

# Impact of Injection-Molding Processing Parameters on the Electrical, Mechanical, and Thermal Properties of Thermoplastic/Carbon Nanotube Nanocomposites

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**ABSTRACT:** Thermoplastic nanocomposites, based on high-density polyethylene, polyamide 6, polyamide 66, poly(butylene terephthalate), or polycarbonate and containing multiwalled carbon nanotubes (CNTs), were compounded with either neat CNTs or commercial CNT master batches and injection-molded for the evaluation of their electrical, mechanical, and thermal properties. The nanocomposites reached a percolation threshold within CNT concentrations of 2–5 wt %; however, the mechanical properties of the host polymers were affected. For some nanocomposites, better properties were achieved with neat CNTs, whereas for others, master batches were better. Then, polycarbonate and poly(butylene terephthalate), both with a CNT concentration of 3 wt %, were injection-molded with a screening design of experiments (DOE) to evaluate the effects of the processing parameters on the

properties of the nanocomposites. Although only a 10-run screening DOE was performed, such effects were clearly observed. The volume resistivity was significantly dependent on the working temperature and varied up to 4 orders of magnitude. Other properties were also dependent on the processing parameters, albeit in a less pronounced fashion. Transmission electron microscopy indicated that conductive samples formed a percolation network, whereas nonconductive samples did not. In conclusion, injection-molding parameters have a significant impact on the properties of polymer/CNT nanocomposites, and these parameters should be optimized to yield the best results. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 70–78, 2011

**Key words:** injection molding; nanocomposites; thermoplastics

## INTRODUCTION

Composite materials, including polymeric matrices filled with carbon nanotubes (CNTs), have been found to be efficient for the improvement of mechanical, thermal, and electrical properties. A great deal of scientific work has been done in this field and summarized in various extensive reviews.<sup>1–4</sup> However, because of the high cost and low availability of CNTs, most research has been performed with small samples produced with constrained laboratory production techniques,<sup>5–16</sup> so comparisons between the results and actual practical applications are limited. In industrial production processes, such as injection molding, there are significant effects of the processing parameters on the properties of the final product that cannot be fully assessed by small-scale laboratory research. Lately, advances in CNT production technologies have made them available in higher quantities, and this has allowed higher scale research

using conventional polymer production techniques such as injection molding.<sup>17–21</sup> Undoubtedly, CNTs have high technological potential, and the study of their behavior in one of the most common polymer and polymer composite production processes (i.e., injection molding) is important. The injection-molding process is controlled by a variety of processing parameters known to affect the product morphology and quality through effects on mixing, orientation, and crystallization.<sup>22</sup> Injection processing parameters have become even more important in the case of high-aspect-ratio CNTs, whose effects and efficiency are influenced by the degree of dispersion and orientation within the polymeric matrix.

The design of experiments (DOE) methodology uses designed experimental runs to evaluate the effects of selected independent variables on the properties of products.<sup>23–25</sup> Screening designs use a small number of runs to evaluate the effects of several variables. This kind of basic design is able to detect only first-order (linear) effects and does not detect higher order effects (nonlinear; e.g., parabolic effects) or interactions between variables. However, screening designs have been found to be an economical and efficient way of screening and ranking

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relatively large numbers of variables with a low number of runs; this feature is very convenient when we are dealing with limited quantities of material, this work being an example. DOE methodologies were used in previous research by Villmow et al.<sup>18</sup> and Pegel et al.<sup>19</sup> to study the influence of injection-molding parameters on the electrical properties of polycarbonate (PC)/multiwalled CNT composites. They found that processing parameters such as the injection velocity and melt temperature affect the electrical resistivity of nanocomposites by several orders of magnitude.

In the first part of this work, thermoplastic nanocomposite compounds, based on high-density polyethylene (HDPE), polyamide 6 (PA6), polyamide 66 (PA66), poly(butylene terephthalate) (PBT), or PC and containing multiwalled CNTs at a concentration of 2 or 5 wt %, were prepared with neat CNTs or commercial master batches with the objective of assessing the influence of the master-batch preprocessing on the nanocomposite properties. The resulting compounds were injection-molded into standard test specimens, and the electrical, mechanical, and thermal properties were evaluated.

In the second part of this work, two selected formulations, one for PC and one for PBT, were injection-molded with a 10-run, 5-variable, 2-level screening DOE. The objective was to evaluate the effects of the injection-molding parameters, if any, on the electrical, mechanical, and thermal properties of the nanocomposites. Transmission electron microscopy (TEM) was used to investigate CNT dispersions in samples with different levels of electrical resistivity.

## EXPERIMENTAL

### Materials

Five thermoplastic materials were used: HDPE (Polene R1760, IRPC, Bangkok, Thailand), PA6 (Grilon BS23, EMS Chemie, Domat/EMS, Switzerland), PA66 (Polynil P50 FI, Nilit, Migdal HaEmek, Israel), PC (Makrolon 2407, Bayer, Leverkusen, Germany), and PBT (Ramster PF-100, Polyram, Moshav Ram-on, Israel).

