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The development and analysis of electrical and electromagnetic interference shielding effectiveness of titanium carbide (TiC)-coated carbon nanofiber (CNF) reinforced liquid crystalline polymer composites are presented. The studied samples consisted of different weight percentages (5, 10, and 15 wt %) of CNFs distributed and dispersed homogeneously within the polymeric matrix. A titanium carbide layer was deposited using pulsed laser deposition, and was conducted at room temperature, which eliminated possible thermal degradation of the polymer matrix. The effect of the thickness of the TiC layer on the electrical properties of the polymeric composites was analyzed. A synergistic behavior between the TiC coating and the polymer composite was observed for samples containing 10 wt % of NFs (within the percolation range), and the ability of the composite to shield electromagnetic interference was increased by 20–30 db. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3130397]

I. INTRODUCTION

Polymeric materials have started to replace metals and other materials in many applications given their advantages such as resistance to corrosion, ease of fabrication, lightweight, and low cost. With the discovery and production of fullerenes, carbon nanofibers (CNFs), carbon nanotubes, nanoparticles, and a variety of nanowires (lead, bismuth, and gallium-arsenide to mention some), numerous researchers turned their attention into the development and analysis of nanoreinforced polymer composites.[1–4] These nanosized reinforcements offer attractive properties that include superior electrical and thermal conductivity, enhanced strength, and low density. These properties can significantly alter the properties of the polymeric matrix such as kinetics of crystallization, optical absorbance, electromagnetic interference (EMI) shielding behavior, electrical, mechanical, thermal, and rheological properties.[5–7]

Conductors and their composites are suitable materials to shield EMI due to their high conductivity and dielectric constant.[8] Metals are excellent materials for EMI shielding, but offer several disadvantages such as, high weight, poor processibility and corrosive susceptibility. Metal coatings are therefore commonly used for shielding, but they still suffer wear and poor scratch resistance. Reinforced polymer composites could be the best alternative to replace metals. A great deal of research has been conducted on the use of polymeric composites for EMI shielding applications.[9,10] Das *et al.*[9] prepared carbon-black and carbon-fiber filled ethylene-vinyl acetate copolymer and natural rubber, and studied their potential applications for EMI shielding in both the microwave (100–2000 MHz) and *X*-band region (8–12 GHz). They reported that the composites with fiber loading ($\geq$20 phr) can be used for EMI shielding with shielding effectiveness (SE) of more than 20 dB. Similarly, Yonglai *et al.*[10] reported frequency independent SE for CNF-reinforced polystyrene composites. The SE increased with NF concentration. The study demonstrated that the loading of 20 wt % of NF resulted in a SE value of 30 dB.

This paper reports the electrical and EMI shielding results of NF-reinforced polymer composites with a deposited titanium carbide (TiC) film. TiC was chosen based on its excellent mechanical, thermal, and chemical stability.[11,12] This material is also used as a heat shield for atmospheric re-entry of the space shuttle. A thin film of TiC was deposited using modified pulsed laser deposition (PLD) process.[13] EMI SE of these TiC-coated composites were measured in the frequency range of 300 kHz to 1.3 GHz.

II. EXPEIMENTAL

A. Sample preparation

The vapor grown CNFs, Pyrograf-III™ (PR-24-AG), with diameters from 50 to 200 nm were supplied by Applied Sciences Inc. The thermotropic liquid crystalline polymer (LCP), Vectra® A950 was supplied by Ticona Inc.

To remove amorphous carbon and open up entangled nests, the NFs were purified following the procedure described by Lozano *et al.*[14] The NFs were refluxed in dichloromethane for five days, followed by filtration in de-ionized water and additional reflux in de-ionized water for 24 h. The NFs were then rinsed and vacuum filtered and dried in a vacuum oven at 110 °C for 48 h. After purification, disper-

