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Electrical, EMI shielding and tensile properties of PP/PE blends filled with GNP:CNT hybrid nanofiller

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ABSTRACT

Polypropylene (PP)/polyethylene (PE) blends filled with 5 vol% graphene nanoplatelets: carbon nanotube (GNP:CNT) hybrid nanofiller were prepared by melt mixing. The blends' microstructure and the influence of GNP:CNT volume ratio on the electrical, electromagnetic interference (EMI) shielding and tensile strength were investigated. The scanning electron microscopy analysis showed that the CNT and GNP are localized in the PE phase. The electrical conductivity and EMI shielding were found to increase with the increase in CNT volume fraction due to the 1D geometry of the CNT that is more effective than the 2D geometry of the GNP in building conductive networks. This finding indicates that not only the nanofiller conductivity but also the nanofiller geometry should be considered in designing hybrid nanocomposite materials. Moreover, the tensile strength was found to increase with the decrease in GNP:CNT volume ratio due to the good adhesion between the CNT particles and the PE phase compared to the almost no adhesion between the GNP particles and the PE phase.

1. Introduction

Conductive polymer nanocomposites (CPN) have wide range of applications in the electronics and energy sectors [1]. CPNs can be used as light-weight shields to maintain the electromagnetic compatibility of electronic devices and as electrodes in batteries and fuel cells [1,2]. Nonetheless, the wide commercial use of CPN is very limited due to the relatively high cost of the high aspect ratio conductive nanofillers. Thus, CPN with high electrical conductivity should be formulated at the lowest possible nanofiller content to enhance CPN competitiveness. In order to achieve this objective many ideas have been investigated such as the double percolation of immiscible polymer blends [3–5], selective localization of nanofiller at the external surface of polymer powder [6] and using hybrid nanofiller mixture [7–11]. Herein, the focus is on investigating the concepts of double percolation and hybrid nanofiller together on the electromagnetic interference (EMI), electrical and mechanical properties of polymer polypropylene (PP)/polyethylene (PE) blends filled with graphene nanoplatelets (GNP): carbon nanotube (CNT) hybrid mixture. GNP and CNT are of the most promising carbon nanofillers due to their high electrical conductivity and aspect ratio.

CPNs based on two different conductive nanofillers have been investigated by many researchers [11–18]. For example at nanofiller content of 0.5 wt%, GNP:CNT/polyetherimide (PEI) nanocomposite exhibited higher electrical conductivity than GNP/PEI and CNT/PEI nanocomposites [16]. This finding was ascribed to the creation of interconnected network, in which the CNT particles connected the GNP particles. On the other hand, for copper nanoparticles (CuNP):CNT/polypropylene (PP), no synergistic effect of using hybrid nanofiller mixture on the electrical percolation threshold was reported. However, it was observed that the affinity of CuNP towards the CNT particles facilitated the dispersion of CuNP nanoparticles.

Herein, immiscible polymer blend filled with hybrid nanofiller mixture is investigated. Two carbon nanofillers, GNP and CNT, of almost similar electrical conductivity but different geometries are used. In immiscible polymer blends, nanofiller particles will selectively localize in one of the blends' phases or at the blends' interface leading to higher effective concentration in the nanofiller-rich phase. If the nanofiller-rich phase is continuous, the blend's electrical percolation threshold will be lower than that of the nanofiller/single-phase composite [19–23]. There are limited number of studies about immiscible polymer blends filled with at least two different fillers [2,23–29]. For example, Besco and coworkers [29] found that for polycarbonate/acrylonitrile-butadiene-styrene filled with organically modified clay (OMC) and CNT, both nanofillers were selectively localized in the PC phase and the

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addition of OMC was found to hinder the formation of CNT conductive network and consequently increased electrical percolation threshold. However, Zhang et al. [30] found that the addition of glass fiber (GF) enhances the electrical conductivity of CNT filled polyoxymethylene (POM)/maleic anhydride-grafted polyethylene (MA-PE) blend. In the CNT/POM/MA-PE mixture [30], the CNT was found to reside in the dispersed MA-PE phase. However upon the addition of 20 wt% GF, the CNT/MA-PE phase was found to coat the 3D network of GF particles leading to formation of continuous network. In this work, the influence GNP:CNT volume ratio on the microstructure, electrical, EMI shielding and mechanical properties of 50/50 and 90/10 polypropylene/polyethylene (PP/PE) blend are investigated. PP/PE blend was selected because PP, PE and their blends are of the most widely used polymeric materials due to their cost advantage and unique properties over many other materials. Since it was predicted that in a PP/PE blend the nanofillers will reside in the PE phase, the 50/50 and 90/10 PP/PE volume ratios were selected in order to investigate the properties of the blend when nanofillers/PE is a major phase (i.e. the 50/50 PP/PE blend) and when the nanofiller/PE is a minor phase (i.e. the 90/10 PP/PE blend). In addition in all experiments, the nanofiller volume percent was constant at 5.0 vol%. This level of nanofiller concentration was selected in order to obtain a composite by melt mixing and with adequate level of EMI shielding [31].

2. Experimental details

2.1. Materials and fabrications

Two polymers were used in this study, namely: PP and PE. The main properties of these two polymers are listed in Table 1. The nanofillers were multi-walled CNT (Nanocyl^{TM} NC7000, Nanocyl S. A., Sambreville, Belgium) and GNP (xGnP-Grade M, XG Sciences, USA). The nanotubes are 9.5 nm in diameter and 1.5 μm in length and GNP particles have a disc-shape geometry with average thickness of 7 nm and diameter of 5 μm. For the calculations of the nanofiller volume fraction, the density of CNT and GNP were set at 1.66 g/ml and 2.2 g/ml, respectively. In all experiments, the total nanofiller content was 5.0 vol%.

