Research Article

Studies on Nanocomposite Conducting Coatings

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Received 30 March 2013; Accepted 24 June 2013

Academic Editor: Masahiro Fukumoto

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Nanocomposite conducting coatings can impart stable surface electrical conductivity on the substrate. In this paper, carbon nanofiber (CNF) and nanographite (NG) are dispersed in thermoplastic polyurethane matrix and coated on the surface of glass and polyethylene terephthalate (PET) film. The nanoparticles dispersion was studied under TEM. The coating thicknesses were estimated. Further, their resistance and impedance were measured. It has been observed that the 5 wt% CNF dispersed nanocomposite coatings show good conductivity. The use of NG can bring down the amount of CNF; however, NG alone has failed to show significant improvement in conductivity. The nanocomposite coating on PET film using 2.5 wt% of both CNF and NG gives frequency-independent impedance which indicates conducting network formation by the nanoparticles. The study was carried out at different test distances on nanocomposite coated PET films to observe the linearity and continuity of the conducting network, and the result shows reasonable linearity in impedance over total test length (from 0.5 cm to 4.5 cm). The impedance of nanocomposite coatings on glass is not frequency independent and also not following linear increase path with distance. This indicates that the dispersion uniformity is not maintained in the coating solution when it was coated on glass.

1. Introduction

Conducting coatings are essentially required for conducting, sensing, and actuating purposes mostly in biomedical, defense, and printed electronics applications. Several classes of conducting coatings exist in the market such as metallic, ceramic, carbon, and electroactive polymers. Conducting coatings are also used for applications like static charge control, electromagnetic pollution control, electromagnetic interference shielding, and so forth, [1]. Among the electroactive and conducting polymers, except for polyaniline, other conducting polymers such as polypyrrole and polythiophene are insoluble in common solvent and thus offer less choice in processing. However, electrochemical deposition and vapor phase polymerization of organic conducting polymers have been carried out on almost all surfaces which give significant rise in conductivity and electroactivity [2, 3]. The limitations of conducting polymers and metal deposition can be overcome using nanocomposite coatings in this field. Nanocomposite coatings may be advantageous over a single metal or conducting polymer coating as this possesses several features

like durability, flexibility, and stability on environmental exposure. Suitable nanocomposite coating (e.g., conducting, gas barrier, microwave absorbent, superhydrophobic, etc.) on a polymer, glass, or any other substrate can impart various functional properties on the surface of the substrate [4].

The conducting nanofillers such as carbon nanotube show improvements in polymer conductivity and strain responsive property as they start to align or orient along stretch direction [5]. Nanocomposite film prepared by dispersing CNF in polypropylene shows significant improvement in conductivity after 5 wt% CNF addition [6]. CNF based nanocomposite coatings on fabric surface have also been reported to improve the conductivity [7].

Although the multistimuli responsive nanocomposite coatings are promising candidates for high-end products, an intensive research needs to be carried out to explore their potential. Nanocomposite coatings with conducting nanofillers are still not investigated in great detail. This work aims to study carbon nanofiber and nanographite based nanocomposite conducting coatings developed on PET and glass surface. The developed coatings are evaluated for their

FIGURE 1: TEM images of polymer dispersions: (a) CNF dispersed, (b) NG dispersed, and (c) both CNF and NG dispersed.

resistance and impedance to show the nature of conductivity. The performance of such coating is evaluated at various test distances to ensure the conducting network continuity.

2. Experimental

2.1. Materials and Methods. Nanographite (NG) was procured from M/s Kaiyu Inc., Hong Kong, having average platelet size of 200 nm. Carbon nanofiber (CNF) (commercial name: Pyrograf III) was purchased from Pyrograf Products Inc., USA, having diameter 60–150 nm and length 30–100 μm . Nanocomposite coating solutions were prepared using thermoplastic polyurethane (TPU) supplied by Bayer Inc., Germany (commercial name: Texin 945 U, ether type, extrusion grade).