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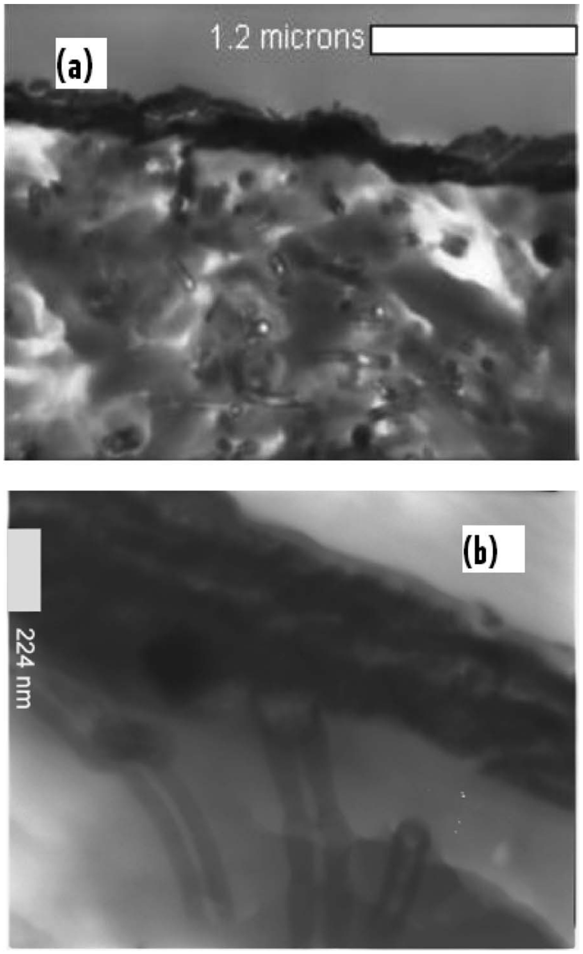

FIG. 1. (a) TEM micrograph of 15 wt % LCP-NF with a 300 nm TiC coating and (b) shows the composite TiC interface.

sion and distribution of NFs were obtained by following previously published procedures.[15,16] The polymeric matrix and the NFs were mixed in a Haake Rheomixer 600 miniaturized internal. Concentrations of 5, 10, and 15 wt % of NFs were prepared.

NFs were observed to be homogeneously dispersed in the matrix. Composites were pressed into squares of 3.81×3.81 cm^2 with thickness of about 1.3 mm. One side of the samples was coated with a thin film of TiC using a magnetic field PLD technique. A TiC target was ablated with an excimer laser (Lambda Physik 210 I) operating at 248 nm. Laser fluences of 14–16 J/cm^2 were typically employed. The depositions were carried out with the substrate at room temperature and at a base pressure of 1×10^{-8} torr. In order to eliminate particulates from being codeposited, a magnetic field was used to divert ions in the laser ablation plume to a nonline-of-sight substrate. Details of this technique have been described elsewhere.[13] For this study, two thicknesses were selected for the TiC films, namely, 300 ± 5 nm and 150 ± 5 nm. Figure 1(a) is a typical transmission electron microscopy (TEM) micrograph of 15 wt % NFs dispersed in LCP with a deposited TiC thin film. Figure 1(b) is a higher magnification TEM image that shows interfacial contact between the TiC thin film and the end of a NF.

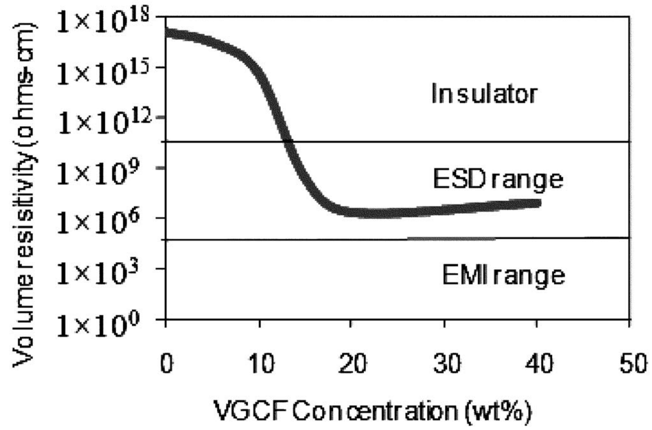

FIG. 2. Typical volume resistivity vs filler concentration curve observed in conductive filler reinforced polymer composites. Depending on the shape, size, and conductivity of the filler, the percolation shifts to lower concentrations and/or lower electrical resistivity.

B. Testing

1. Electrical testing

Polymers matrices reinforced with conductive fillers go through a percolation (formation of a filler network) process as observed in Fig. 2. This figure provides a representative curve for nanoreinforced composites and indicates the three traditional ranges for resistivity values, namely, insulator ($>10^{11}$ Ω cm), electrostatic discharge range (10^5–10^{11} Ω cm), and EMI range ($<10^5$ Ω cm). The percolation threshold is indicated with a dashed line, but can shift left or right, i.e., percolation can occur at lower or higher wt %, and can also shift to lower or higher resistivity values. Given this situation, two methods were used to obtain electrical resistivity: ASTM-257 and four-point probe. The ASTM-257 method focuses on the resistivity values of insulating materials, while the four-point probe covers resistivity values lower than 10^7 Ω cm.

