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Thin-Film Layering of Conductive Polymer Composite 2-wt% Multiwalled Carbon Nanotube (MWCNT)/Poly (3,4-ethylenedioxythiophene):Poly (Styrenesulfonic Acid) (PEDOT:PSS) for Electromagnetic Interference Shielding

by Eugene Zakar, Theodore Anthony, and Madan Dubey

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14. ABSTRACT We investigated the cumulative effects of layering a thin film of conductive polymer composite 2-wt% multiwall carbon nanotube filler in poly (3,4-ethylenedioxythiophene):poly (styrenesulfonic acid) on a transparent and flexible Mylar substrate for application to electromagnetic interference (EMI) shielding. The optical transmittance of spin-coated composite layers is 90%, 45%, and 20% with a thickness of 0.05, 0.15, and 0.45 μm, respectively. However, when the same composition of composite formula is drop casted, the film thickness increases tenfold and the optical transmittance drops to 0%. This study also shows that the cumulative effects of composite layering are additive, but the electrical properties do not scale the same way. A significant increase in the EMI shielding effectiveness in the Ku-band is mainly attributed to the enhanced electrical conductivity of the composite layering.					
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1. Introduction

Electromagnetic interference (EMI) has emerged as a major concern in the development of electronic, optoelectronic, and wearable devices because of the increasing use of high frequencies and broad bandwidths. Although all electronics emit magnetic and electrical energy, if this energy unintentionally interacts with another device and causes it to malfunction, then it is considered interference.

The recent development of nano-carbon-decorated composites provides a revolutionary approach to the mitigation of high EMI radiation owing to its superior conductivity, flexibility, and corrosion resistance characteristics in harsh environments compared to traditional metallic Faraday cages and structures.¹ Poly (3,4-ethylenedioxythiophene):poly (styrenesulfonic acid) (PEDOT:PSS) is a water-based conductive polymer that enhances the dispersion of nano-carbon-based materials²⁻⁶ and makes very thin films possible. The combination of conductive polymers with multiwall carbon nanotubes (MWCNTs) has become an attractive material for EMI shielding applications recently.⁷

Removal of solvents in the polymers by evaporation and in improving the structural integrity of printed layers without delamination or distortion upon drying⁸ are a great concern during processing. Isopropyl alcohol (IPA) is a common solvent that has a low boiling point (92.5 °C) compared to other dopants like glycerol (290 °C) or DMSO (189 °C) and has the potential to speed up the drying of composite layers during additive manufacturing. However, the effects of multilayering MWCNT/polymer composites and mixing IPA on the shielding properties have not been measured. In this study, we examine and correlate the electrical conductivity, which has a major effect on EMI shielding,⁹ and optical properties of the composites during additive layering, as well as determine the effects of the IPA mixtures to better optimize the performance of the EMI shielding.

We prepared a solution of 2-wt% MWCNT in PEDOT:PSS for layering using the spin-coating method and drop-casting method on Mylar substrates. We investigate the effects of IPA and drying time of the composite with substrate heating, determine its optical properties, and correlate the electrical resistivity with measured EMI shielding effectiveness (SE) values.

2. Experimental Details

2.1 Substrate and Solution Preparation

A 50- μm -thick Mylar substrate was used for this study due to its mechanical flexibility, optically transparency, and most importantly its insensitivity to EM waves in the Ku-band being tested. The Mylar surface does not easily wet, making it difficult for any film adhesion and requiring additional preparation steps to convert it to a hydrophilic surface by soaking in acid or treating in oxygen plasma, which can be cumbersome and time consuming. We instead used an alternative approach of coating the substrate with a glue layer of polymethyl methacrylate (PMMA) (NANO 950 PMMA A4, Micro Chem), which is simpler to apply and provides good reproducibility. Spin-coating PMMA at 3000 rpm for 30 s followed by hot plate soaking at 95 °C for 60 s in air produces a film of 1 μm .

Filler material, 0.2 g of MWCNTs (Cheap Tubes), was added to a 5-mL PEDOT:PSS solution (1.3 wt% in water, conductive grade; Sigma Aldrich). We compared this to a mixture of 0.2-g MWCNT in a PEDOT:PSS solution with IPA (PEDOT:PSS 5 mL + IPA 5 mL). The difference in the second solution is the addition of the IPA for faster evaporation and drying time of the composite film. The composite solutions were mixed using a high shear speed mixer (PRO250 Scientific) at 800 and 2000 rpm each for 5 min, followed by ultrasonic bath (Branson 2510) for 6 h. Spin coating of the layers was performed at room temperature, but for drop casting the substrates were heated with aid of a hot plate.