Two forms of multiwalled CNTs were used: neat CNTs (Nanocyl 7000, Nanocyl, Sambreville, Belgium) and commercial master batches of CNTs. The master batches included an HDPE/CNT master batch with a CNT concentration of 31.6 wt % (Nanocyl 9000, Nanocyl), a PA6/CNT master batch with a CNT concentration of 20 wt % (PA6 20BN, Hyperion, Cambridge, MA), a PA66/CNT master batch with a CNT concentration of 15 wt % (Plasticyl PA1501, Nanocyl), a PC/CNT master batch with a CNT concentration of 15 wt % (PC 15BN, Hyperion), and a PBT/CNT master

batch with a CNT concentration of 15 wt % (PBT 15BN, Hyperion).

### Sample preparation

Before processing (compounding or injection molding), all thermoplastics, master batches, and composites (excluding those containing HDPE) were predried overnight in a vacuum drier at standard temperatures. Neat CNTs were predried overnight at 150°C. All formulations were dry-blended and compounded in a 25-mm screws, 25 length/diameter, corotating, twin-screw extruder (APV MP2030, APV, Saginaw, MI) with standard extrusion parameters suitable for each thermoplastic. Neat thermoplastics were also processed through the compounder to be used as references with the same thermal history as their respective nanocomposites. Then, test samples were injection-molded in a 30-mm screw, 50-ton injection-molding machine (Arburg 320C, Arburg, Lossburg, Germany). In the first part of this work, HDPE, PA6, PA66, PC, and PBT composite formulations with CNT concentrations of 2 or 5 wt % (neat or master-batch CNTs) were prepared. In the case of master batches, the concentrations were calculated so that the final formulation had a net CNT concentration of 2 or 5%. The sample notation includes the abbreviation for the thermoplastic followed by the net CNT concentration and the letter N for neat CNTs or the letters MB for master-batch CNTs. For example, for HDPE, the following formulations were evaluated: HDPE (the neat thermoplastic used as a reference), HDPE-2N (98 wt % HDPE and 2 wt % CNTs in neat form), HDPE-2MB (the same as HDPE-2N but with CNTs in the master-batch form), HDPE-5N (95 wt % HDPE and 5 wt % CNTs in neat form), and HDPE-5MB (the same as HDPE-5N but with CNTs in master-batch form). These formulations were repeated for the four other thermoplastics. All formulations were compounded and further injection-molded with standard injection-molding parameters suitable for each thermoplastic, with modifications made when they were needed. For each formulation, the injection-molding processing parameters were recorded. In the second part of this work, two formulations, PC and PBT with a CNT concentration of 3 wt % in master-batch form (PC-3MB and PBT-3MB, respectively), were compounded and then injection-molded. Injection molding was conducted with a 5-variable, 2-level, 10-run screening DOE. The high and low levels of the DOE variables were chosen according to the experience gained in the first part of this work.

### DOE

Five injection-molding parameters (those affecting mainly mixing and orientation) were chosen as

**TABLE I**  
**DOE for PC-3MB**

Run	Independent variables (inputs)				
	$Q$ (cm <sup>3</sup> /s)	$V_s$ (mm/min)	$T$ (°C)	$P_b$ (bar)	$P_h$ (bar)
1	60	15	280	50	1000
2	75	15	280	250	700
3	60	35	280	250	700
4	75	35	280	50	1000
5	60	15	310	250	1000
6	75	15	310	50	700
7	60	35	310	50	700
8	75	35	310	250	1000
9	75	15	310	50	700
10	75	15	310	50	700

Runs 9 and 10 were replicates of run 6.

independent variables for the DOE: the screw speed ( $V_s$ ) and backpressure ( $P_b$ ), which affect mixing; the injection flow rate [i.e., injection speed ( $Q$ )] and working temperature ( $T$ ), which affect the mixing, flow, and orientation; and the holding pressure ( $P_h$ ), which affects general product quality. A 10-run, 2-level experimental design was chosen with 8 different runs and 2 replicates (runs 9 and 10), which were used to generate the statistical experimental error of the process. Runs that produced the highest quality samples, which were chosen at the time of the experiment itself, were used for replication: run 6 for PC-3MB and run 5 for PBT-3MB. Tables I and II describe the experimental designs for formulations PC-3MB and PBT-3MB, respectively.

