

Effect of Carbon Nanofiller Amounts on the Electrical and Thermodynamic Properties of Polypropylene Nanocomposite

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ABSTRACT

PP reinforced with two types of carbon nanostructures were prepared via melt mixing. The effects of the carbon nanofiller type with different compositions on the electrical conductivity and dynamical analysis of the nanocomposites were investigated. The results showed that the influence of MWNTs on the properties of PP composites is different with CB, which is due to the structure and aspect ratio difference between MWNTs and CB.

Keyword: Polypropylene, multi-walled carbon nanotubes, electrical conductivity, dynamic mechanical properties

Introduction

Conductive polymer composites (CPC) can be obtained by the combination of an insulating polymer matrix with electrically conductive fillers (Kalaitzidou *et al.*, 2007, Yoonessi *et al.*, 2010, Grossiord *et al.*, 2010, Dweiri *et al.*, 2007, and Chen *et al.*, 2011). Among these conductive fillers, carbon-based materials such as carbon black (CB) (Maiti *et al.*, 2005, and Naiti *et al.*, 1981) and carbon nanotubes (CNTs) (Hadjiev *et al.*, 2010, Sun *et al.*, 2008, Sun *et al.*, 2010, and Warren *et al.*, 2009) have been used extensively because of their wide availability, low density, high electrical conductivity, and resistance to corrosion. The critical content of conductive of filler required to form continuous conducting paths and impart electrical conductivity to the polymer matrix is called percolation threshold. Carbon black (CB) is the most widely used conductive filler because of its abundant source, low density, predominant electrical property, and low cost. But the CB content at percolation threshold of many CPC is high, such as ~ 10.88 vol % CB content for high density polyethylene/CB (Yoon *et al.*, 2004), ~ 20 vol.% CB content for poly(vinyl chloride)/CB (Saad *et al.*, 2003) and 20 vol.% CB content for polyurethane/CB (Fengkui *et al.*, 2000). However, a higher electrical conductivity can be produced by using a much lower volume of carbon nanotubes (CNTs), due to its very high aspect ratio. Polypropylene (PP) is one of the most widely used commodity thermoplastics. PP has been widely used in the household appliances, food packaging, automotive components, and medical devices. PP nanocomposites have been extensively investigated over a wide range of applications during the past few decades.

In particular, significant property enhancements were reported when carbon nanofillers were incorporated into PP (Grooiord *et al.*, 2010, Kalaitziou *et al.*, 2007, and Li *et al.*, 2011).

A better understanding of the dynamic thermo-mechanical properties of the composite will help to define structure/property relationships and subsequently to relate these properties to the product final performance (Yang *et al.*, 2007). Dynamic mechanical analysis (DMA), measures the response of a given material to a cyclic deformation as a function of temperature (Jamaliah, 2005). It also provides information about storage modulus, loss modulus and damping factor behavior of materials. The dynamic storage modulus is approximately similar to the Young's or elastic modulus, or material stiffness. It provides the information on elastic response to the deformation resistance (Liao, 2003). The type of polymers (semicrystalline or amorphous), the glass transition temperature of the polymers, the filler type, geometry (including aspect ratio), concentration and the interaction of the fillers to the matrix molecular chains are all the factors which affecting the molecular motions within the matrix (Yang *et al.*, 2007). In addition they affect the behavior of the storage modulus curve. Loss modulus indicates the materials ability of the material to dissipate energy, often in the form of heat or molecular rearrangements when there is deformation occurred (Khalina, 2005). It also indicates the viscous nature of the polymer and gives information about the viscous or energy dissipation during the flow (Greenand Wilkes, 1995). It is also directly related to the amount of amorphous PP chain involved in the transition (Khalina, 2005). As the filler loading increased, there is a little mobility of the PP chain. This limitation in the mobility of chain was indicated by little amplitude differences, which leads in turn to an increase in the viscosity of polypropylene (PP) filled carbon nanofiller composites (Abdel-Goad & Potschke, 2005). The damping factor ($\tan\delta$) is the ratio of the loss modulus to the storage modulus. It is very useful for determining the occurrence of

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molecular mobility transition such as the glass transition temperature which also represents the ability to the heat resistance (Yang *et al.*, 2007).

