Effect of Solid State Grinding on Properties of PP/PET Blends and Their Composites with Carbon Nanotubes

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ABSTRACT: In this study, it was aimed to improve electrical conductivity and mechanical properties of conductive polymer composites, composed of polypropylene (PP), poly(ethylene terephthalate) (PET), and carbon nanotubes (CNT). Grinding, a type of solid state processing technique, was applied to PP/PET and PP/PET/CNT systems to reduce average domain size of blend phases and to improve interfacial adhesion between these phases. Surface energy measurements showed that carbon nanotubes might be selectively localized at PET phase of immiscible blend systems. Grinding technique exhibited improvement in electrical conductivity and mechanical properties of PP/PET/CNT systems at low PET compositions. Ground composites molded below the melting temperature of PET exhibited higher tensile strength and modulus values than those prepared above the melting temperature of PET. According to SEM micrographs, micron-sized domain structures were obtained with ground composite systems in which PET was the minor phase. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 3041–3048, 2010

Key words: conductive polymer composites; carbon nanotubes; grinding; electrical resistivity; mechanical properties

INTRODUCTION

Most of the polymeric materials, which are used in many applications, are homopolymers. However, sophisticated applications require more complicated material systems, possessing combination of properties not attainable with simple homopolymer.¹ Development of new polymer systems to meet demands for high performance materials will take too long and will be too expensive. An alternative to the development of new polymer systems is the development of blends, which are a physical combination of two or more polymers to form a new material.² They are prepared to reduce the cost of an expensive homopolymer, to improve processability of an heat-sensitive homopolymer or to improve impact resistance.³

The simplest and economical technique to produce polymer blend is the physical blending of two or more polymers. The properties of physical blend depend on the degree of compatibility of homopolymers forming the blend system. Most of the physical blends are highly incompatible. In incompatible blend system, constituents tend to form aggregations, resulting in separated phases. Two phase morphological system possesses large and inhomogeneous domains of homopolymers with poor interphase adhesion, inducing poor mechanical properties. Large domains of phases result in stress concentrations at the phase boundaries. Hence, tensile strength, impact strength, and elongation at break values of incompatible blend are relatively low.¹ In spite of poor mechanical properties, incorporation of conductive filler into incompatible blend systems improves electrical conductivity of their composites at much lower filler contents due to the double percolation phenomenon, which results from heterogeneous distribution of conductive filler in one phase of the incompatible blend system and/or at the interface of the polymers.⁴⁻⁵

In literature, several techniques, such as reactive extrusion, in situ polymerization and mechanical milling, have been developed to reduce coarse domains of blend phases to nanoscale range.⁶⁻¹⁴ Additionally, a new approach, solid-state shear pulverization method has been applied to obtain well dispersed and stable blend microstructure, composed of immiscible polymer phases.¹⁵⁻¹⁷ Microstructured or nanostructured blend morphology is important in terms of electrical conductivity and mechanical properties of conductive polymer composites. However, conventional melt mixing methods, e.g., extrusion, have limitations in preparation of
Grinding, a type of solid-state processing method, can be applied to reduce average domain size of conductive polymer composite, composed of two immiscible polymer phases, following the conventional melt mixing process. Grinding method will improve both electrical and mechanical properties of conductive polymer composite by increasing the contact probability between domains of blend phases.

In this study, carbon nanotubes (CNT) were melt mixed with polypropylene (PP)/poly(ethylene terephthalate) (PET) immiscible blend systems. After melt-compounding process, grinding was carried out to improve both electrical conductivity and mechanical properties of PP/PET/CNT systems by decreasing domain size of PP and PET phases in the blend. Blends and composites were ground through a Wiley mill intermediate model grinder (Arthur H. Thomas Co., Philadelphia, PA) at room temperature for 30 min and pellets were turned into powder with grinding.