All blends were prepared by melting mixing using a batch mixer (Plastograph EC, Brabender, Germany). Polymer pellets, prior to mixing, were dried in a vacuum oven for 16 h at 80 °C. The CNT and GNP powders were also pre-dried at 130 °C for 16 h. The melt mixing was conducted at 100 rpm and 180 °C for 13 min. In a typical experiment, X g of polymer pellets were fed to the pre-heated mixer and mixed for 3.0 min. For the 50/50 (vol/vol) PP/PE blends, the amounts of PP and PE were 13.3 g and 14.1 g, respectively. While for the 90/10 (vol/vol) PP/PE blends, the PP and PE amounts were 24.6 g and 2.9 g respectively. Then, Y amount of the nanofillers were fed into the mixer. Tables 2 and 3 lists the amounts of the GNP and CNT used in preparing the 5 vol% filled 50/50 PP/PE and 90/10 PP/PE blends, respectively.

The nanofillers were added to the mixer following three different sequences. In the first sequence, both fillers were fed at the same time. In the second sequence, GNP was first fed and after 5.0 min the CNT was fed. In the third sequence, CNT was first introduced then after 5.0 min the GNP was fed. At the end of the mixing process, the blend was collected and sent to a compression molding machine (Carver Inc., Wabash-IN, USA) to prepare specimens for electrical, EMI shielding and mechanical properties characterization. The molding was conducted under 27.5 MPa and 200 °C for 10 min. For the electrical conductivity and EMI shielding characterizations, the samples were (40 mm × 20 mm × 1 mm) rectangles. For tensile tests, initially (65 mm × 65 mm × 1 mm) plates were produced; then ASTM D628-5-IMP die was used to cut type V ASTM D638-03 specimens.

Table 1
Information about PP and PE used in this study.

	PP	PE
Manufacturer	SABIC	ExxonMobil Chemical
Brand name	PP 504P	HTA 001HD
Specific Gravity	0.9	0.952
Melt flow rate (g/10 min)	3.2[a]	0.32[b]

[a] 230 °C and 2.16 kg load.
[b] 190 °C and 5.0 kg load.

Table 2
Amounts of GNP and CNT used to formulate the 5 vol% GNP:CNT filled 50/50 PP/PE blends.

GNP:CNT	GNP (g)	CNT (g)	GNP wt%	CNT wt%	GNP vol%	CNT vol%
5:0	3.420	0.000	11.1%	0.0%	5.0%	0.0%
4:1	2.710	0.515	8.8%	1.7%	4.0%	1.0%
3:2	2.020	1.030	6.6%	3.4%	3.0%	2.0%
2:3	1.340	1.550	4.4%	5.1%	2.0%	3.0%
1:4	0.660	2.065	2.2%	6.9%	1.0%	4.0%
0:5	0.000	2.580	0.0%	8.6%	0.0%	5.0%

Table 3
Amounts of GNP and CNT used to formulate the 5 vol% GNP:CNT filled 90/10 PP/PE blends.

GNP:CNT	GNP (g)	CNT (g)	GNP wt%	CNT wt%	GNP vol%	CNT vol%
5:0	3.520	0.000	11.3%	0.0%	5.0%	0.0%
4:1	2.816	0.531	9.1%	1.7%	4.0%	1.0%
3:2	2.112	1.062	6.9%	3.5%	3.0%	2.0%
2:3	1.408	1.593	4.6%	5.2%	2.0%	3.0%
1:4	0.704	2.124	2.3%	7.0%	1.0%	4.0%
0:5	0.000	2.655	0.0%	8.8%	0.0%	5.0%

2.2. Characterization tools

The microstructure of the PP/PE blends was investigated using Environmental Scanning Electron Microscope (Quanta 450 FEG, FEI). Prior to SEM analysis, samples were fractured in liquid nitrogen and sputtered with a thin layer of gold using sputtering machine (Q150R ES, Quorum Technologies, UK). The blends electrical conductivity was measured using two different set-ups. Conductive samples were characterized using digital multimeter (Keithley 2010 DMM, Keithley Instruments, USA) connected to a 4-wire probe test fixture, while the non-conductive samples were characterized using Keithley 6517A electrometer connected to Keithley 8009 test fixture (Keithley Instruments, USA). The reported electrical resistivity represents the average of at least six specimens. The EMI shielding effectiveness (SE) in the X-band (8.0–12.0 GHz) frequency range was conducted using E5071C ENA network analyzer connected to a WR-90 rectangular waveguide. The rectangular ($2 \times 4\,cm^2$) specimens were inserted between the two sections of the waveguide and the S-parameters (S_{11}, S_{12}, S_{22}, S_{21}) of each sample were recorded. The total EMI SE was calculated as follows:

$$EMISE = 10log\frac{1}{|S_{12}|^2} = 10log\frac{1}{|S_{21}|^2} \quad (1)$$

The tensile tests were conducted according to the ASTM standard D638-03 using WDW-20 (Jinan Testing Equipment IE Corporation, China) tensile testing machine. For each formulation, at least six specimens (Type V ASTM D638-03) were tested and the average of those was reported. The crosshead speed for all tests was 10 mm/min.