000$ . The density is approximately  $1.75 \text{ g/cm}^3$ . One grade of MA-PP modified polypropylene, OREVAC PPC (melt flow index (MFI)

equal to 2 g/10min with 2.16 kg at 230°C, density ( $d$ ) equal to 0.98 g/cm<sup>3</sup>, from Arkema Inc., France, as well as unmodified polypropylene, NOVOLEN 1106H (MFI = 2 g/10 min with 2.16 kg at 230°C,  $d = 0.90$  g/cm<sup>3</sup>) from Basell, Germany, were used. The maleic anhydride content in MA-PP is 0.14 wt. % as determined by titration method. The nanocomposites were prepared by melt mixing the starting masterbatch with the pure polymer in the 30 ml mixing chamber of a Plasti-Corder kneading machine PLE 331 (Brabender, Germany) at 190°C for 10 minutes at a mixing speed of 35 rpm. Slabs with a thickness of 1 mm were prepared by compression moulding of the mixed composites using a laboratory hydraulic press SRA 100 (Fontijne, The Netherlands) at 2.4 MPa and at 190°C for 2 minutes.

The final obtained concentration of CNT in the prepared nanocomposites varies from 0.3 to 8 wt.%.

## 2.2 Nonisothermal DSC Analysis

Differential scanning calorimetry (DSC) measurements were carried out in the temperature range -70 to 200°C, using a Perkin–Elmer Pyris 6 apparatus. A cooling rate of 10 K/min and a heating rate of 10 K/min were used. The weight of the samples varied from 4 to 6 mg. It is noted that PP and its composite samples containing various MWCNTs contents were formerly heated at 200°C for 5 min in order to remove the previous thermal history. All measurements were carried out in nitrogen atmosphere. The exothermic crystallization and endothermic melting were recorded as a function of temperature.

## 2.3 Dielectric Relaxation Spectroscopy

Dielectric relaxation spectroscopy (DRS) measurements were carried out in the frequency range 10<sup>-2</sup>–10<sup>6</sup> Hz by a Novocontrol Alpha analyzer.

The real part of the complex conductivity ( $\sigma'$ ) and the real ( $\epsilon'$ ) part of the complex dielectric permittivity are measured as a function of frequency. Golden thin electrodes were sputtered on both sides of the samples, in order to assure good electrical contact between the samples and the electrodes of apparatus capacitor cell.

# 3 RESULTS AND DISCUSSION

## 3.1 Thermal transitions of PP/CNT and MA-PP/CNT nanocomposites

DSC results are reported in Table 1 for the melting, crystallization, and the glass transition, where  $T_m$  is the melting temperature,  $T_c$  the crystallization temperature,  $T_g$  the glass transition temperature,  $T_{c,onset}$  and  $T_{c,end}$  the end temperatures of crystallization,  $\Delta H_m$  the enthalpy change of melting,  $X_c$  the degree of crystallinity, and  $\Delta C_p$  the change between heat capacity. It should be

noticed that  $\Delta H_m$ ,  $X_c$ , and  $\Delta C_p$  are normalized to the sample mass and to the polymer content of nanocomposites. The degree of crystallinity of PP is calculated from the following equation

$$X_c (\%) = \frac{\Delta H_m}{\Delta H_0} \times 100 \quad (1)$$

where  $\Delta H_0$  is the heat of fusion for 100% crystalline PP (isotactic) which is 209 J/g [7]. The value of  $\Delta C_p$  is also normalized to the amorphous portion of PP, noted as  $\Delta C_p^*$ .

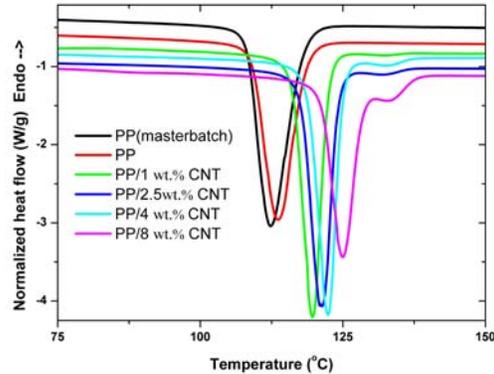


Figure 1: DSC thermograms of crystallization for the PP, PP(masterbatch), and PP/CNTs composites at a cooling rate of 10 K/min.