2.2 Characterization Methods

Electrical resistance was measured using a Keithley 2400 source meter and the electrical conductivity using an automatic four-point probe system (4-Dimensions Inc.). The thickness of both the spin-coat and cast composite layer(s) was determined by a step height method using a surface profiler (KLA-Tencor P-15). In this method, a masking tape (3M brand) is first applied to the surface of the substrate, followed by coating of the composite, then lift-off of the tape, consequently leaving a physical step height of the composite layer(s) for the surface profiler to scan across for the thickness measurement. The optical properties in the UV-visible (vis) spectra (500–800 nm) was measured by NanoSpec (Nanometrics). The EMI SE was measure using the wave-guide method, with the help of a two-port programmable vector network analyzer (Agilent N5242A) in the frequency range of 12–18 GHz (Ku-band). The bandwidth of the WR-62 waveguide adapter used in this study is determined by the longest side of the rectangular cavity cross section, 0.3 \times 0.6 inches. The composite

samples were cut slightly larger than these dimensions, and the thickness of the film samples varied depending on the number of layers.

3. Results and Discussion

Attenuation is one of the principal indicators for measuring the effectiveness of EMI shielding. It refers to the difference between an electromagnetic signal's intensity before shielding and its intensity after shielding. The EMI SE is a measurement of a material's ability to block electromagnetic waves. Experimentally, EMI SE is measured in decibels and defined as the logarithmic ratio of incident power (P_I) to transmitted power (P_T), as shown in Eq. 1.

$$SE = 10 \log (P_I/P_T) = 20 \log (E_I/E_T), \quad (1)$$

where $P_I(E_I)$ and $P_T(E_T)$ are the power (electric field) of incident and transmitted EM waves, respectively.

3.1 Spin-Coat Shielding

Spin coating the composite solution with IPA produces extremely thin films of $0.05 \mu\text{m}$ ($1\times$ spin coat), $0.15 \mu\text{m}$ ($3\times$ spin coat), and $0.45 \mu\text{m}$ ($9\times$ spin coat) with a measured optical transmittance of 75%–90%, 35%–45%, and 10%–20%, respectively, as shown in Fig. 1. The spin-coated composite layers dry immediately during the spinning cycle and adhere uniformly to the substrate. On non-IPA solutions, the composite layers are nonuniform across the substrate. The transmittance decreases with increasing number of passes and thickness of the composites. From these results, we can anticipate a film beyond $9\times$ passes becomes opaque with the same solution composition. The spin-coat method offers a wide latitude in UV-vis spectra depending on the number of spin coatings. In comparison, a fixed film thickness of $70 \mu\text{m}$ prepared by the spreading blade technique with 0.5 to 3 wt% MWCNT/PDMS composite has a narrow transmittance of 40%–50%.¹⁰

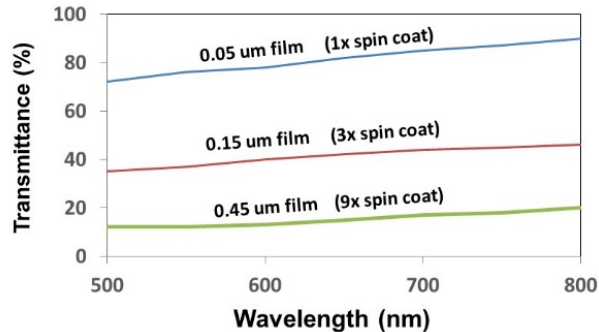


Fig. 1 Transmittance (%) of UV-vis spectra for composite film using the spin-coat method

All the spin-coated films have very high measured film resistance values in the kilohms range and not surprisingly produce very low EMI SE values, below the single digits range (not shown).

3.2 Drop-Cast Coat Shielding

When switching from spin-coating method to the drop-casting method, the same composition solution produces a tenfold increase in composite film thickness but at the cost of increased drying time to 24 h, which is impractical for most additive manufacturing. The addition of IPA to the composite solution cuts down the drying time to below 60 min according to our plot in Fig. 2. The drying time is accelerated when the substrate temperature reaches a critical point of approximately 40 °C. Above this critical temperature, our composite films become less reproducible in terms of uniformity and conductivity. As the substrate temperature increases nearer to the boiling point of IPA (89 °C), the deposited solution dries faster and the volume shrinks at a more rapid rate. Due to these early results, we prepared all our composite layers with IPA at a substrate temperature of 40 °C.

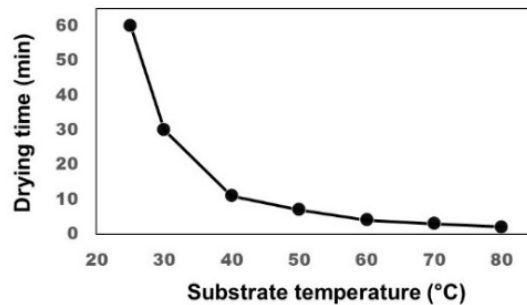


Fig. 2 Drying time for the composite layers decrease with increasing substrate temperature during the drop casting

A drop-cast solution with IPA produces a film of 4.4 μm with an electrical conductivity of 12 ± 1 S/m and EMI SE of approximately 14 dB, as shown in Fig. 3. Interestingly, when we removed the IPA, there was a substantial decrease in the conductivity to 8 ± 1 S/m and the EMI SE to approximately 5 dB. It appears that an IPA solution yields a three-times improvement in EMI SE of the same thickness, due in part to the higher conductivity. The 4.4- μm composite film appears opaque to the naked eye, and the measured optical transmittance is 0% in the UV-vis spectra, 500–800 nm (not shown).