The nanoparticles were taken into the solution as dry weight of TPU. The nanofillers, NG and CNF were dispersed in 80 : 20 ratio of $\text{N,N}'$ -dimethyl formamide (DMF) and acetone solvent mixtures through 30 min ultrasonic treatment (37 kHz) and 2 h mechanical stirring (500 rpm). Dried TPU chip taken as 10 wt% of the solvent (w/v) was dissolved in nanoparticles dispersion at 60°C by continuous stirring for

4 h to prepare the coating solutions. The solutions were coated on PET film (20 mm $\times$ 60 mm) and glass substrate (20 mm $\times$ 20 mm) and dried at 80°C for 4 h.

2.2. Characterization of Coatings. To investigate the dispersion of nanoparticles in TPU coating solutions, transmission electron microscope (model: JEM2100 from Jeol Inc., Japan) images were taken at 80 kV. The coating surfaces were observed in reflection mode of optical microscope (Axio Scope.A1 from Carl Zeiss, Germany). The coating thickness was measured using optical microscope LEICA DM750P from Leica Microsystems, Germany. The surface resistances of the nanocomposite coatings were tested in multimeter (model: GW Instek GDM8246 from Goodwill Inc., Taiwan), and surface impedances were measured in LCR meter (model: NB 9304 from Nvis Technologies, India).

3. Results and Discussion

3.1. Dispersion of Nanoparticles. The transmission electron microscope images of the nanocomposite films reveal reasonable good dispersion of nanoparticles in the polymer matrix

FIGURE 2: Coated PET films.

TABLE 1: Thickness of samples and coatings.

Sample	Thickness (μm)	Coating thickness (μm)
Uncoated glass	140 ± 0.3	
CNF coated glass	153 ± 1	13 ± 1
NG coated glass	150 ± 2	10 ± 2
Both CNF and NG coated glass	144 ± 0.3	4 ± 0.3
Uncoated PET film	93 ± 0.3	
CNF coated film	100 ± 1	7 ± 1
NG coated film	110 ± 2.5	17 ± 2.5
Both CNF and NG coated film	130 ± 3	37 ± 3

(Figure 1). Figure 1(a) indicates that CNF was dispersed in the polymer and form a good continuous conducting network which is also evident when both CNF and NG was used in combination (Figure 1(c)). However, only NG cannot form continuity in the matrix, dispersed as isolated islands in the matrix without any conducting bridge or connection between them (Figure 1(b)). As the polymer has very poor conductivity, the conducting nanofillers continuity in the matrix is essential to have significant reduction in coating resistance. In Figure 1(c), NG acts as connector between the CNF network and this also induce good conducting network in the nanocomposite.

3.2. Nature of Coating. The coated PET films are shown in Figure 2. The pure TPU coating is transparent, while the CNF, NG, and both dispersed nanocomposite coatings are nontransparent. Under reflection mode of phase contrast polarizing optical microscope, at high resolution, the surface shows some unevenness in pure TPU coating (Figure 3(a)), while the nanocomposite coatings show contrasting images (Figures 3(b) and 3(c)) that may be due to the nanofillers present in the matrix. The surface of the coating is visible under phase contrast microscope which contains both the filler as well as the matrix polymer; thus the contrast in surface image can be attributed to the nanofillers.

Table 1 describes the different coating thicknesses on glass and PET film substrate. Thickness of coatings was measured

using optical microscope. The uncoated and coated sample thicknesses were determined as shown in Figure 4 and then the respective coating thickness was calculated from that.

From Figure 4, it can be observed that coatings on both the glass and PET films are reasonably even, and the variation is less which is required for any inference on conductivity as the electrical properties are also dependant on thickness of coatings. Too thin coating may lead to nonuniformity as well as loss in continuation of conducting network.

3.3. Resistance and Impedance of Coatings. The conductivity of pure TPU is very poor (in the order of 10^{-8} S/m) [8]. So, this study concentrates only on coatings which offer a reasonable high conductance or low resistance (in kilo-ohm order). The 5 wt% NG dispersed nanocomposite coatings show high surface resistance (in Mega-ohm order) which usually gives high standard error, so it is not taken into consideration for network continuity understanding. Figure 5 shows the surface resistance of nanocomposite coatings on PET film. Nanocomposite coatings of 5 wt% CNF show less resistance as compared to 2.5 wt% of both CNF and NG. Both coatings show linearity in resistance increase with increase in test length; however, pure CNF shows better linearity. A linear increase in resistance indicates the reliability of the conducting coating system. For metal deposition, it is always a perfect linear. The linear increase denotes the uniformity in nanofiber network continuity in case of nanocomposite coatings. Thus, the conducting network seems to be uniform up to the distance of 4.5 cm.