The aim of the present study is to prepare PP nanocomposites by using carbon nanofillers synthesized by melt mixing via twin extruder, in order to evaluate the effect of various loadings of MWNTs and CB on the electrical conductivity and the thermodynamic analysis of the prepared nanocomposites.

Materials and Methods

Materials:

PP was supplied by oriental petrochemicals company, Egypt (in the form of homopolymer pellets). It has density of 0.9 g/cm³, and melt flow rate of 12 g/10min (at 230°C/2.16 kg load). MWNTs were supplied from Nanoscience and Nanotechnology unit, Beni-Suef University, Egypt. It is synthesized by chemical vapor deposition (CVD) method. Iron-Cobalt/Calcium carbonate, Fe-Co/CaCO₃, was used as catalyst/support mixture. Carbon black (SAF) is used, and supplied from transporting and engineering company, Egypt. MWNTs and CB are used as nanofillers with various concentrations in the PP mixes. Irganox 1010 was supplied from Ciba (Geigy, Switzerland) in white powder form. It has a specific gravity of 1.45, and melting point of 110-125°C. It is used to prevent thermomechanical degradation during mixing and pressing processes.

Methods:

Preparation of Nanocomposites:

All ingredients were accurately weighed and the mixing was carried out using twin-screw extruder, new plast company, Indian. The mixing was continued at 190 °C for 20 min. at a rotor formulations speed of 30 rpm. The mixes are shown in Table 1.

Table 1: Formulations (in wt %) of the PP mixes containing CNTs or CB without treatment.

Ingredient	Sample No.				
	A ^o	A ₁	A ₂	A ₃	A ₄
PP	100	100	100	100	100
CNTs or CB (nanofiller)	0	0.5	1	3	5
Irganox 1010 (Antioxidant)	0.1	0.1	0.1	0.1	0.1

Morphological Characterization:

The morphology of the composites was studied under scanning electron microscope (SEM, Philips XL 30 microscope, U.S.A). Prior to the measurement; the specimens were coated with gold. This analysis shows the shape and size of filler particles.

Thermogravimetric Analysis (TGA):

Thermogravimetric analysis (TGA) was performed on an analyzer (Model TA-50, Shimadzu, Japan) on 5 mg sample for all cases, at a heating rate of 10 °C/min. TGA was conducted with the compounds placed in a high quality nitrogen atmosphere in order to avoid unwanted oxidation. It is used to obtain the thermal stability and degradation temperature of the composite.

Wide-Angle X-Ray Diffractometry (WAXD):

WAXD experiments were performed at room temperature to characterize the crystalline structure of fillers. XRD patterns were collected using a Bruker D8 advance X-ray powder diffractometer at the wave length of copper target= 1.54 Å, a tube voltage of 40 kV and the tube current of 40 mA.

Electrical Conductivity:

The measurements of the DC conductivity were performed at room temperature on disk-shaped specimens of about 2 mm thickness and 16.04 mm diameter. The instrument used is 4-range high voltage insulation resistance tester, Japan.

6. DMA thermodynamical Analysis:

DMA measurements were made in tensile mode at 1 Hz frequency using a DMA Q800 apparatus (TA Instruments, USA). The specimens for DMA tests were molded with a compression machine and the specimens' dimensions were 30 mm x 8 mm x 2 mm (length x width x thickness). The storage modulus (E'), loss modulus (E'') and tangent delta ($\tan \delta$) were determined as a function of temperature in the range of -20 to 70°C, and the heating rate was set for 3°C/min.

Results and Discussion

Characterization of Nanofillers:

Carbon nanotubes and carbon black were characterized by transmission electron microscope (TEM) and thermogravimetric analysis (TGA) to detect their surface morphology and thermal stability, respectively.

Morphology of the Nanofillers:

The morphology of the CB and MWNTs fillers was investigated with transmission electron microscopy (TEM) as shown in Fig.1. It shows TEM images of the original nanotubes and carbon black. Due to the large aspect ratio of nanotubes (Deng *et al.*, 2009), the network formed by MWNTs is more likely to be entangled than the networks based on CB. As can be seen from this figure, the nanotubes have outside diameters of about 36 nm, and CB is nanoparticles with diameter of about 28 nm, which form aggregates with considerable branching and chaining.