Figure 1 shows the thermograms for PP, PP(masterbatch), and PP/MWNT nanocomposites at a cooling rate of 10 K/min, where the crystallization exotherms are observed. The addition of 1 wt.% of nanotubes in PP causes a significant shift of the crystallization peak to higher temperature which increases further as the concentration of CNT increases. The latter indicates that CNT act as nucleating agents, increasing the rate of crystallization of PP [8, 9]. Additionally, a second crystallization peak is observed at higher temperatures for the nanocomposites only, and its position gradually shifts to higher temperatures with a steady increase in magnitude at the same time, as the concentration of CNT increases. This indicates that the second peak is closely related to the addition of CNT to PP matrix. The degree of crystallinity also increases as the content of nanotubes increases (Table 1). The glass transition analysis shows that  $T_g$  remains invariable on addition of CNT at about -9°C while at the same time the heat capacity decreases. The reduction of  $\Delta C_p^*$  is an indication that less part of amorphous PP contributes to the glass transition. This observation could be explained considering that an amount of amorphous PP remains immobilized around nanotubes or trapped between them. The percentage of immobilized PP has been estimated by the equation:

$$\chi_{im}(\%) = (1 - \Delta C_p^* / \Delta C_{p,0}^*) \times 100 \quad (2)$$

where  $\Delta C_{p,0}^*$  is the value for the pure polymer.

Sample	Melting			Crystallization			Glass Transition		
	T <sub>m</sub> (°C)	ΔH <sub>m</sub> (J/g)	X%	T <sub>c</sub> (°C)	T <sub>onset</sub> (°C)	T <sub>end</sub> (°C)	T <sub>g</sub> (°C)	ΔC <sub>p</sub> <sup>*</sup> (J/gK)	χ <sub>im</sub> (%)
PP(masterbatch)	161	102	49	112	118	108	-9	0.23	
PP	159	91	44	114	118	109	-9	0.34	
PP/1 wt.% CNT	161	95	46	120	123	116	-10	0.28	18
PP/2.5 wt.% CNT	161	98	47	121	124	118	-8	0.26	22
PP/4 wt.% CNT	161	100	48	122	125	119	-8	0.22	32
PP/8 wt.% CNT	162	102	49	125	129	121	-9	0.15	51

**Table 1.** Results of DSC study of PP and PP/CNT.

The immobilized portion of PP increases with CNT addition (Table 1).

As masterbatch is diluted with MA-PP in order to get the desirable final concentration of CNTs in the composite, varying from 0.8 wt.% to 8 wt.%, the respective content of PP (masterbatch) varies from 3.2 to 32 wt.%, thus the influence of CNT on thermal transitions is more dicey to predict. Nevertheless, DSC experiments provide useful qualitative results for the MA-PP series.

Decreased regularity of the chains due to the presence of maleic anhydride units causes a reduction of crystallization tendency [10]. Reduced degree of crystallinity and lower melting temperature of 149°C for MA-PP compared to 161°C for isotactic PP is observed. Furthermore, the melting peak shifts to higher temperatures and the degree of crystallinity increases in the nanocomposites from 31 % for the neat MA-PP to 36 % for the MA-PP/8 wt.% CNT. Finally, there is no evidence of phase separation between PP(masterbatch) and MA-PP in the blend since a single melting peak is observed.