To determine electrical resistivity of conductive composite systems, test samples of conventional PP/PET/CNT and ground PP/PET/CNT were prepared by compression molding device at 280°C. PP/PET/CNT pellets were heated for 0.5 min under 50 bar gauge pressure and then they were heated for 2.5 min under 150 bar gauge pressure. Finally, compression molded samples were quenched to room temperature by water. Test samples required for mechanical property characterization were prepared using the laboratory scale injection molding instrument (DSM Micro 10 cc Injection Molding Machine). At the injection molding process of PP/PET and PP/PET/CNT systems, barrel and mold temperatures were 280°C and 30°C, respectively. Additionally, to investigate possible effects of high temperature processing on composite microstructure, ground PP/PET/CNT pellets were molded at 230 and 280°C, respectively. PET does not melt at 230°C and reduced domain structures of this phase should not change during the compression molding and the injection molding processes at this temperature.

### EXPERIMENTAL

#### Materials

In this study, poly(ethylene terephthalate) (PET) and polypropylene (PP) were used to prepare blend systems. Besides, carbon nanotubes (CNT) were added to these systems to obtain conductive composites. Table I summarizes properties of PET, PP, and CNT, respectively.

#### Composite preparation

Before melt compounding, PET and PP pellets were dried in a vacuum oven for 12 h at 80°C and 4 h at 60°C, respectively. PP/PET/CNT systems were prepared by using a twin screw extruder (Thermo PRISM TSE-16-TC (L/D = 24)). PP and PET pellets were mixed in solid form and fed into the extruder through the main feeder. In addition, CNT were fed into the extruder through the side feeder to obtain conductive composite systems with the compositions of 90/10/1, 80/20/1, 70/30/1, 60/40/1, 40/60/1, 20/80/1 (PP/PET/CNT) in weight %. Same blend compositions were also prepared in the absence of CNT to observe the effect of the conductive filler on the blend systems. Additionally, CNT content of the composite system, 70/30/1 (PP/PET/CNT), was varied among the compositions: 70/30/0.25, 70/30/0.5, 70/30/2, 70/30/4 (PP/PET/CNT). The extrusion processes of PP/PET and PP/PET/CNT systems were performed at a processing temperature of 260°C with a screw speed of 200 rpm. After melt compounding, certain amounts of blend and composite pellets were exposed to grinding process to decrease domain size of PP and PET phases in the blend. Blends and composites were ground through a Wiley mill intermediate model grinder (Arthur H. Thomas Co., Philadelphia, PA) at room temperature for 30 min and pellets were turned into powder with grinding.

### Composite characterization techniques

Contact angle measurements were carried out to obtain information about surface energy components (total surface energy, $\gamma_{\text{Tot}}$, London dispersive component, $\gamma_{\text{LW}}$, and acid/base component, $\gamma_{\text{AB}}$) of PP, PET and CNT, used to determine selective
TABLE II
Surface Energy Components of Probe liquids,

<table>
<thead>
<tr>
<th>Liquid</th>
<th>$\gamma_{L}^{\text{Tot}}$</th>
<th>$\gamma_{L}^{\text{AB}}$</th>
<th>$\gamma_{L}^{\text{AB}}$</th>
<th>$\gamma_{L}^{\text{A}}$</th>
<th>$\gamma_{L}^{\text{B}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIM</td>
<td>50.80</td>
<td>-</td>
<td>-</td>
<td>2.30</td>
<td>30.10</td>
</tr>
<tr>
<td>EG</td>
<td>48.00</td>
<td>29.00</td>
<td>19.00</td>
<td>3.00</td>
<td>30.10</td>
</tr>
<tr>
<td>Formamide</td>
<td>58.00</td>
<td>39.00</td>
<td>19.00</td>
<td>2.30</td>
<td>39.60</td>
</tr>
</tbody>
</table>

where $\gamma_{\text{PET-CNT}}$, $\gamma_{\text{PP-CNT}}$, $\gamma_{\text{PET-PP}}$ are the interfacial tension between CNT and polymer phases, $\gamma_{\text{PET-PP}}$ is the interfacial tension between two phases. If $W_a$ is greater than 1, CNT are located within poly(ethylene terephthalate) phase. If $W_a$ is less than $-1$, CNT are located within PP phase. If $W_a$ is between $-1$ and 1, than the conductive filler is distributed at the interface.28-30

The electrical resistivity of conventional and ground PP/PET/CNT systems was measured by two point probe method with a constant current source (Keithley model 2400). For better electrical contact in two point probe method, copper wires were placed into the compression molded composites during sample preparation. Conductivity measurement was performed by contacting probes with these copper wires. All measurements were done at room temperature, and the average of six measurements was taken into account for each composition of conventional PP/PET/CNT and ground PP/PET/CNT.