### Characterization

The tensile properties were measured with a tensometer with an external extensometer (Instron 4481, Instron, Norwood, MA) according to the ASTM D 638 standard procedure (type 1 test sample). The modulus of elasticity ( $E$ ) was measured at a speed of 1 mm/min, and the strength and elongation were measured at a speed of 50 mm/min for HDPE, PA6,

PA66, and PBT and at a speed of 10 mm/min for PC. The flexural properties were measured according to the ASTM D 790 standard procedure at a speed of 1.3 mm/min. The Izod impact strength was measured with an impact tester (Ceast Resil 5.5, Instron, Norwood, MA) according to the ASTM D 256 standard procedure (notch type A, impact speed = 3.46 mm/s). Samples were tested in the injection direction (the notch perpendicular to the material flow). The thermal properties were evaluated with a heat deflection temperature (HDT) testing instrument (Ceast HDT 3, Instron, Norwood, MA) according to the ASTM D 648 standard procedure (1.82 MPa). The volumetric resistivity (VR) was measured with an electrometer (Keithley 610C/240A/6105, Keithley, Cleveland, OH) according to the ASTM D 257 standard procedure on a 3-mm-thick circular sample, and finally the CNT dispersion within the host polymer matrix was studied with a transmission electron microscope (TEM) (Philips CM-120, Philips, Eindhoven, Netherlands) with a 120-kV accelerating voltage on 50-nm-thick ultramicrotomed cross sections (Ultracut UCT, Leica) parallel to the injection direction.

## RESULTS AND DISCUSSION

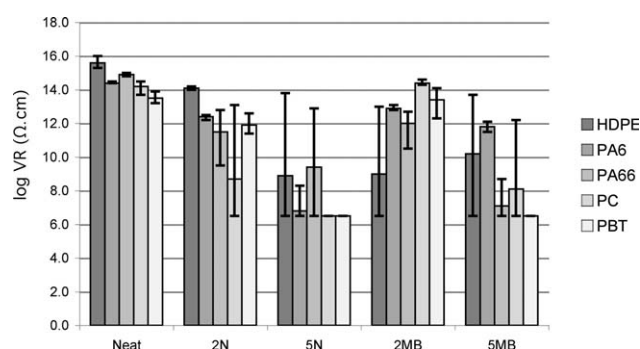
All nanocomposites were compounded and injection-molded without difficulty. Figure 1 shows the average values (bars) and maximum and minimum values (error bars) of the logarithm of VR of HDPE, PA6, PA66, PC, and PBT for neat polymer samples, samples with neat CNT concentrations of 2 and 5 wt % (2N and 5N), and for samples with master-batch CNT concentrations of 2 and 5 wt % (2MB and 5MB).

For HDPE, sample HDPE-2N showed only a small VR reduction; however, a significant VR reduction was observed for samples HDPE-5N, HDPE-2MB, and HDPE-5MB. These three samples showed a broad range of resistivity values spanning from less

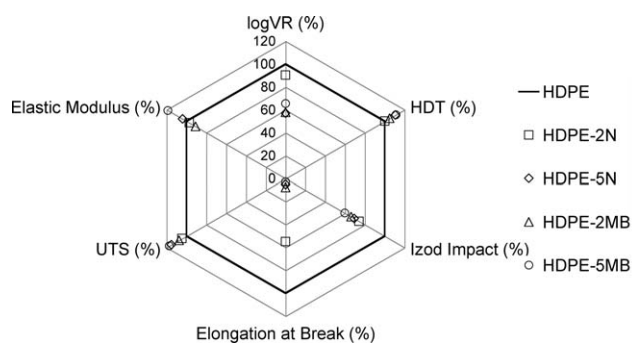
**TABLE II**  
**DOE for PBT-3MB**

Run	Independent variables (inputs)				
	$Q$ (cm <sup>3</sup> /s)	$V_s$ (mm/min)	$T$ (°C)	$P_b$ (bar)	$P_h$ (bar)
1	60	15	260	50	1000
2	75	15	260	250	700
3	60	35	260	250	700
4	75	35	260	50	1000
5	60	15	290	250	1000
6	75	15	290	50	700
7	60	35	290	50	700
8	75	35	290	250	1000
9	60	15	290	250	1000
10	60	15	290	250	1000

Runs 9 and 10 were replicates of run 5.



**Figure 1** Average values (bars) and maximum and minimum values (error bars) of the logarithm of VR for different nanocomposite formulations.

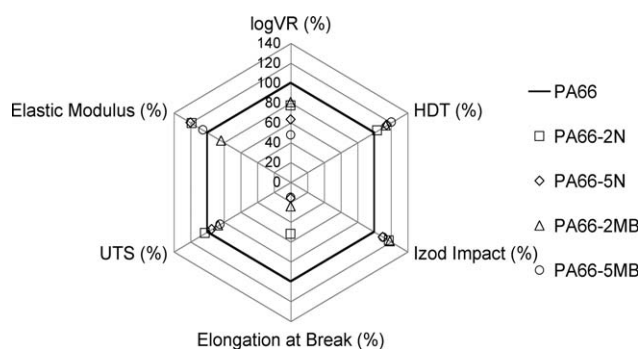


**Figure 2** Electrical, mechanical, and thermal properties of HDPE/CNT nanocomposites and neat HDPE (taken to be 100%).

than  $10^{6.5}$  (the minimum instrument detection value) to  $10^{13}$ – $10^{14}$   $\Omega$  cm (for neat HDPE, the average measured VR value was  $10^{15.6}$   $\Omega$  cm). For samples containing neat CNTs, a significant VR reduction was observed only with a CNT concentration of 5 wt % (HDPE-5N), whereas for samples based on master batches, the reduction was observed already with a CNT concentration of 2 wt % (HDPE-2MB). This demonstrated that in the case of HDPE, the CNT master batch was more effective.