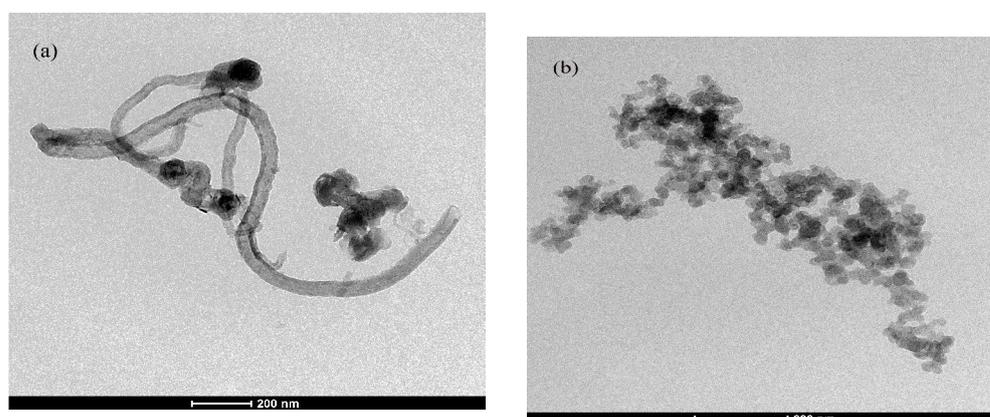


Fig. 1: TEM micrographs of (a) MWNTs and (b) CB.

Thermal Degradation Behavior of Nanofillers:

Fig. 2 represents thermogravimetric results of pure multiwall carbon nanotubes and carbon black in nitrogen atmosphere. The onset of degradation of MWNTs starts at about 472°C, which is attributed to the degradation of graphene walls (Shanmugharaj *et al.*, 2007), while CB starts to loss mass at 394°C. The residual weights at 750°C are about 79 and 34 % for MWNTs and CB, respectively. At the end of the analysis, the degradation process of MWNTs is not completed. This difference can be attributed to the unique properties of MWNTs. This result indicates the higher thermal stability of carbon nanotubes than that of carbon black.

Characterization of the Polypropylene Nanocomposites:

The characterization of PP nanocomposites by different techniques was discussed elsewhere (Darwish *et al.*, 2014). The results clarified that composites filled with CB showed better dispersion than that filled with MWNTs. They also showed that the thermal stability increases with increasing filler loading and that MWNTs enhanced the thermal stability of the composites rather than CB filler.

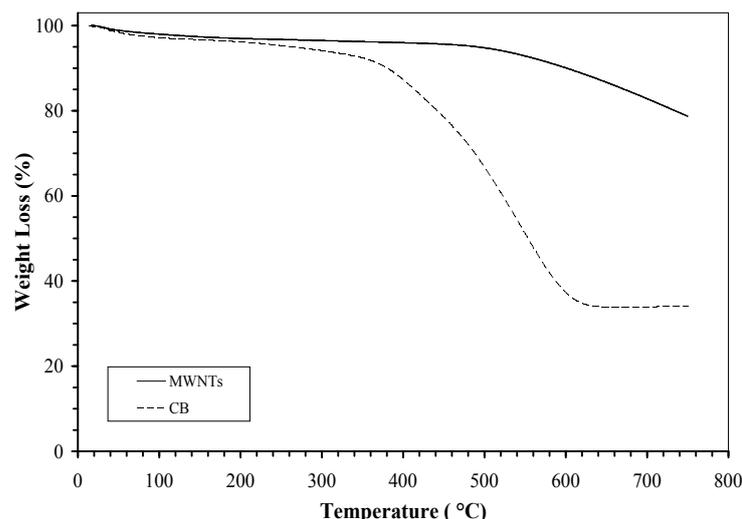


Fig. 2: TGA curves of pure multiwall carbon nanotubes and carbon black under nitrogen atmosphere.