The tensile properties of PP/PET blend systems and PP/PET/CNT composite systems were measured using a tensile testing instrument (Shimadzu Autograph AG-100 KNIS MS) according to ISO 527-25A standard. Five specimens of each composition were tested and average of these five test results were illustrated in tables with their standard deviations. Injection molded specimen had a thickness of 2 mm and width of 4 mm with a gauge length of 20 mm. According to the gauge length and a strain rate of 0.1 min$^{-1}$, the crosshead speed of testing instrument was set at 2 mm/min. Charpy impact strength of PP/PET and PP/PET/CNT systems was measured by a pendulum impact tester (Ceast Resil Impactor 6967) according to ASTM D 5942 standard. Fractured surfaces of impact specimens were analyzed by Scanning Electron Microscope (JEOL JSM-6400). Before morphology analysis, conventional and ground PP/PET/CNT systems were exposed to chemical etching with trifluoroacetic acid for 6 h to separate PET phase of blend systems.

RESULTS AND DISCUSSION

Surface energies of polymer phases are effective in selective localization of filler in blend systems.28,29

To determine the distribution of carbon nanotube particles in PP/PET blend systems, surface energy values of PP and PET at the extrusion process temperature, 260°C, are essential and it is difficult to measure these values at this temperature with contact angle method. However, surface energies of molten PP and PET can be calculated using eqs. (1) and (2) (Table III). To check reliability of surface energies calculated using these equations, surface
energies of PP and PET are also calculated for 20°C with contact angle method (Table IV) and by using eqs. (1) and (2) (Table III). These values are quite close to each other. Hence, surface energies, calculated using eqs. (1) and (2), can be used to determine selective localization of nanotube particles in PP/PET systems. For this purpose, interfacial tension values, given in Table V, are calculated using eq. (3) and utilized to calculate the wetting coefficient, \( W_w \).

The wetting coefficient, \( W_w \), is calculated as 1.44 after substituting calculated interfacial energies into eq. (4). As the wetting coefficient is greater than 1, CNT may prefer PET phase rather than PP phase in the blend.

PP-based composite containing 1 wt % CNT is electrically insulating, and it has an average electrical resistivity value of 10\(^{11}\) ohm.cm; whereas PET-based composite containing 1 wt % CNT is not electrically insulating, and it has an average electrical resistivity value of 50 ohm.cm. Additionally, conventional PP/PET/CNT systems at low PET compositions have insulating resistivity values. These results support the same idea that CNT may locate in PET phase of PP/PET/CNT systems.

Electrical conductivity of PP/PET/CNT systems strongly depends on the double percolation phenomenon. The percolation of nanotube particles in PET phase, which is the first percolation threshold, is provided as electrical resistivity of PET based composite containing 1 wt % CNT is in semiconductive range. The continuity of PET phase in blend system, which is known as the second percolation, is significant on account of the formation of conductive pathways throughout the blend sample. Additionally, conventional PP/PET/CNT systems at low PET compositions have lower electrical resistivity than those of ground systems at high PET compositions. The reason for this reverse trend may be the difference in domain size of composites. Starting with 40 wt % PET composition, PET domains start to form the continuous structure in blend systems. As PET content in the blend is less than 40 wt %, most of PET domains may disperse in PP phase (Figs. 1–3) and the conductive pathways throughout the blend sample cannot be formed and their electrical resistivity values are in insulator range, even if CNT content in PET phase is above percolation threshold concentration. For the blend systems exposed to grinding, applied to decrease average domain size of phases, the second percolation threshold is shifted to lower PET content. SEM micrographs reveal the difference in morphologies of ground and conventional composites (Figs. 1–3). Average domain size of the minor phase, PET, in ground system of 10 wt % composition is around 1 μm or smaller (Fig. 1); whereas average domain size of PET in conventional composite is around 100 μm, two orders of magnitude larger than that obtained in the ground composite. As the domain size decreases, probability of contact between domains of phases increases. Ground composites containing 10, 20, and 30 wt % PET are in semiconductive level (Fig. 4), which shows that PET domains with nanotube particles are in contact and charge transfer may be provided throughout the samples. Hence, grinding technique is successful to some extent as there is a significant difference between electrical resistivity values of conventional and ground composites up to 40 wt % PET composition.