### 3.2 Dielectric properties of MA-PP/CNT

Figure 2 shows the frequency dependence of the real part of the complex electrical conductivity  $\sigma(f)$  for various CNTs weight content in MA-PP measured at room temperature. Two distinct behaviors depending on the CNT

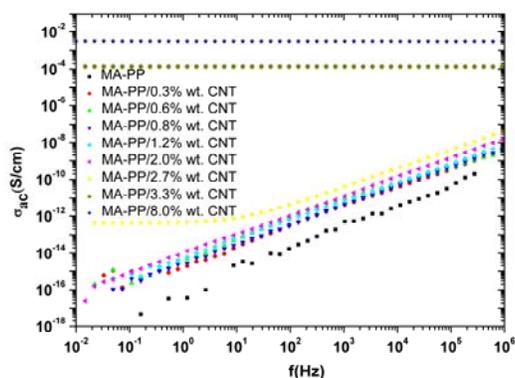


Figure 2: ac conductivity against frequency for the MA-PP series.

content are observed. Ac conductivity increases linearly as frequency increases for the samples with compositions between 0.3 and 2 wt.% CNT as well as for the neat MA-PP, which is typical for insulating materials.

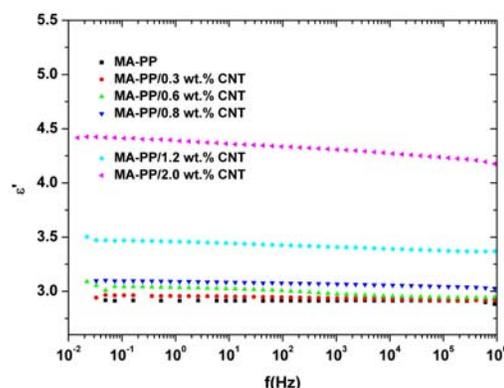


Figure 3:  $\epsilon'$  against frequency for the MA-PP samples below percolation threshold.

Contrary, the sample with 2.7 wt.% CNT exhibits a plateau where  $\sigma_{ac}$  is independent of frequency below a critical value. For the samples with higher content of CNT the independence of ac conductivity on frequency, which is characteristic for conductive materials, is extended in the whole frequency range. It is clearly seen that the transition from insulating to conductive phase takes place between 2 wt.% and 2.7 wt.% of CNT. Thus, the percolation threshold ( $\phi_c$ ), being the critical composition of conducting inclusions where the first network forms, is located between these values. According to percolation theory [9, 10] of composite materials, conductivity above  $\phi_c$  is described by the equation:

$$\sigma(\phi) \sim (\phi - \phi_c)^t \quad (3)$$

where  $\phi$  is the volume fraction of the conductive component and  $t$  is the critical exponent [6]. The dc conductivity  $\sigma_{dc}$  values for the samples above the percolation threshold can be estimated from the plateau values of conductivity in the  $\sigma(f)$ - $f$  plot for  $f \rightarrow 0$ . The dc conductivity value for the MA-PP/8 wt.% CNTs is equal to  $2 \cdot 10^{-3}$  S/cm.

Percolation threshold could alternatively be studied from  $\epsilon'$  values of insulating samples below the percolation threshold. Figure 3 presents the real part of complex permittivity versus frequency for the samples presenting insulating behavior. PP, as a non polar polymer, does not exhibit dielectric relaxation mechanisms, therefore the real part of dielectric function is practically frequency invariant in the whole frequency range. Maleic anhydride is a polar group which is attached to the polypropylene backbone, nevertheless its content is very low (0.14 wt.%), hence the contribution to dielectric function is insignificant, as depicted in Figure 3. In the same figure the increase of  $\epsilon'$  on addition of carbon nanotubes, is also depicted. Below  $\phi_c$ , the real part of dielectric permittivity  $\epsilon'$  increases as  $\phi$  approaches  $\phi_c$  following a power law [11]:

$$\epsilon'(\phi) = A(\phi_c - \phi)^{-s} \quad (4)$$

where A is a constant,  $\phi$  the content of carbon nanotubes, and s is a critical exponent.

The fit of equation (4) to the values of  $\epsilon'$  obtained from the samples with different content of CNT, is presented in Figure 4.