For PA6, samples PA6-2N and PA6-2MB did not show a significant VR reduction, sample PA6-5MB showed a slight reduction, and sample PA6-5N showed a significant reduction within a small range of resistivity values spanning from less than  $10^{6.5}$  to  $10^{8.3}$   $\Omega$  cm (for neat PA6, the average measured VR value was  $10^{14.4}$   $\Omega$  cm). In the case of PA6, a CNT concentration of 2 wt % in neat or master-batch form was not enough to produce a significant VR reduction, and a CNT concentration of 5 wt % was needed. Moreover, contrary to the case of HDPE, for PA6, neat CNTs were found to be more effective than master-batch CNTs.

For PA66, samples PA66-2N and PA66-2MB showed a VR reduction to a level of  $10^{9.5}$ – $10^{13}$   $\Omega$  cm (for neat PA66, the average measured VR value was  $10^{14.9}$   $\Omega$  cm), whereas samples PA66-5N and PA66-



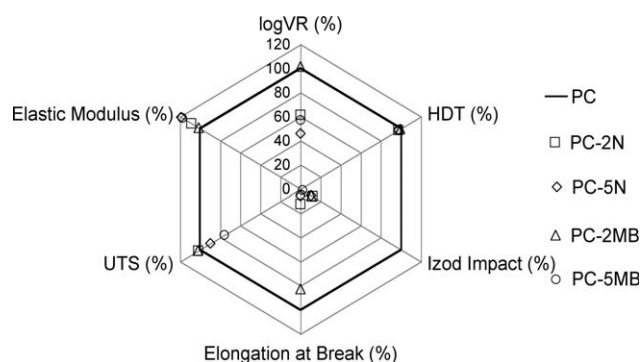
**Figure 3** Electrical, mechanical, and thermal properties of PA66/CNT nanocomposites and neat PA66 (taken to be 100%).

5MB showed a more significant reduction. Sample PA66-5MB showed the highest reduction within a smaller range of resistivity values spanning from less than  $10^{6.5}$  to  $10^{8.7}$   $\Omega$  cm. Similarly to PA6, a CNT concentration of 2 wt % in neat or master-batch form was not enough to produce a significant VR reduction, and a CNT concentration of 5 wt % was needed. For PA66, the best results were obtained when a CNT concentration of 5 wt % was introduced through a master batch.

For PC, no VR reduction was observed in sample PC-2MB; however, significant VR reductions were observed for samples PC-2N, PC-5N, and PC-5MB. Sample PC-2N reached an average VR of  $10^{8.7}$   $\Omega$  cm but showed a wide range spanning from less than  $10^{6.5}$  to  $10^{13.5}$   $\Omega$  cm (for neat PC, the average measured VR value was  $10^{14.2}$   $\Omega$  cm). Likewise, PC-5MB showed a slightly lower average VR of  $10^{8.1}$   $\Omega$  cm and a slightly narrower range spanning from less than  $10^{6.5}$  to  $10^{12.2}$   $\Omega$  cm. However, sample PC-5N showed a very significant VR reduction, and all measurements rendered a VR lower than  $10^{6.5}$ . In the case of PC, a VR reduction could be obtained with a neat CNT concentration of 2 wt % or with a CNT concentration of 5 wt % in neat or master-batch form. The best results were obtained when a CNT concentration of 5 wt % was introduced in the neat form.

Finally, for PBT, both samples with a CNT concentration of 2 wt % showed a slight VR reduction (PBT-2N was a little better than PBT-2MB); however, both samples with a CNT concentration of 5 wt % reached the minimum instrument detection value of  $10^{6.5}$  (for neat PBT, the average measured VR value was  $10^{13.5}$   $\Omega$  cm). In the case of PBT, a VR reduction could be obtained only with a CNT concentration of 5 wt % in neat or master-batch form. For PBT, neat CNTs seemed to be a little more efficient than the master batch.