Electrical Properties of PP Nanocomposites:

Like other electrically conductive fillers, carbon nanofillers are excellent candidates for preparing electrically conductive composites (Kalaitzidou *et al.*, 2007, and Wakabayashi *et al.*, 2010). It is well known that dispersion state of MWNTs and CB in the polymer matrix affects electrical properties of polymer composites directly. In general, electrical conductivity (σ) depends on size, shape, concentration, distribution, and surface treatment of fillers. Aspect ratio and loading of the fillers play an important role in the electrical conductivity of a composite and there is often a percolation threshold concentration beyond which the electrical conductivity is shown. Compared with the carbon black or carbon fiber as conductive fillers, MWNTs can form the effective conductive pathway in polymer composites at a relatively low volume fraction because they have very high aspect ratio (Potschke *et al.*, 2003).

Fig. 3 represents the electrical conductivity of neat PP, PP/MWNTs and PP/CB nanocomposites with various loadings. As compared to neat PP, a slight increase in the electrical conductivity (σ) was observed at lower MWNTs loading (0.5 wt.%) which is very close to the value of pure PP and the composites are still insulating. In the vicinity of the percolation threshold, the conductivity increases dramatically, by several orders of magnitude, and a transition from insulating to conductive material occurs. The percolation threshold value is about 1 wt.% of MWNTs. This is achieved because the filler particles agglomerate and this causes the formation of the conducting paths or network in the PP matrix (Zois *et al.*, 2001). After the percolation is achieved, the electrical conductivity of the PP composites does not greatly change with the increasing filler content. While incorporation of CB filler into PP affects slightly the conductivity of the composite compared to neat PP and the composite is still insulating. This is because CB particles cannot form agglomerates and therefore there is no distinct increase in the electrical conductivity. At higher loadings (i.e. >1 wt.%), the MWNTs-based composites show better electrical conductivity values when compared to those of CB filler, as can be seen from Fig. 3.

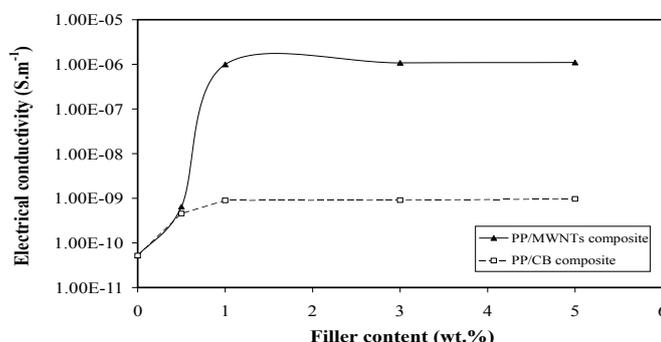


Fig. 3: Electrical properties of PP/MWNTs(a) and PP/CB(b) nanocomposites as a function of MWNTs and CB loadings.

Thermodynamic Properties (DMA):

DMA is an effective tool to determine the viscoelastic parameters, such as dynamic storage modulus (E'), loss modulus (E''), damping ($\tan\delta$) and glass transition temperature (T_g) characteristics of polymeric materials. Storage modulus is a measure of the maximum energy stored in the material during one cycle of oscillation. Loss modulus is the viscous component and is related to the samples' ability to dissipate mechanical energy through molecular motion. The ratio between the viscous modulus (loss modulus) (E'') to storage modulus (E') is termed as $\tan\delta$ ($\tan\delta$), which is normally used to quantify the dissipation of the viscoelastic material. The T_g is defined as the region where storage modulus increases with increasing frequency at a constant temperature or the temperature at which maximum of the $\tan\delta$ occurs. In a DMA test, the sample is subjected to a sinusoidal mechanical deformation at a fixed frequency of 5 Hz. For pointing similarities and differences between the composites with different compositions, dynamic mechanical data for the unfilled PP, PP/MWNTs and PP/CB were collected and discussed.

