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Enhanced Electromagnetic Interference Shielding Effectiveness of Hybrid Fillers by Segregated Structure

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Abstract. Polymer nanocomposites seem to be promising candidate for the electromagnetic interference (EMI) shielding material because of its loss cost, lightweight, flexibility, and ease of production. However, to achieve high shielding, there are concerns about the nanofiller concentration and dispersion of nanofillers in the polymer matrix. To overcome this issue, implementing the effective filler dispersion technique by segregated structure were investigated. In this study using miscible mixing and precipitation method (MSMP), polystyrene (PS) matrix was fabricated by incorporation of multiwall carbon nanotubes (CNT) as primary filler and nickel nanowires (NiNW) or zinc oxide nanowires (ZnONW) as secondary filler. Preparing a hybrid structure of the dielectric/magnetic nanofiller along with CNT led to significant increase in EMI shielding effectiveness (SE) when compared to the single filler systems. For instance, PS/2.0vol% CNT nanocomposites showed EMI SE of about 16.6dB (in X-band frequency) for 1.1 mm thick shield. By adding 0.5vol% of the secondary filler either NiNW or ZnONW, it enhanced the EMI SE to 23.2dB and 24.0dB respectively. This excellent EMI SE of the hybrid nanocomposites was attributed to both selectively distributed conductive nanofillers in a segregated structure and excellent magnetic/dielectric properties of the synthesized NiNW/ZnONW, respectively. Details of the dielectric loss mechanisms for the architectures were studied. Besides achieving reliable dielectric properties, CNT/NiNW or CNT/ZnONW nanocomposite shield can be prepared with low thickness and low filler content, making them useful for various shielding applications.

Keywords: Carbon Nanotubes, Nanowires, Segregated Structure, Hybrid Nanocomposite, Electromagnetic Shielding Effectiveness.
PACS: 88.30.rh, 81.07.Gf, 81.05.Qk, 72.80.Le.

INTRODUCTION

The miniaturization trend in electronics has required the feature sizes of the electronic components to shrink suitably. Thus, the close approximation of electronic components leads to a new form of pollution called electromagnetic interference (EMI). This electromagnetic interference will decrease the efficiency of the electronics or cease its functions. Because of these consequences, it is now mandatory to protect the electronic and its components from this electromagnetic pollution. Metals have excellent electrical and magnetic properties, and so they are traditionally used to shield the components. Nowadays, polymer nanocomposites are substituting metals for EMI shielding application owing to their low cost, lightweight, flexibility, easy processing, high corrosion resistant and easy tailoring based on the required shielding application [1]. The EMI shielding effectiveness of composite material depends on the filler's intrinsic properties (e.g. conductivity, aspect ratio, magnetic and dielectric), filler concentration and dispersion state, and shield's thickness. Thus, a strong conductive network in the polymer matrix, which makes an electrically conductive nanocomposite, seems to be the propitious candidate for the EMI shielding applications. Various electrical conductive fillers such as graphene nanoplatelets, single-walled carbon nanotubes, multi-walled carbon nanotubes, vapor grown carbon nanofibers, carbon nanoparticles, metallic nanowires, metallic nanorods, metallic nanoparticles and nanostructures of intrinsically conductive polymers have been used in the studies of novel conductive polymer nanocomposites [2]. Among those aforestated fillers, multiwall carbon nanotubes (CNT) seem to be most intensively used nanomaterials for conductive applications due to its low cost, high aspect ratio, and excellent electrical properties [3].

Kim et al. (2004) reported the first study of multi-walled carbon nanotubes polymer nanocomposites as an EMI shield material, showing ~27 dB for 40.0 wt% MWCNT/PMMA composite [4]. Since then extensive research has been carried on those type of composites for EMI shielding applications. The EMI shielding properties depend on the distribution, dispersion and intrinsic properties of the conductive fillers in the composite materials. High CNT loading is required to attain desirable EMI shielding effectiveness, which in turn leads to increase in cost and weight of the

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materials, and deterioration of the mechanical properties. Therefore, achieving higher EMI shielding at low filler concentration for CNT/polymer nanocomposites is desirable. The filler network formation seems to be significant for the EMI shielding applications. From the literature, it is clear that the segregated structure helps in improved network formation, which enhances the EMI shielding properties. In the segregated structure of conductive polymer nanocomposites, the conductive fillers stays at the interface of the polymer domains, which helps in decreasing the filler concentration and increase in EMI shielding effectiveness by ordered filler distribution. Gelves et al. (2011) was the first to report about the miscible solvent mixing and precipitation (MSMP) method to achieve high EMI shielding at low filler loading; the authors had successfully obtained 26 and 42 dB for 10.0 and 13.0 wt% of copper nanowires/polystyrene nanocomposite respectively for 0.21 mm thick samples [5]. In another case, Yan et al. (2014) reported EMI SE of 28.3-32.4 dB for 0.66 Vol % of thermally reduced graphene oxide in polyethylene matrix for 2.5 mm thick sample [6].