There is a reverse trend when PET content of composites is more than 40 wt % (Fig. 4). Conventional composites have lower electrical resistivity than those of ground systems at high PET compositions. The reason for this reverse trend may be the difference in domain size of composites. Starting with 40 wt % composition, PET domains start to form the continuous structure in blend systems. As PET composition of blend increases, conductive networks are enhanced along PP/PET/CNT samples. Conductive networks may be destroyed after grinding. When PET is the continuous phase, grinding increases both the probability of contact of PET domains and the contact resistance between PET phases by decreasing the domain size.

PP and PET phases are subjected to high compressive and shearing forces during grinding, which causes fragmentation and dispersion of micron-sized domains. Reduced polymer domains combine to form larger domains with a net reduction in interfacial area during high temperature processing above
melting points of polymers. Compression and injection molding processes were also performed above melting temperatures of both PP and PET. Coalescence is the major drawback of high temperature processes as high temperature and long term processes enlarge the domains of phases. Reduced domain structures of PP and PET phases might tend to coalesce during molding processes as electrical resistivity of ground composites, molded at 280°C, is higher than that of ground composites, molded at 230°C (Fig. 5). Molding temperature of 280°C, above the melting point of PET, is adequate to change microstructure of blends. However, the effect of high temperature processing on blend morphology should be limited, that is, reduced domain structures might not coalesce too much during molding processes since ground systems, containing less than 40 wt % PET and molded at 280°C, have electrical conductivity in semiconductive level (Fig. 5).

An increase in carbon nanotube content of the conventional composite, containing 30 wt % PET, does not change its electrical resistivity as carbon nanotube particles may localize in PET phase of the blend, and conductive PET phases do not provide the continuity at this composition of the conventional PP/PET/CNT system. On the other hand, the ground system provides the continuity at 30 wt % PET composition, and an increase in carbon nanotube content enhances electrical conductivity of this ground composite (Fig. 6).

![Figure 1](image1.png)  
**Figure 1** SEM micrographs of impact fractured samples of PP/PET/CNT (90/10/1) systems, etched with trifluoroacetic acid, (a) ground and (b) conventional.

![Figure 2](image2.png)  
**Figure 2** SEM micrographs of impact fractured samples of PP/PET/CNT (80/20/1) systems, etched with trifluoroacetic acid, (a) ground and (b) conventional.
Immiscible PET/PP blend system exhibits poor adhesion between phases and has poor mechanical properties. Reduced domain structure, attained by solid state processing, has a distinct effect on the mechanical properties of blend systems. Ground blends have higher tensile strength values than conventional ones (Table VI). Average domain size of PP and PET phases might be reduced after grinding, which results in enhanced tensile strength due to advanced interfacial interaction between phases. Tensile strength values of neat PET and neat PP are 46.3 MPa and 30.5 MPa, respectively. With increasing PET content of both blend systems, tensile strength decreases slowly (Table VI). Blend systems containing less than 40 wt % of PET have higher tensile strength values compared to neat PP.

Tensile modulus values of neat PET and PP are 948 MPa and 511 MPa, respectively, and tensile modulus values of ground and conventional blend systems fluctuate between these values (Table VI). They do not exhibit a distinct trend. Ground blends have higher tensile modulus values compared to conventional blends except 40 and 80 wt % PET containing systems.