Storage Modulus (E') of PP/MWNTs Nanocomposites:

Fig.4 (a,b) displayed the plot of storage modulus (E') as a function of temperature for the PP/MWNTs and PP/CB nanocomposites with different weight percentage addition of MWNTs and CB, respectively. Storage modulus curve for pure PP is overlaid as for the comparison purpose. Basically, at the initial stage of analysis, the storage modulus of the MWNTs samples increases from about 2.717×10^3 to 3.090×10^3 MPa with the increasing amount of MWNTs, while the storage modulus of CB samples increases from 2.717×10^3 to 2.954×10^3 MPa. This indicates that mechanical reinforcement effects are increasing with the nanotubes content than CB (Dalmás *et al.*, 2007, and Choi *et al.*, 2005). The stiffness effects introduced by MWNTs enable the PP to sustain higher storage modulus value than that introduced by CB (Yang *et al.*, 2007). This also will suggest that the MWNTs added behaves as good reinforcement and allow homogeneous stress transferred from the matrix to the filler. As the filler loading increased, the stress is more evenly distributed and thus will increase the storage modulus (Jose *et al.*, 2003). As can be seen from the figure, the initial value of storage modulus is higher for each sample at the sub-ambient temperature due to the fact that, at this stage the molecules are in the frozen state, therefore they retain high stiffness properties in the glassy condition (Jamaliah *et al.*, 2005). Therefore, E' is higher when the molecular movement is limited or restricted which in turn leads to an increase in the storage of mechanical energy increased (Fateme *et al.*, 2006, and Zhang *et al.*, 2007). The stiffening effect was more remarkable at lower temperature. This phenomenon was explained by the mismatch in coefficient of thermal expansion between the matrix and inorganic fillers, which might allow better stress transfer between matrices and fillers at low temperatures (Zhang *et al.*, 2007). The storage modulus curves for each sample decrease dramatically with the increase of temperature from -20 to 70°C . This finding is in agreement with the works done by many researchers (Dalmás *et al.*, 2007, Fateme *et al.*, 2006, Jamaliah *et al.*, 2005, Khalina *et al.*, 2005, and Yang *et al.*, 2007). The pattern of decrement in the storage modulus value with the increasing temperature is due to the fact that PP reaches its softening point therefore reduced the elastic response of the material. With the increase of temperature to the melting temperature, the storage modulus of the composites was dominated by the matrix intrinsic modulus (Yang *et al.*, 2007). As the temperatures approaches the glass transition temperature region, there is a large drop in the storage modulus values, indicating the phase transition from the rigid glassy state where the molecular motions are restricted to a more flexible rubbery state and the molecular chains have greater freedom to move.

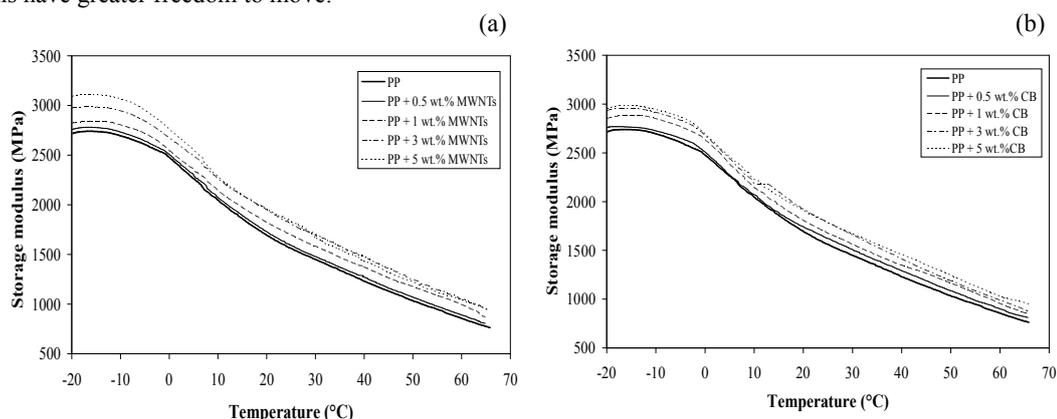


Fig. 4: Variation of storage modulus (E') of PP/MWCNTs (a) and PP/CB (b) nanocomposites as a function of temperature.

The Figure showed that the presence of different loading of fillers in the PP matrix even at lower percentages of weight is still capable to keep retains the pattern of the curve. This result is in agreement with the work done by McNally et al., where they found that addition of low loadings of MWNTs were also more effective at increasing the dynamic mechanical storage modulus of polyethylene composites (Mcnallya *et al.*, 2005).