EMI Shielding has three underlying mechanisms, such as reflection, absorption and multiple reflection [1]. Reflection of the EM radiation depends on the free mobile charges on the surface of the shield material; it is directly proportional to the conductivity of the material. Absorption depends on electric and magnetic dipoles in the shield material, while multiple reflection refers to reflection at various interfaces or surfaces of the shield (if the distance between the reflecting surfaces or interfaces is considerable when compared to the skin depth, then it can be neglected). Enhancement of attenuation through absorption would be achieved by incorporation of either high dielectric materials such as ZnO, $BaTiO_3$, MnO_2, $SrTiO_3$, etc., or high magnetic materials such as Ni, Fe, Fe_3O_4, etc., into the polymer matrix [7, 8]. However, using dielectric materials or magnetic materials as a single filler in the polymer matrix does not significantly improve the shielding effectiveness by absorption. For instance, Gong et al. (2008) reported 25 dB for 50 wt% Ni in resin-based matrix [9]. The electrical conductivity of CNT decreases in the core-shell structure approach due to the decoration of the secondary fillers using the chemical method. Hence combining dielectric/magnetic materials, as the secondary filler, along with a primary conductive filler such as CNT seems to be a promising approach to enhance EMI shielding effectiveness.

In this study, multiwall carbon nanotubes (CNT) were incorporated as primary conductive filler; zinc oxide nanowire (ZnONW) and nickel nanowire (NiNW) were used as a secondary filler because of their dielectric and magnetic properties, respectively. In addition to the large aspect ratio of ZnONW, its low production cost and strong absorption capacity of EM waves, ZnONW have attracted attention towards EMI shielding applications. Similarly, NiNW is both electrically conductive and ferromagnetic with high aspect ratio, which makes it a useful significant secondary magnetic filler for the hybrid system. The primary objective of this work is to study the effects adding different secondary nanofillers (dielectric or magnetic fillers) with similar geometry to primary conductive filler (CNT) in a segregated structure polymer nanocomposite. To best of our knowledge, until now, there is no study on the effect of addition ZnONW or NiNW to CNT polymer nanocomposites using segregated structure. The results of this study show that the fabricated hybrid nanocomposites are promising materials for high-performance EMI shielding, with superior shielding effectiveness, lower filler content, and thickness comparing to the materials reported in the literature.

METHODOLOGY

All the chemicals (ACS reagent) were purchased from the Sigma-Aldrich. ZnONW was synthesized via the hydrothermal method [10]. For the synthesis of nanowires, 0.4g of $ZnCl_2$ (zinc source) was dispersed into 90 mL of distilled water by constant stirring. Then 3.0 g of sodium dodecyl sulfonate (morphology controller agent) and 40.0 g of sodium bicarbonate (mineralizer) were added to the mixture and stirred vigorously for another 30 minutes. The mixture was transferred into a 100 mL Teflon-lined stainless steel autoclave, which was heated up to 140 ºC and maintained for 12 hours. Later, the autoclave was cool down to room temperature, and the obtained white precipitate was washed several times with hot distilled water followed by ethanol and then filtered. The white powder was dried in a vacuum oven at 60 ºC for 4 hours. NiNW was prepared by template-assisted synthesis. Porous aluminum oxide (PAO) template used in this method was made by two-step anodization method. Details about PAO template preparation can be found elsewhere [11]. The PAO templates were immersed in the electrodeposition solution for 5 minutes. The electrolyte solution was heated and maintained at 35 ºC; the solution consists of nickel (II) sulfate hexahydrate ($NiSO_4.6H_2O$, 300 gL^{-1}), boric acid (H_3BO_3, 40 gL^{-1}), and sodium dodecyl sulfate ($NaC_{12}H_{25}SO_4$, 8 mgL^{-1}). During the electrodeposition, the solution was stirred continuously using magnetic stirrer for active deposition of nickel ions. Two nickel foils were used as counter electrodes positioned at 2cm from both faces of the PAO; the electrodeposition was carried out by continuous 200 Hz sine wave AC of 20 V_{rms} for about 30 minutes. Then nanowires were liberated from the PAO template by immersing them in 1.0M NaOH solution for 10min. The liberated nanowires collected from the sodium hydroxide solution were washed with methanol several times to remove the base. The nanowires were filtered from the methanol solution using nylon membrane and dried in a vacuum oven at 60 ºC.