For the ASTM measurements, a Monroe electronics model 272, resistivity meter was used to test the sample. The sample was inserted in the resistivity adapter with a conveniently dimensioned electrode configuration. This model provides guarded shielded electrodes making sample contact easier, and it accounts for the flatness of the sample. In the case of testing with the four-point probe, the sheet resistance (R_s) was measured on both sides of the samples (coated and noncoated) using a Jandel resistivity apparatus model RM2 incorporated with a hand-applied four-point cylindrical probe. The probe spacing of this apparatus is 1.016 mm and the probe radius is 100 μm. The probes were placed in different areas of the sample.

2. EMI SE testing

EMI SE of the samples was measured using a flanged coaxial tester connected to a Hewlett-Packard 8752C Network Analyzer. SE was measured in a frequency range of 300 kHz to 1.3 GHz. SE is defined by ASTM D4935-99 as the ratio of power transmitted with a material present (P_1)

TABLE I. Resistivity (Ω cm) of 150 nm thick pure LCP and LCP-NF composites

	Ref. sample (LCP)	5% NF in LCP	10% NF in LCP	15% NF in LCP
TiC-coated side	2.0×10^2	1.1×10^2	1.2×10^2	1.2×10^2
Noncoated side	2.6×10^{13}	7.8×10^{12}	4.0×10^{12}	1.0×10^2

and without the material present (P_2) for the same incident power. It is usually expressed in decibels and is given by the following equation:

$$SE = -10 \log \frac{P_1}{P_2}. \quad (1)$$

SE is defined as the ability of a material to block electromagnetic radiation. A SE of 40 dB, the targeted minimum in most applications, provides 99% attenuation of the electromagnetic radiation. In automotive and computer applications a SE of 30 dB is sufficient for 50% of their applications, and 40 dB would satisfy 95% of their needs.[17]

III. RESULTS AND DISCUSSION

A. Electrical testing results

The results of the measured resistivity of reference LCP and LCP-NF composites are presented in Table I. The measurements were taken both on the front side coated with TiC film (150 nm) and on back side, which is the uncoated side.

It was found that upon coating, the resistivity of the coated side of the composites remained unchanged from that of TiC. However, the resistivity of the uncoated side decreased significantly for 15 wt % NF loaded LCP relative to all the other samples and in fact it was nearly the same as measured on its coated side. The resulting decrease in resistance in the noncoated side of the composite at higher NFs loading is due to the formation of a NF conducting path (percolation effect).

The effect of the thickness of the TiC layer in the resistivity was also investigated. The resistivities of two samples with equal concentration of NFs but different TiC film thicknesses (150 and 300 nm) were analyzed. The conductivity did not improve with the increase in the film thickness (not shown). This result is consistent with previous results on the resistivity for a titanium film of thickness from 150 to 300 nm where negligible changes were observed above 150 nm.[18]

B. EMI SE results

There are three mechanisms for EMI attenuation: reflection, absorption, and multiple reflections.[19] Reflection requires the existence of mobile charge carriers which interact with the electromagnetic radiation. Absorption requires the presence of magnetic and/or electric dipoles that interacts with the electromagnetic fields. The last mechanism, multiple reflections, refers to the reflections at various surfaces or interfaces in the shield. If the mechanism of multiple reflections is ignored (as is usually the case for metals), the electromagnetic SE of materials is commonly obtained from Simon formalism[17]

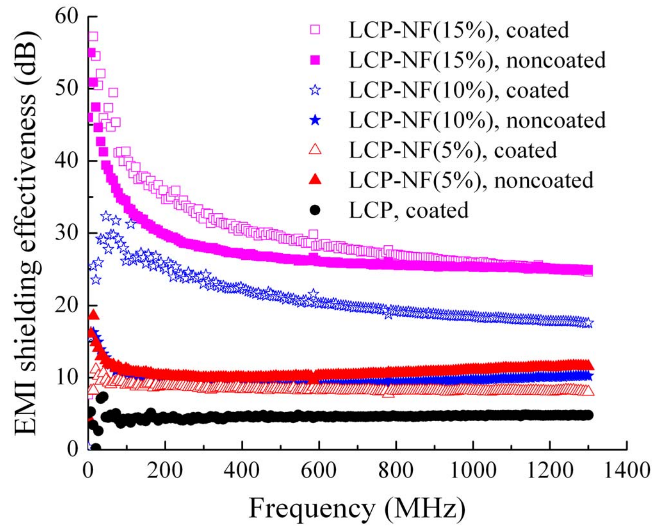

FIG. 3. (Color online) SE of LCP and its composites. Note: coated refer to TiC (150 nm) coating and all mixing are based on weight percentage.

$$SE = 50 + 10 \log_{10}(\rho f)^{-1} + 1.7t(f/\rho)^{1/2}, \quad (2)$$

where SE is expressed in decibels, ρ is the resistivity (Ω cm) at room temperature, t is the thickness of the sample (centimeter) and f is the frequency (megahertz).