Loss Modulus (E'') of PP/MWNTs and PP/CB Composites:

E'' is used to indicate the rheological change (phase and flow) which occur during the processing of materials. Fig.5(a,b) represented loss modulus of unfilled PP, PP/MWNTs and PP/CB composites, respectively. The loss modulus of unfilled PP increased with addition of MWNTs and CB for composites, respectively. This finding seems to agree the finding by Yang *et al.*, 2007 where they found that E'' value was increased along with the inclusion of nanofiller. Also, Khalina, 2005 reported that the increase pattern of loss modulus amplitude with the presence of fibers indicating that the filled PP system was experiencing the increasing amount of amorphous part of PP chain which involved in the transition. This indicates higher viscosity as a result of the molecular movement restriction due to the presence of the fillers (Khalina, 2005). Thus, the higher the CNTs content, the higher the viscosity, which at the end requires higher needs for energy dissipation (Abdel-Goad & Potschke, 2005).

Additionally, similar to the storage modulus results, when approaching the melting temperature of PP, the curves tend to converge and exhibit the intrinsic properties of PP matrix. Fig.5 (a,b) showed that the inclusion of MWNTs and CB had negligible effect to the peak temperature of loss modulus. i.e. the peak was not significantly shifted with regard to the effect of different loadings. This condition indicates that the inclusion of carbon nanofillers did not significantly affect the relaxation behavior of PP. The relaxation transition peak shown in E'' curves is around 5 to 7°C. Fig.5 (a) showed that there is an apparent increase in the transition peak value of PP/5 wt.% MWNTs composite than that of other nanotube contents.

The E'' peak reached a maximum peak (T_g) and then decreased sharply with the increasing temperature. The temperature range from -10 to 10°C represents a transition region from the glassy state to a rubbery state (Khalina, 2005). Above the phase transition region, the decrease in the E'' is sharper indicating a sharp decrease in the viscosity of the composites with the increasing of temperature until ~ 40°C, before the curves form stabilization plateau prior to the convergence of the curves caused by the melting temperatures.

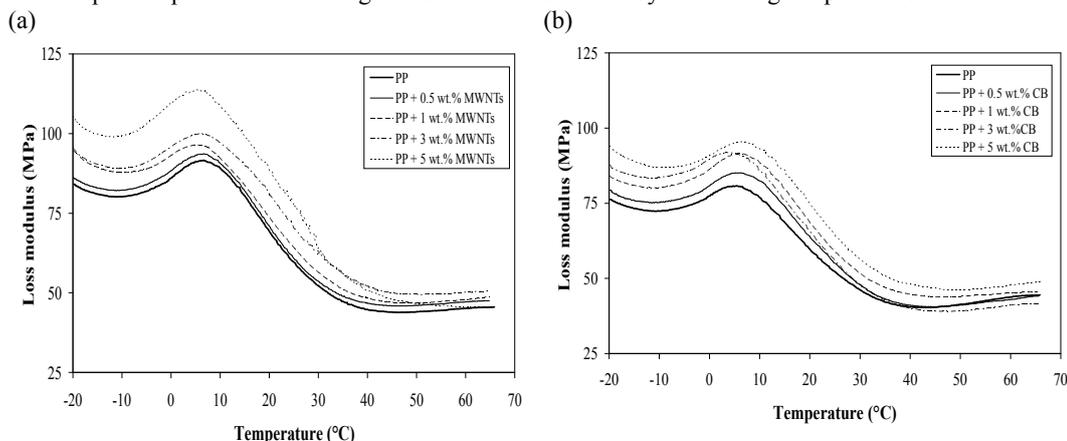


Fig. 5: Variation of loss modulus (E'') of of PP/MWCNTs (a) and PP/CB (b) nanocomposites as a function of temperature.

Damping Factor ($\tan\delta$) of PP/MWNTs and PP/CB Composites:

$\tan\delta$ indicates the relative importance of both viscous and elastic behaviors of materials, whereby $\tan\delta < 1$ exhibits more elastic behavior and may behave like solid, while $\tan\delta > 1$ exhibits more viscous behavior and behaves more like liquid (Fateme, 2006).