In this study, we employed MSMP technique to prepare the polymer nanocomposites. Polystyrene (PS, Styron 666D, M_w 200,000 g/mol) were generously provided by Dow Chemical Canada, and CNT with an average tube length of 1.5 µm and the diameter of 9.5 nm, purchased from the Nanocyl (MWCNT NC7000). Segregated nanocomposites with different concentration of single and dual fillers were prepared by MSMP approach. In this approach, the different volumes of ~0.64 mg/ml MWCNT/CH_3OH,~3.3 mg/ml NiNW/CH_3OH,~3.3 mg/ml ZnONW/CH_3OH were mixed with 20 mg/ml Polystyrene/CH_2Cl_2. Before mixing the nanofiller dispersion with the polymer solution, each solution was mixed and bath-sonicated. Later, the obtained precipitate was filtered and dried for 16 hours in the fume hood. This was followed by drying in the vacuum oven for 2 hours to remove the residual solvent. Then the dried nanocomposites were ground using a mortar and compressed into mold size of 22.86 x 10.16 x 1.1 mm^3 using Carver compression molder at 220 ºC, 35 MPa for 5 minutes.

We investigated the morphology of the nanowires and nanocomposites by transmission electron microscope (TEM) using Technai F20 (FEI, Hillsboro, Oregon, USA). For the TEM analysis, thin sections of approximately 70 nm of nanocomposites were ultramicrotomed using Leica EMUC7. X-ray analysis was performed using a Rigaku Ultima III X-ray diffractometer with Cu K-alpha radiation as the X-ray source, operating at 40 kV and 44 mA to obtain the full diffractogram for each analyzed material. The electrical conductivity of the nanocomposites was measured using Loresta GP resistivity meter (MCP-T610 model, Mitsubishi 48 Chemical Co., Japan) coupled to an ESP four-pin probe (MCP-TP08P model, Mitsubishi 48 Chemical Co., Japan). EMI shielding effectiveness (EMI SE) in the X-band frequency range was measured using S-parameters obtained from the E5071C network analyzer (ENA series 300 kHz to 20 GHz).

RESULTS AND DISCUSSION

A typical XRD spectrum of the as-synthesized ZnONW and NiNW are shown in Figure 1(a). All the characteristic diffraction peaks were assigned to wurtzite structure of ZnO and face center cubic nickel, respectively. XRD result indicates no impurities in the ZnONW, suggesting high purity of the ZnONWs. Figure 1(b) and 1(c) show the TEM images of synthesized nanowires. The image analysis indicated that ZnONW had an average length of 11.0µm and an average diameter of 80nm. This gives an aspect ratio of 137. Furthermore, statistical analysis of the TEM images of NiNW revealed that the average length and diameter were 1.4µm and 15nm, respectively (aspect ratio of 93). The electrical conductivity and EMI shielding performance of the polymer nanocomposites are influenced by the dispersion and distribution of the filler. To have a better insight into the dispersion state of fillers in the polymer matrix, dispersion states were investigated by TEM. Figure 1(d) to 1(i) illustrate the microstructure of prepared nanocomposites contacting 2.0vol% CNT (hybrid nanocomposites contain 0.5vol% secondary nanofiller). In all polymer nanocomposites, it is apparent that the fillers have a non-uniform distribution and form a segregated network. It has been demonstrated that such segregated structure constructs a dense conductive network which improves the electrical conductivity as well as the shielding effectiveness [5]. This observation also indicates that using MSMP is an effective approach on developing polymer nanocomposites with segregated structure.