Tensile strength value of PET composite containing 1 wt % CNT is 21.9 MPa, and tensile strength value of PP composite containing 1 wt % CNT is 31.5 MPa. When PET content of PP/PET/CNT systems increases, tensile strength of both ground and conventional composites diminishes slightly. Domain size of minor phase seems to be a little higher as PET content of ground systems increases from 10 to 30 wt % (Figs. 1–3). As the domain size of blend phases decreases, tensile strength increases as interfacial area between phases increases and the probability of finding a large flaw, resulting stress concentration, in blend structure decreases. Except for 60 wt % PET containing system, ground composites provide higher tensile strength values when compared with conventional composites. Especially, at 10 wt % composition, there is a distinct difference in tensile strength values of conventional and ground composite systems (Table VII).

Figure 3  SEM micrographs of impact fractured samples of PP/PET/CNT (70/30/1) systems, etched with trifluoroacetic acid, (a) ground and (b) conventional.

Figure 4  Electrical resistivity of conventional and ground PP/PET/CNT systems.

Figure 5  Electrical resistivity of ground PP/PET/CNT systems, prepared at 230°C and 280°C.
As stated previously, coalescence of reduced domains attained by grinding is the major drawback of long term and high temperature processing. Most of ground composites prepared at 230°C have slightly higher tensile strength values than those of ground composites prepared at 280°C. Because of poor interfacial adhesion between blend phases, PET domains in ground systems may enlarge during molding processes at 280°C, resulting in lower tensile strength values. However, the difference in tensile strength values of ground systems prepared at 230 and 280°C, respectively, is not significant (Table VII), which may be due to short term molding processing.

Tensile modulus values of PET composite containing 1 wt % CNT and PP composite containing 1 wt % CNT are 910 MPa and 749 MPa, respectively. Tensile modulus values of both conventional and ground composites change as PET content of PP/CNT changes from 10 to 80 wt % (Table VII). Furthermore, CNT do not have a distinctive effect on tensile modulus values of both composite systems (Tables VI and VII). When PET content is more than 30 wt %, tensile modulus values of both blend systems start to increase.

If the domain size of blend phases diminishes, tensile modulus increases. Ground PP/PET/CNT systems molded at 230°C may have smaller domain structures than ground systems molded at 280°C as the systems prepared at 230°C have higher tensile modulus values (Table VII). The difference in tensile modulus values of ground systems prepared at 230 and 280°C, respectively, are much more than the difference observed in tensile strength results (Table VII).

Impact strength values of conventional and ground blend systems are close to each other except for 20 wt % PET composition. Contribution of PET phase decreases impact strength of both blend systems, as this phase of PP/PET system is highly

![Figure 6](https://example.com/figure6.png)  
**Figure 6** Electrical resistivity of conventional and ground PP/PET/CNT systems containing 30 wt % PET and different amount of carbon nanotubes.
crystalline and rigid (Table VI). The explicit difference in impact strength values of conventional and ground blend systems containing 20 wt % PET may be due to the decrease in domain size of the phases. On the other hand, impact strength behavior of composite systems does not change with CNT contribution (Table VI and VII). Impact strength of both composite systems decreases with increasing PET composition. Low compositions of ground composites, containing 10 and 20 wt % PET, have higher impact strength values compared to conventional composites.

CONCLUSIONS

CNT might be selectively localized at PET phase of PP/PET/CNT composite systems. Electrical resistivity of conventional composite systems, which was in insulating range, was reduced to semiconductive level with grinding technique. The most distinctive difference in mechanical properties of conventional and ground systems was observed in the tensile strength. Ground PP/PET and PP/PET/CNT systems provided better tensile strength values for all PET compositions. Electrical conductivity, tensile strength, and modulus values of ground composite systems molded at 280°C were lower than those of ground composite systems molded at 230°C. Based on the enhanced electrical conductivity and tensile strength values, grinding technique can be applied to conductive polymer composites, consisting of incompatible blend phases.

References