Samples under this study, besides being coated with a TiC layer, are reinforced with nanosized fibers, considerably increasing the interfacial states due to larger surface area of NFs in contact with polymer. EMI shielding values from these samples should also include results from multiple reflection mechanisms. The SE of the LCP-CNF composites with and without the TiC coating as a function of frequency is presented in Fig. 3.

For the control sample (TiC-coated LCP), a small value in SE is observed (5 dB). This is mainly due to the contribution of the TiC thin film given the transparency (0 dB) of the polymer to EMI. Even though in the 5 wt % sample (coated and uncoated) the SE nearly doubled to 10–13 dB, it is still not enough to provide effective shielding. Increasing NFs loading to 10 wt % did not improve the shielding behavior of the uncoated sample. On the other hand, the TiC coating on this composite (10 wt %) provided a significant increase in shielding behavior reaching SE ~32 dB at low frequencies (75–100 MHz) and a gradual decrease in about 20 dB at 1300 MHz. Further increasing NFs concentration to 15 wt % increased SE to 55 dB at low frequencies and leveled off at 28 dB at higher frequencies. The decrease in SE with increasing frequency has been previously reported by Yang *et al.*[20] It is possible that the difference in the size of CNFs is also contributing to the SE frequency dependence.

The addition of TiC thin film in this composite showed some increase at frequencies of up to 800 MHz but did not change the shielding values significantly at frequencies greater than 1 GHz. These results demonstrate that the use of a TiC coating did not significantly improve the shielding behavior for composites containing 5 and 15 wt % of NFs.

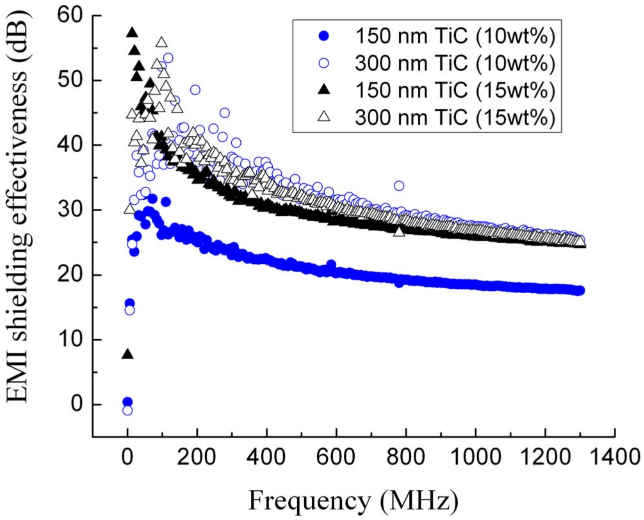

FIG. 4. (Color online) SE of composites with different TiC thicknesses.

From the resistivity measurements it can be determined that these samples are the two extreme cases in terms of percolation as previously observed. The composite containing 5 wt % of NFs is far below the percolation threshold (as in Fig. 2). However, the 15 wt % NFs composite has already reached percolation and the combination of low resistivity and increased interfaces promote higher values of SE. It is therefore consistent that in this case, the deposition of a TiC layer did not provide an additional shielding effect. The 10 wt % CNFs composite is at the percolation threshold. Hence, the deposition of the TiC film promotes a synergistic effect by facilitating the formation of a conducting path, as clearly observed in Fig. 1(b), where the NFs bridge into the TiC layer.

TiC thickness dependence of the SE was also analyzed. Figure 4 shows the resulting SE of 150 and 300 nm thick TiC for 10 and 15 wt % LCP-NF composites. In the case of the 15 wt % sample, a small increase is observed and expected as the second term in Eq. (2) is increased. However, in the case of the 10 wt % sample, a significant SE increase in 10–15 dB is observed for the 300 nm TiC-coated sample over the 150 nm TiC-coated sample.

The TiC thickness dependence behavior of the 10 wt % NF reinforced LCP composite and its overall SE increase is remarkable. As explained above, this composite is right at the threshold for percolation through the formation of a conductive network. The deposited TiC coating further facilitated the conducting path formation and enhanced the multiple reflection mechanism.