Figures 2–4 show graphical multiproperty descriptions of the mechanical properties [ $E$ , ultimate tensile strength (UTS), elongation at break ( $\epsilon_B$ ), and



**Figure 4** Electrical, mechanical, and thermal properties of PC/CNT nanocomposites and neat PC (taken to be 100%).

TABLE III  
Summary of the Effects of CNTs on Nanocomposite Properties

Polymer	Best balance of properties	Resistivity ( $\Omega$ cm)	Stiffness	Strength	Impact	Thermal	Ductility
HDPE	2 wt % master batch	$<10^{6.5}-10^{13}$	Increases	Increases	Decreases	Increases	Good
PA6	5 wt % neat	$<10^{6.5}-10^{8.3}$	Increases	Decreases	Increases	Increases	Good
PA66	5 wt % master batch	$<10^{6.5}-10^{8.7}$	Increases	Decreases	Increases	Increases	Low
PC	2 wt % neat	$<10^{6.5}-10^{13.5}$	Increases	Decreases	Decreases	Similar	Good
PBT	5 wt % neat	$<10^{6.5}$	Increases	Increases	Increases	Increases	Fair

Izod impact], thermal properties (HDT), and VR of HDPE, PA66, and PC for neat polymers, samples with a neat CNT concentration of 2 or 5 wt % (2N and 5N), and samples with a master-batch CNT concentration of 2 or 5 wt % (2MB and 5MB). All values are presented as percentages of the value for the neat polymer (taken to be 100%).

For HDPE (Fig. 2), with a CNT concentration of 2 wt %, the modulus of the samples decreased versus that of the neat polymer; with a concentration of 5 wt %, the modulus increased. Slight increases in the UTS and HDT and significant decreases in  $\epsilon_B$  and the impact resistance were observed for all samples. Altogether, in the case of HDPE, the introduction of CNTs reduced the VR, increased the stiffness, strength, and thermal resistance, and decreased the elongation and impact; however, samples stayed reasonably ductile. The sample that seemed to present the best balance of properties was HDPE-2MB, which had low VR values and other properties similar to those obtained with a CNT concentration of 5 wt % but with a lower CNT loading.

For PA66 (Fig. 3), the modulus increased for all samples except PA66-2MB. The UTS tended to decrease, whereas the HDT and the Izod impact slightly increased. A significant reduction in  $\epsilon_B$  was observed for all samples. Similar behavior was observed for PA6. Altogether, for the polyamides, the introduction of CNTs reduced the VR, slightly increased the stiffness, impact, and thermal resistance, and decreased the elongation. PA6 samples remained ductile for all CNT concentrations, whereas PA66 samples with a CNT concentration of 5 wt % showed brittle behavior. In the case of PA6, the best balance of properties was obtained for sample PA6-5N, and in the case of PA66, the best balance was obtained for sample PA66-5MB. It is possible that good properties could be obtained with a lower CNT concentration such as 4 or 3 wt %.

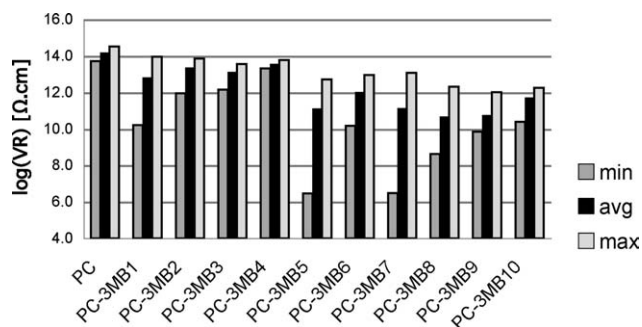
For PC (Fig. 4), the modulus increased for all samples, the UTS slightly decreased, and the HDT remained more or less unchanged. The  $\epsilon_B$  and Izod impact values decreased significantly. PC is known to have a very high impact strength, and although CNTs reduced its impact resistance significantly, all samples except PC-5MB retained reasonable proper-

ties. Altogether, for PC, the introduction of CNTs reduced the VR, increased the stiffness, reduced the strength slightly, did not change significantly the thermal resistance, and decreased significantly the elongation and impact strength. Samples with a CNT concentration of 2 wt % remained ductile, whereas samples with a CNT concentration of 5 wt % showed brittle behavior. For PC, the lowest VR was observed for sample PC-5N, but this sample became brittle; however, sample PC-2N, having a somewhat higher VR, remained ductile. It seems that in the case of PC, the best balance of properties could be obtained using neat CNT concentrations between 2 and 5 wt %, such as 4 or 3 wt %.

Finally, for PBT, the UTS (strength), HDT (thermal resistance),  $E$  (stiffness), and impact increased slightly; however, the elongation decreased significantly. Samples remained ductile, except for PBT-5MB, which became brittle. The best balance of properties was obtained for sample PBT-5N, but it is possible that good properties may be obtained with a lower CNT concentration such as 4 or 3 wt %.

A summary of the effects of the CNTs on the different properties with respect to the neat polymer forms is presented in Table III. General trends can be discerned. CNTs reduced the VR, increased the stiffness and thermal resistance, and reduced the ductility. The strength and impact resistance increased or decreased according to the polymeric matrix and the CNT concentration and type.