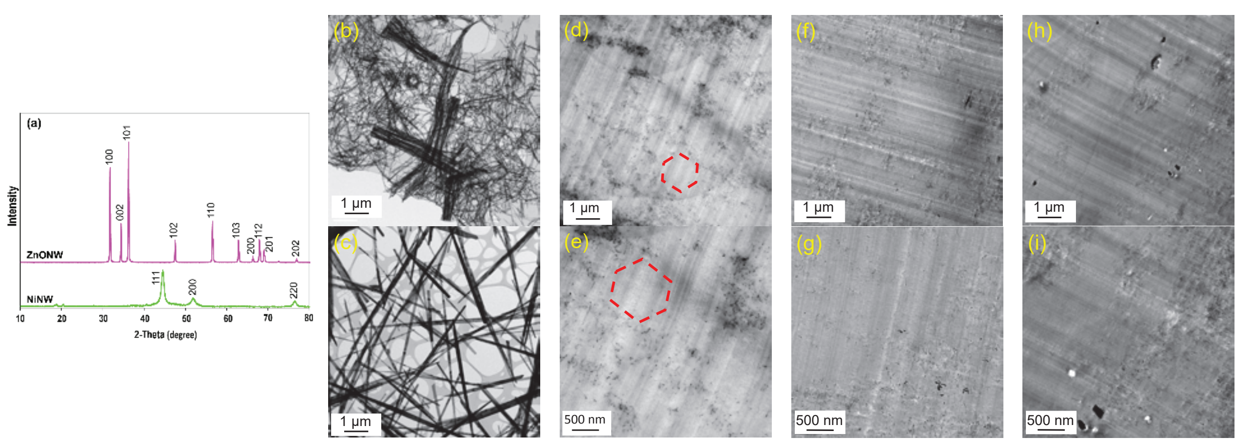

FIGURE 1. (a) XRD pattern of synthesized nanowires; TEM images of: (b) NiNW, (c) ZnONW, (d, e) PS/2.0vol% CNT nanocomposite, (f, g) PS/2.0vol% CNT/0.5vol% NiNW hybrid nanocomposite, and (h, i) PS/2.0vol% CNT/0.5vol% ZnONW hybrid nanocomposite at low (d, f, h) and high (e, g, i) magnification.

Major shielding mechanisms, absorption and reflection, are closely related to conductivity [12]. In the case of reflection, free charge carriers (electron or holes) interact with the electromagnetic wave leading to significant electromagnetic loss. On the other hand, the absorption mechanism originates from the interaction of electromagnetic wave with electric or magnetic dipoles [13]. So, the electrical conductivity of the prepared nanocomposites was studied. As seen in Figure 2(a), the electrical conductivity of PS nanocomposites increases with increasing the CNT content. Furthermore, the hybrid nanocomposites have higher electrical conductivity comparing to PS/CNT nanocomposites. For example, the electrical conductivity of PS/2.0vol% CNT is 26 S m^{-1}, while PS/2.0vol% CNT/ 0.5vol% NiNW reaches 56 S m^{-1}, which is close to the electrical conductivity of PS/3.0vol% CNT. The results indicate that the conductive properties of nanocomposites can be improved by fabrication of hybrid nanocomposites. The higher electrical conductivity of hybrid nanocomposites can be ascribed to stronger electrical network [5, 11, 14]. To investigate the effect of CNT/secondary filler ratio on the hybrid nanocomposite conductivity, different amount of ZnONW (or NiNW) were added to the nanocomposites. In this study, the best results are presented by taking the fillers content and EMI shielding performance into consideration.