The obtained results definitively show the importance of considering multiple reflections contributions to the SE value. If multiple reflections are ignored, according to Eq. (2), the SE of the 10 wt % sample (at 1000 MHz) would be negative, transparent to EMI, while the SE of the 15 wt % sample would be 30 db which is basically the observed experimental value. Given that the 5 wt % and especially the 10 wt % sample showed high values of SE without an "appropriate" low resistivity value, it is concluded that the main contribution comes from multiple reflection mechanisms. Thus, it is imperative to consider these contributions in theoretical approaches given the growth in the field of nanoreinforced composites. These composites prove that high conductivity is not a required criteria for shielding of EMI.[21]

IV. CONCLUSION

This study showed a combination of materials where a synergistic effect considerably increased the SE of EMI. An extremely thin layer of TiC (150 or 300 nm) was deposited on a NF reinforced thermotropic LCP. The TiC layer prompted the formation of a conductive network. The sample containing 10 wt % (right below the percolation threshold) showed to be more susceptible to such formation as demonstrated by the significant increase in SE from 10 to 50 db (in the lower frequency range). The sample containing 15 wt % of NFs showed negligible increases when coated with TiC given that percolation was already achieved. The fact that the TiC layer increased the SE considerably at lower NF concentrations promotes the use of TiC for multifunctional purposes. TiC is hard and possesses superior wear properties. TiC-coated polymer composite devices could be used in adverse environments such as in high working temperatures as heat shields (i.e., critical application for the space shuttle). The opportunity to achieve SE at lower filler contents allows for preserving the resilience and toughness of the polymer (higher contents such as the 15 wt % in this study, significantly decrease strain values of the composite) such that the use of the polymer's inherent properties in various applications can be maximized. Because the deposited TiC layer is extremely thin (150–300 nm), the mechanical properties of the NF-reinforced composite are preserved; however, as observed, such thin TiC layers have a significant and valuable effect on the electrical properties of the composite.

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[1]K. Lozano, J. Bonilla-Rios, and E. V. Barrera, J. Appl. Polym. Sci. **80**, 1162 (2001).
[2]P. M. Ajayan, L. S. Schadler, C. Giannaris, and A. Rubio, Adv. Mater. (Weinheim, Ger.) **12**, 750 (2000).
[3]E. Kymakis, I. Alexandrou, and G. A. J. Amaratunga, Synth. Met. **127**, 59 (2002).
[4]P. Glatkowski, P. Mack, J. L. Conroy, J. W. Piche, and P. Winsor, U.S. Patent No. 6,265,466 (July 24, 2001).
[5]G. G. Tibbetts, M. L. Lake, K. L. Strong, and B. P. Rice, Comp. Sci. Tech. **67**, 1709 (2007).
[6]O. Breuer and U. Sundararaj, Polym. Compos. **25**, 630 (2004).
[7]Y. Yang, M. C. Gupta, K. L. Dudley, and R. W. Lawrence, J. Nanosci. Nanotechnol. **5**, 927 (2005).
[8]J. Joo and A. J. Epstein Appl, Appl. Phys. Lett.l **65**, 2278 (1994).
[9]N. C. Das, T. K. Chaki, D. Khastgir, and A. Chakraborty, J. Appl. Polym. Sci. **80**, 1601 (2001).
[10]Y. Yonglai, M. C. Gupta, K. L. Dudley, and R. W. Lawrence, J. Nanosci. Nanotechnol. **7**, 549 (2007).
[11]G. Radhakrishnan, R. E. Robertson, R. C. Cole, and P. M. Adams, Appl. Phys. A **77**, 175 (2003).
[12]S. Lee, S. Perry, S. Didziulis, P. Frantz, and G. Radhakrishnan, J. Vac. Sci. Technol. B **18**, 69 (2000).
[13]G. Radhakrishnan and P. M. Adams, Appl. Phys. A **69**, 33 (1999).

[14] K. Lozano, B. Files, F. Rodrigues-Macias, and E. V. Barrera, Proceedings of the Symposium on Powder Materials, Current Research, and Industrial Practices, Cincinnati, OH, 1999 (unpublished) pp. 333.
[15] K. Lozano and E. V. Barrera, J. Appl. Polym. Sci. **79**, 125 (2001).
[16] H. Vasquez, K. Lozano, R. V. Soto, and A. Rocha, Measurement **41**, 870 (2008).
[17] R. M. Simon Polym.-Plast. Technol. Eng. **17**, 1 (1981).
[18] E. Lee, N. Truong, B. Prater, and J. Kardokus, Semicond. Int. (2006).
[19] D. D. L. Chung, Carbon **39**, 279 (2001).
[20] S. Yang, L. Espinoza, H. Foltz, R. Jones, and K. Lozano, Composites, Part A **36**, 691 (2005).
[21] G. Lu, X. Li, and H. Jiang, Compos. Sci. Technol. **56**, 193 (1996).