CNTs are nanoparticles; thus, if they are well dispersed, they will intimately interact with the polymer matrix and affect the properties of the host polymer with lower loadings in comparison with conventional fillers. Moreover, CNTs are nanofibers with a high aspect ratio, so their effects can be further enhanced by proper orientation. Electrical conduction/dissipation will be achieved when CNTs form a percolation network, a kind of electrical web that allows electricity to be conducted through a nonconducting polymer matrix. The formation of this web depends on the CNT dispersion and orientation within the polymer matrix, which in turn depend on various parameters such as the CNT type and structure, CNT/polymer mutual affinity, polymer melt viscosity, polymer solid morphology, and crystallinity (fillers tend to preferentially locate



**Figure 5** Average logarithm of VR for DOE PC-3MB samples.

themselves in amorphous areas) and, as shown in the second part of this work, on the processing parameters. The results obtained in the first part of this work were expected and are similar to those described in previous articles.<sup>1–4</sup> Electrical conduction/dissipation was achieved with lower CNT loadings (between 2 and 5 wt %) in comparison with those needed with conventional conductive fillers (to produce similar effects with carbon black, loadings > 10 wt % would be needed<sup>26</sup>); however, because of the multiple factors affecting CNT/polymer interactions, the specific loadings were different for each polymer. Similar behavior was observed for the mechanical properties. Lower loadings of CNT versus those used with conventional reinforcements were needed to affect the mechanical properties. Again and for the same reasons described previously, although the general effect trends were similar for all the polymers, specific effects changed from polymer to polymer. Finally, changing from neat CNTs to master-batch CNTs changed not only the thermal history of the material but also the CNT type (two different master-batch suppliers that produced two different CNT types were used). In all cases, the best results were obtained for one CNT type (either in the neat form or in the commercial master-batch form). This led to the conclusion that this specific CNT structure was favorable under the conditions of this work, and with a favorable CNT structure, the effects of a different thermal history were less significant.

It has been shown in the first part of this work that multiple factors may affect the properties of polymer/CNT composites. In the second part of this work, the CNT and polymer type were kept constant within each DOE, and only the processing parameters were changed.

Figures 5 and 6 show the VR results for PC-3MB and PBT-3MB DOE samples, respectively, from run 1 to run 10. Values for neat polymeric samples are also included for comparison. In both cases, although the formulation was unchanged during the

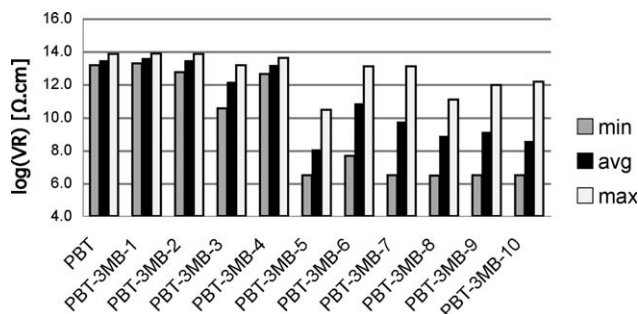
entire experiment (a CNT concentration of 3 wt %), the results varied significantly from run to run. For PC-3MB (Fig. 5), the average VR was  $10^{13.6} \Omega \text{ cm}$  in run 4 and close to that of neat PC ( $10^{14.2} \Omega \text{ cm}$ ), whereas the average VR was  $10^{10.7} \Omega \text{ cm}$  in run 8, that is, 3 orders of magnitude less. For PBT-3MB (Fig. 6), the average VR was  $10^{13.6} \Omega \text{ cm}$  in run 1 and close to that of neat PBT ( $10^{13.5} \Omega \text{ cm}$ ), whereas the average VR was  $10^8 \Omega \text{ cm}$  in run 5, that is, more than 5 orders of magnitude less.

In the DOE used in this work, the injection-molding parameters were changed in runs 1–8 according to the design (Tables I and II), and the obtained results were used to calculate the first-order effects of the injection-molding parameters on the properties of the nanocomposites. Runs 9 and 10 were replicates (i.e., the same processing parameters) of run 6 for PC-3MB and run 5 for PBT-3MB. Replicates were used to generate statistical error data intrinsic to the process. Effects that were smaller than the statistical intrinsic error of the process were discarded. In this way, eqs. (1)–(8) were obtained. In eqs. (1)–(8), the processing parameter values are encoded; this means that +1 should be inserted into the equations for high values of the processing parameters, and –1 should be inserted for low values.<sup>23</sup>

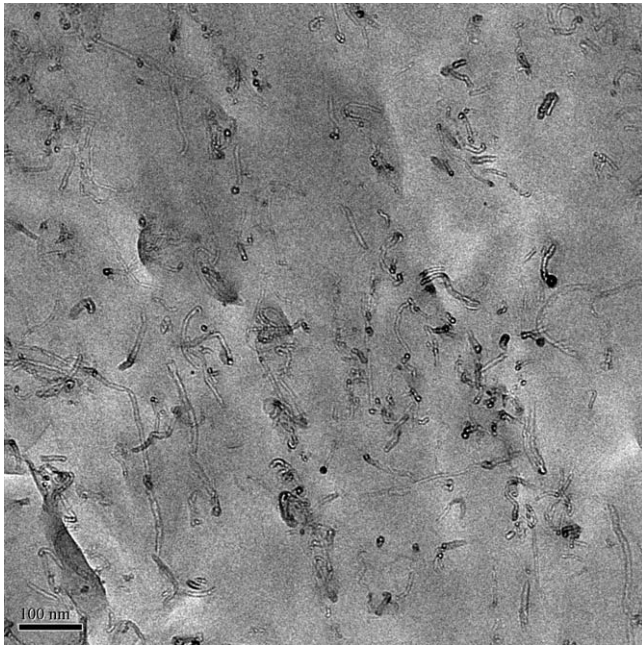
For the average VR of the PC-3MB formulation, all effects except for  $T$  were found to be smaller than the statistical intrinsic error of the process and therefore were discarded; this led to the following model:

$$\log \text{VR} = 12.0 - 1.1T \pm 0.6 \quad (1)$$

where  $\log \text{VR}$  is the average logarithm of VR ( $\Omega \text{ cm}$ ) and  $T$  is the working temperature in encoded values of +1 for the high level and –1 for the low level. The VR depended inversely on  $T$ ; that is, the higher the  $T$  value was, the lower the VR value was. An increase of  $30^\circ\text{C}$  in  $T$  (the difference between the high value of  $310^\circ\text{C}$  and the low value of  $280^\circ\text{C}$ ) led to a decrease of more than 2 orders of magnitude in the average VR  $\{[12.0 - 1.1(+1)] - [12.0 - 1.1(-1)] = -2.2\}$ .



**Figure 6** Average logarithm of VR for DOE PBT-3MB samples.



**Figure 7** TEM image of a nonconductive PBT-3MB sample from DOE run 1 ( $VR = 7.31 \times 10^{13} \Omega \text{ cm}$ ).

For PBT-3MB, the effect of  $T$  on the average VR was even more significant:

$$\log VR = 10.8 - 1.8T \pm 0.6 \quad (2)$$

Also in this case, the VR was found to be not significantly affected by the processing parameters except for  $T$ . Similarly to formulation PC-3MB,  $T$  affected the VR inversely. An increase of  $30^\circ\text{C}$  (the difference between the high value of  $290^\circ\text{C}$  and the low value of  $260^\circ\text{C}$ ) led to a decrease of almost 4 orders of magnitude in the average VR  $\{[10.8 - 1.8(+1)] - [10.8 - 1.8(-1)] = -3.6\}$ .

Similarly, the model equations for  $E$  (MPa),  $\varepsilon_B$  (%) and the Izod impact strength ( $\text{KJ/m}^2$ ) for formulation PC-3MB were calculated:

$$E = 2828 + 60P_b \pm 31 \quad (3)$$

$$\varepsilon_B = 17.8 - 4.4V_s - 9.2T \pm 3.3 \quad (4)$$

$$\text{Izod impact} = 8.0 \pm 0.4 \quad (5)$$

According to eq. (3),  $E$  was found to be dependent mainly on  $P_b$  (i.e., improved melt mixing). All other processing parameters were found to have insignificant effects. An increase of 200 bars in  $P_b$  (the difference between the high value of 250 bar and the low value of 50 bar) resulted in an increase of 120 MPa in the modulus  $\{[2828 + 60(+1)] - [2828 + 60(-1)] = 120 \text{ MPa}\}$ .  $\varepsilon_B$  was found to be inversely dependent

primarily on  $T$  and secondarily on  $V_s$ . Thus, although increasing  $T$  was favorable for electrical conductivity, it caused a detrimental loss of ductility. However, this unwanted effect could be somewhat moderated by a reduction of  $V_s$ .

As shown in eq. (5), the Izod impact was found to be independent of the processing parameters. The same behavior was found for the HDT.

Equations (6)–(8) are the model equations for  $E$  (MPa),  $\varepsilon_B$  (%) and the Izod impact strength ( $\text{KJ/m}^2$ ) for the PBT-3MB formulation:

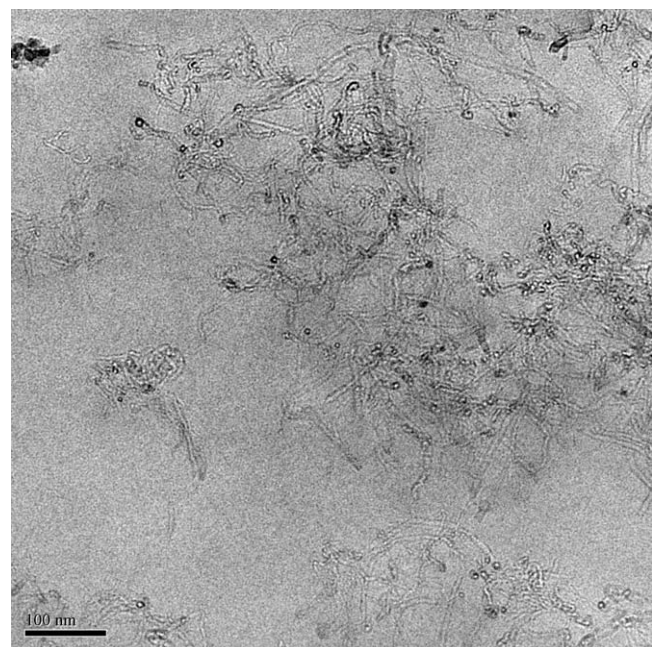
$$E = 3314 + 13Q + 12V_s - 28T + 10P_b \pm 6 \quad (6)$$