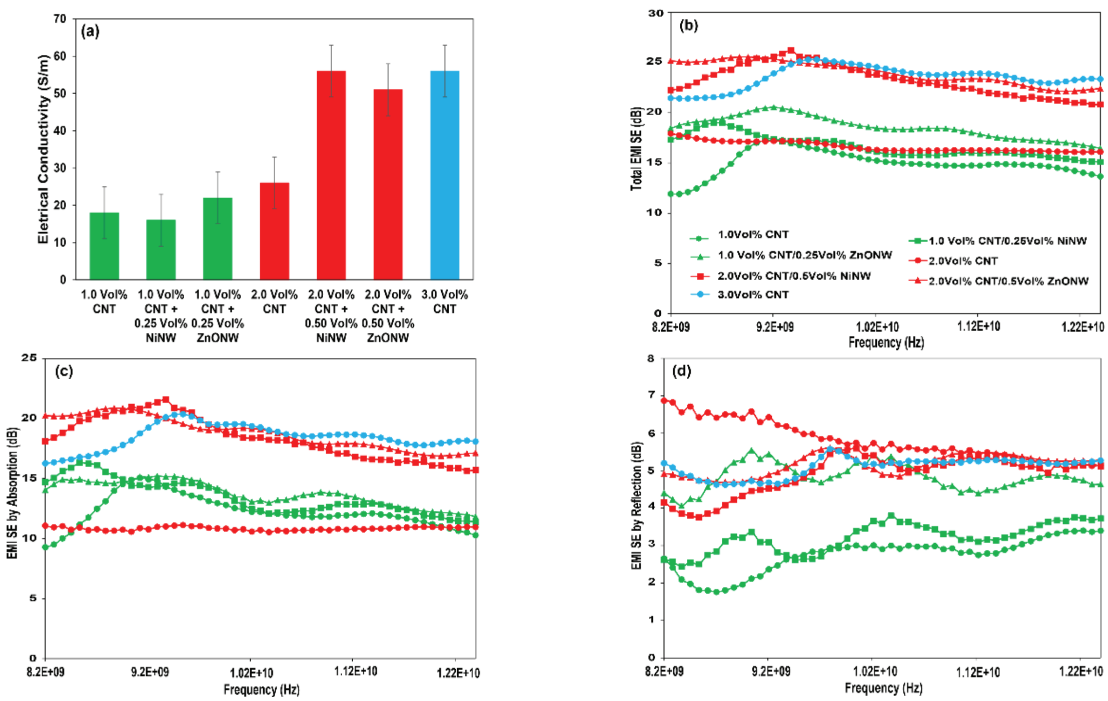

FIGURE 2. (a) Electrical conductivity of the prepared samples, (b, c, and d) total, absorption, and reflection shielding effectiveness of PS/CNT, PS/CNT/ZnONW, PS/CNT/NiNW hybrid nanocomposites. Figure 2(c) and 2(d) have the same legend as figure 2(b).

Figure 2(b-d) illustrate the EMI shielding effectiveness of the nanocomposites. As seen, hybrid nanocomposites show a higher EMI shielding comparing to PS/CNT nanocomposites. For example, the average total EMI shielding over the X-band frequency for PS/2.0vol% CNT/0.5vol% ZnONW is 24dB, while PS/2.0vol% CNT shows an average of 16.6dB. It points out that developing the hybrid structure with employing magnetic/dielectric secondary filler can be an effective approach to prepare high performance EMI shields with lower filler content. The increased EMI SE can be attributed to the increased conductivity of the hybrid nanocomposites. The higher concentration of CNT can result in a thicker conductive interface between PS multi-facets leading to stronger conductive network and interaction with incoming electromagnetic waves, improving the shielding effectiveness. On the other hand, dielectric properties of the nanocomposites is a significant parameter on shielding performance interpretation. To have a better insight on the shielding performance of studied polymer nanocomposites, dielectric (dielectric permittivity (ε') and imaginary permittivity (ε'') properties were investigated (Figure 3). The terms ε' and ε'' are associated with energy storage and dielectric loss, respectively. The latter is a consequence of energy dissipation resulting from conduction, resonance and relaxation mechanisms. Higher EMI shielding can be achieved with higher dielectric and imaginary permittivity. Increasing the amount of conductive filler leads to the formation of a greater amount of micro-capacitors in the polymer matrix, and a higher dielectric permittivity arose [14]. Interestingly, in case of hybrid nanocomposites, negative dielectric permittivity was found for hybrid nanocomposites containing 2.0vol% CNT at the higher frequency. The formation of a strong conductive network, the summation of an induced electrical field, and polarization electrical field which exceeds incident electric field can result to the appearance of negative permittivity [15]. This negative permittivity can be effectively used in attenuation of EMI. On the other hand, ZnONW and NiNW significantly enhanced ε'' compared to PS/CNT over the full range of X-band frequencies. Same trend was observed for shielding by absorption. This suggests that the developed hybrid nanocomposites attenuate the electromagnetic waves mainly through dielectric loss via absorption.

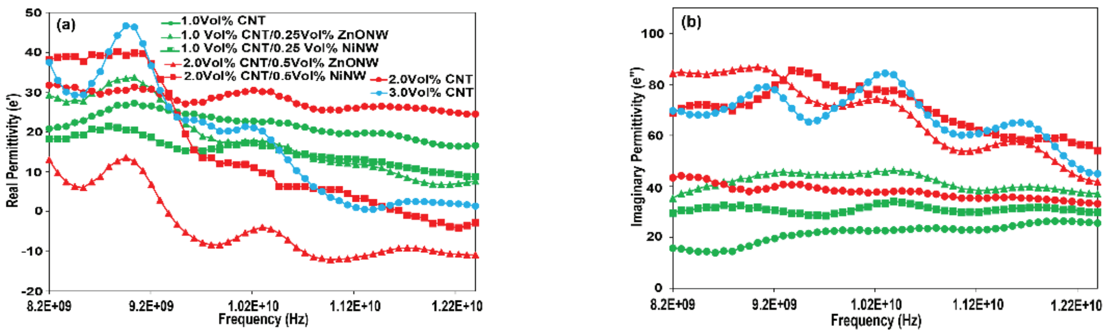

FIGURE 3. (a) Dielectric permittivity and (b) imaginary permittivity of PS/CNT nanocomposites and hybrid nanocomposites. Both figures have the same legend.

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