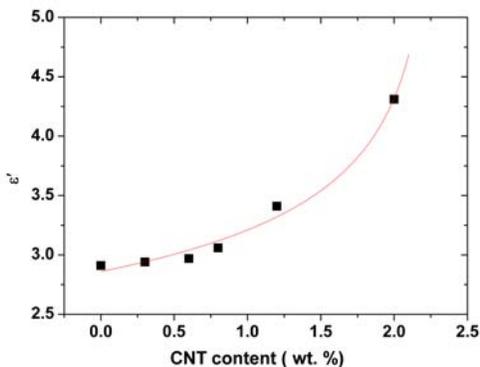


Figure 4:  $\epsilon'$  against CNT content for the MA-PP samples below percolation threshold, measured at 1.19Hz. Fit of equation (4).

The best fit gives a value of 2.2 wt.% for the percolation threshold and  $s = 0.22$  for the critical exponent. The latter value diverges significantly from the commonly accepted value of 0.7 for three-dimensional percolation, therefore further investigation based on similar composites is needed.

Preliminary results obtained for the PP/CNT series show that percolation threshold lies between 3 and 4 wt.% CNT and the maximal dc conductivity value is  $6 \cdot 10^{-2}$  S/cm for the PP/8 wt.% CNT nanocomposite.

## 4 CONCLUSIONS

MWCNT act as nucleating agent for iPP crystallization resulting in an increase of crystallization temperature and of the degree of crystallinity. Melting temperature and glass transition temperature remain

unaffected while an increasing percentage of immobilized amorphous PP appears on addition of CNT. Furthermore, good mixing of masterbatch granules with MA-PP and iPP is assumed, implying that melt mixing is an effective method for nanocomposite preparation. No phase separation between PP and MA-PP is detectable when they are blended, since co-crystallization takes place. Percolation threshold for MA-PP series is estimated from the  $\epsilon'$  values of samples below percolation threshold to be 2.2 wt.% of CNT. For the PP/CNT series the percolation threshold is higher (between 3-4 wt.% CNT), indicating better nanotube dispersion for the MA-PP/CNT series, while the maximal value of conductivity ( $\sim 10^{-3}$  S/cm for 8 wt. % CNT) is similar in both series.

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## REFERENCES

- [1] E. T. Thostenson, C. Li, T. W. Chou, *Comp Sci Tech*, 65, 491–516, 2005.
- [2] F. Hussain, M. Hojati, M. Okamoto, R.E. Gorga, *J Comp Mat*, 40, 1511-1565, 2006.
- [3] R. Andrews, D. Jacques, M. Minot, T. Rantell, *Macromol Mater Eng*, 287, 395–403, 2002.
- [4] N. Grossiord, J. Loos, O. Regev, C.E. Koning, *Chem Mater*, 18, 1089-1099, 2006.
- [5] A. Menyhard, J. Varga, *E Polym J*, 42, 3257–3268, 2006.
- [6] Y. Seo, J. Kim, K. U. Kim, Y. C. Kim, *Polymer*, 41, 2639–2646, 2000.
- [7] J. Brandrup, E. H. Immergut, E. A. Grulke, A. Abe, D. R. Bloch, *Polymer Handbook*, John Wiley & Sons, 1999.
- [8] L. Valentini, J. Biagiotti, J.M. Kenny, S. Santucci, *Comp Sci Tech*, 63, 1149–1153, 2003.
- [9] M. K. Seo, J. R. Lee, S. J. Park, *Mat Sci Eng A*, 404, 79–84, 2005.
- [10] K.W. Cho, F. Li, J. Choi, *Polymer*, 40, 1719–1729, 1999.
- [11] D. Stauffer, *Introduction to Percolation Theory*, Taylor and Francis, London, 1985.
- [12] S. Kirkpatrick, *Rev Mod Phys*, 45, 574-588, 1973.
- [13] L. Flandin, T. Prasse, R. Schueler, K. Schulte, W. Bauhofer, J.-Y. Cavaille, *Phys Rev B*, 59, 14349, 1999.