The impedance study confirms the uniform network formation by the nanofillers in both nanocomposite coatings (Figure 6). At three different frequencies, the impedance of the nanocomposite coatings lays one above another which indicates the frequency-independent behavior. Both coatings show this behavior. Frequency dependence comes from the complex component of the material, that is, the inductance and capacitance. The real component of the impedance is the resistance which is not dependant on frequency. The two coatings are mostly resistive in nature, which confirms the formation of pure conducting network in the dielectric polymer matrix. The linearity of the curves with increase in test length is also noticeable for confirmation of uniformity in network formation. However, the resistance of the system using NG and CNF is higher than that of the pure CNF based system. As CNF is the key for network continuity due to its very high aspect ratio, higher CNF content lowers down the resistance significantly, while a mixed system of CNF and NG cannot offer such robust network. Again, higher slope of resistance and impedance of mixed nanofillers based coating in Figures 5 and 6 indicates comparatively less stable network over long distance.

However, results on the glass substrate are not as promising as on PET film. Figure 7 describes the impedance of nanocomposite coatings at different frequencies and at different test lengths. In case of 5 wt% CNF dispersed nanocomposite coating, the impedance value increases somewhat linearly with increase in test length (Figure 7(a)), but it is frequency dependant in nature. Again, the impedance shows severe

FIGURE 3: Optical microscope reflection mode phase contrast; top surface images of (a) pure TPU coating, (b) 5 wt% CNF dispersed coating, and (c) 2.5 wt% both CNF and NG dispersed coating.

FIGURE 4: Side view (cross-sectional view) of (a) uncoated glass, (b) 5 wt% CNF nanocomposite coated glass, (c) 2.5 wt% of both CNF and NG nanocomposite coated glass, (d) uncoated PET film, (e) 5 wt% CNF nanocomposite coated PET film, and (f) 2.5 wt% of both CNF and NG nanocomposite coated PET film.

FIGURE 5: Resistance of nanocomposite coatings on PET film over different distances: (a) 5 wt% CNF dispersed; (b) 2.5 wt% of both CNF and NG dispersed.

FIGURE 6: Impedance of nanocomposite coating on PET film at different frequencies and over a distance: (a) 5 wt% CNF dispersed; (b) 2.5 wt% of both CNF and NG dispersed.

instability in Figure 7(b). This may also be due to very low coating thickness in case of both CNF and NG coated glass ($4 \pm 0.3 \mu\text{m}$). But, in both cases, these curves indicate that the nanofillers network formation and their uniformities are not as good as in case of PET film coating. So, there is a substrate dependency on the nanocomposite coatings which may be attributed to the compatibility of the substrate with the coating polymer. This needs to be investigated further to achieve a linear performance of nanocomposite coatings on glass substrate over length.

(a)

(b)

FIGURE 7: Impedance of nanocomposite coating on glass at different frequencies and over a distance: (a) 5 wt% CNF dispersed; (b) 2.5 wt% of both CNF and NG dispersed.

4. Conclusion

The nanocomposite coating on PET film based on 5 wt% CNF shows uniform conducting network over a continuous length as it shows frequency-independent impedance and linear increase in resistance with increasing test length. It has been demonstrated that the use of NG can bring down the CNF content, and a combined use of these nanofillers in coating solution can also serve the purpose of good conductivity. However, the resistance of the coating is higher than that of

pure CNF based coating. Again, only NG based nanocomposite coatings are not successful because of the lack of continuity in conducting nanofillers. Though coating on glass surface should be investigated further, the nanocomposite coating on PET film can be used for various conductivity responsive applications. These conducting nanocomposite coatings can successfully be utilized in different application areas.

Conflict of Interests

None of the authors have a conflict of interests including direct or indirect financial relations with any of the trademarks and companies mentioned in this paper.

Acknowledgments

This work is a part of a project sanctioned under fast track scheme of Department of Science and Technology (DST), Government of India. The authors like to express their deep gratitude to DST and the management of PSG Institutions for their financial and other shapes of support to carry out this work.

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