Fig.6 showed that the range of $\tan\delta$ is < 1 , exhibiting that the fabricated composites behave like a solid. It was also shown that the nanocomposites showed a slightly higher damping than the pure PP in case of PP/MWNTs composites owing to the viscoelastic energy dissipation as a result of filler-filler friction and filler-PP interaction. From the damping factor curves, T_g of the composites can be determined by the $\tan\delta$ peak temperature (Choi *et al.*, 2005). It is clearly shown that the formation of the T_g peaks is in the range of 11 to 13°C, where it is associated to the relaxation of unrestricted amorphous phase in PP (Schawe, 2002).

This relaxation stage is a secondary relaxation due to the movement of short chain segments). However, by referring to Fig.6, it was also shown that there is no significant shift in the T_g temperatures, with respect to the different amounts of MWNTs and CB added into the PP matrix. The maximum peak for each curve falls at slightly the same T_g temperature. The relatively no changes in transition temperature of composites suggest that there is no change in the rigidity of the filler matrix interfacial zone and no change in the mobility of the interfacial region. This situation was consistent with the work done by Zhang, 2007 which found that addition of 1 wt.% MWNTs into PP matrix does not give any significance increase to the glass temperature, where it falls around $\sim 13^\circ\text{C}$ which is almost equivalent with the T_g of the tested virgin PP.

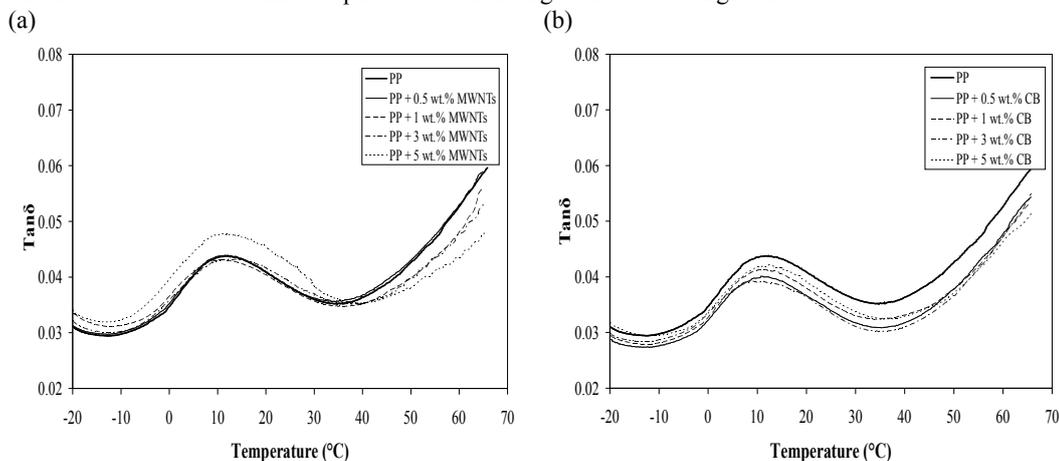


Fig. 6: Variation of damping factor ($\tan\delta$) of PP/MWCNTs (a) and PP/CB (b) nanocomposites as a function of temperature.

Table 2: Glass transition temperature (T_g) as obtained from loss modulus and tan delta data.

Sample	T_g ($^\circ\text{C}$)	T_g ($^\circ\text{C}$)
	As obtained from E''	As obtained from $\tan\delta$
PP	6.62	12.30
PP + 0.5 wt% MWNTs	6.63	12.09
PP + 1.0 wt% MWNTs	5.26	11.25
PP + 3.0 wt% MWNTs	6.24	12.44
PP + 5.0 wt% MWNTs	5.27	11.87
PP + 0.5 wt% CB	6.17	12.20
PP + 1.0 wt% CB	6.36	12.49
PP + 3.0 wt% CB	5.56	12.91
PP + 5.0 wt% CB	6.31	12.46

Conclusion:

PP/carbon nanocomposites were prepared via melt blending PP with two types of carbon fillers: MWNTs and CB. The morphological characterization based on scanning electron microscopy showed that the nanotubes have outside diameters of about 36 nm, and CB are nanoparticles with diameter of about 28 nm, which form aggregates. The nanofiller aspect ratio has a very significant impact on the electrical conductivity and thermodynamic properties of PP nanocomposites.

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