$$\varepsilon_B = 16.7 - 2.5Q - 1.5T \pm 0.9 \quad (7)$$

$$\text{Izod impact} = 4.1 - 0.4T \pm 0.3 \quad (8)$$

Higher  $Q$ ,  $V_s$ , and  $P_b$  values caused an increase in the modulus, and a higher  $T$  value caused a decrease. Higher  $Q$  and  $T$  values caused a decrease in  $\varepsilon_B$ . The Izod impact strength and the HDT were hardly affected by the injection-molding parameters.

The morphologies of a nonconductive PBT-3MB sample obtained from run 1 ( $VR = 7.3 \times 10^{13}$ ) and a conductive PBT-3MB sample obtained from run 5 ( $VR < 3 \times 10^6$ ) were compared with TEM micrographs. For the nonconductive PBT-3MB sample (Fig. 7), the CNTs seemed to adopt a discontinuous dispersion, whereas for the conductive PBT-3MB



**Figure 8** TEM image of a conductive PBT-3MB sample from DOE run 5 ( $VR < 3.0 \times 10^6 \Omega \text{ cm}$ ).

sample, clear network formation (percolation network) could be observed (Fig. 8) in correlation with the VR values measured for these same samples.

Undoubtedly, the processing parameters affect the properties of CNT/polymer composites (mainly the electrical properties but also, to a lesser degree, the mechanical properties). The processing parameters (especially those chosen in this work) affect the degree of dispersion and orientation of CNTs within the polymer matrix and thus affect the properties. The behavior of PBT-3MB seemed to be more complicated than that of PC-3MB, and this was expected because PBT is a crystalline polymer, whereas PC is amorphous. In the case of PBT, crystallization thermodynamics and kinetics play significant roles in the development of the final mechanical properties of nanocomposites, and these can be affected by the injection-molding parameters in complex ways. In the case of the mechanical properties of PBT, further experimentation, including a higher resolution DOE, may be necessary.

## CONCLUSIONS

Thermoplastic nanocomposites based on HDPE, PA6, PA66, PC, or PBT with multiwalled CNTs at a concentration of 2 or 5 wt % (introduced in neat or master-batch form) were compounded and injection-molded into testing samples used to evaluate the electrical, mechanical, and thermal properties of the nanocomposites. Polymer/CNT composites with a CNT concentration as high as 5 wt % could be compounded and injection-molded with normal processing parameters without processing difficulties, and dissipative/conductive polymer composites were obtained. However, the introduction of CNTs, even at these low concentrations, had a significant effect on the mechanical properties: usually, the stiffness and strength increased, and the ductility decreased. For some polymers, nanocomposites prepared with neat CNTs were found to render the best properties; for others, nanocomposites prepared with CNT master batches showed the best results. Optimal formulations with a good balance of properties were identified as follows: sample HDPE-2MB (with a CNT concentration of 2 wt % introduced in master-batch form), sample PA6-5N (with a neat CNT concentration of 5 wt %), sample PA66-5MB (with a CNT concentration of 5 wt % in master-batch form), sample PC-2N (with a neat CNT concentration of 2 wt %), and sample PBT-5N (with a neat CNT concentration of 5 wt %).

In the second part of this work, two selected formulations, PC with a CNT concentration of 3 wt % and PBT with a CNT concentration of 3 wt % (introduced in master-batch form), were injection-molded with a five-variable, two-level screening DOE to evaluate the

first-order effects of the processing parameters on the properties of the nanocomposites. Although only a 10-run screening DOE was performed, a dependence of the properties of the PC/CNT and PBT/CNT nanocomposites on the injection-molding parameters was evident. For both materials, the VR depended significantly on  $T$ ; that is, the hotter the melt was, the lower the VR value was. For PC, an increase of only 30°C in  $T$  resulted in a decrease of more than 2 orders of magnitude in the average VR, and for PBT, the same temperature increase resulted in a decrease of almost 4 orders of magnitude in the average VR. This VR/melt temperature dependence has important practical significance. The modulus and elongation showed more complex behavior and depended on multiple parameters differently for each material according to their intrinsic character (amorphous or crystalline). For both materials, the Izod impact strength and HDT were not significantly affected by the injection parameters. A TEM investigation indicated that conductive samples formed a percolation network, whereas nonconductive samples did not. In conclusion, the injection-molding parameters have a significant impact on the properties of polymer/multiwalled CNT nanocomposites, and not only the formulations but also the processing parameters should be optimized for the best properties.

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