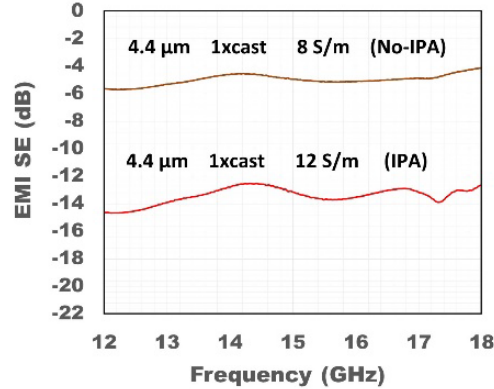


Fig. 3 EMI SE comparison of the 4.4-μm composites (IPA vs. no IPA)

The improvement in electrical conductivity with the addition of IPA to the composite is consistent with observation of other similar works. The PEDOT:PSS binder alone is central to many composites and has been a subject of intense investigations. Wei et al., for example, heated their substrate to 80 °C (close to the boiling point of IPA) but with the addition of a high-boiling-point solvent ethylene glycol (EG).⁸ The combined action of IPA and EG was found to result in a structurally stable transition between each layer. After printing the layers, the interdigital electrodes were further annealed to remove the residuary solvents at 120 °C overnight using a vacuum oven. In another work, spin coating of a PEDOT/PSS in water solution resulted in a decrease of conductivity, while solutions prepared from IPA showed an incremental increase of the conductivity from 1:0.5 to 1:1 dilution.¹¹ Others showed continued improvements in the conductivity with increase in IPA-dilution ratio from 1:6 to 1:18 as well as benefits in homogeneity of the films.¹² Alternatively, methanol has shown superior conductivity enhancements compared to IPA or ethanol.¹³

When we drop cast 4× layers, the total thickness increases to 15 μm, the conductivity increases to 18±1 S/m and the EMI SE improves to approximately 15 dB, as shown in Fig. 4. It is evident from Fig. 4 that the SE increases with the thickness of the sample. The increase in total thickness appears to scale linearly with the additive layer increments, but the total electrical EMI SE for 4× layers is less than the total additive effect of each EMI SE layer increment. A significant increase in the EMI SE is attributed to the enhanced electrical conductivity of the composite. Zhang et al. reported a similar observation when introducing a coating of pristine graphene layer(s) into a carbon fiber composite structure and showed an improved EMI SE in the Ku-band due to the contribution of the superior electrically conductive graphene layer.¹⁴

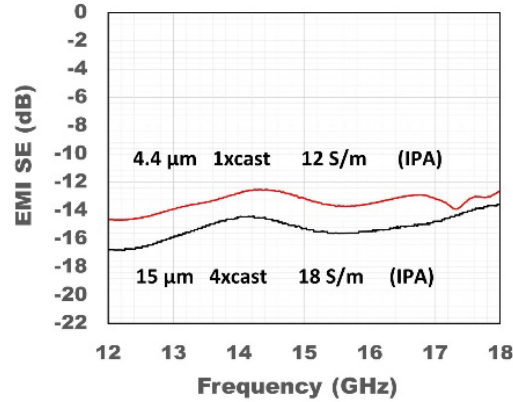


Fig. 4 EMI SE comparison of the 4.4- and 15- μm composites (both IPA)

A good wetting means that the solution is capable of spreading over and maintaining contact with the Mylar surface continuously.¹⁴ Typically, metals with high surface energies such as copper are easy to wet, while plastics and our Mylar substrate with a low surface energy are difficult to wet. When the PMMA glue layer was intentionally left off during our Mylar substrate preparation step for the same composite film (15 μm , 4 \times layers), the EMI SE drops by half its value from approximately 15 dB down to 8 dB, as shown in Fig. 5. This confirms that without a good glue layer, a poor wetting surface leads to a film with lower conductivity of 11 ± 1 S/m.

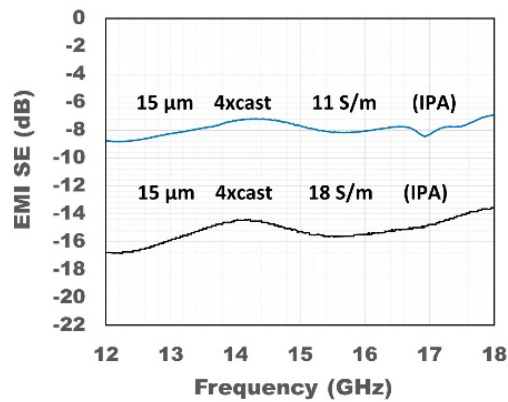


Fig. 5 EMI SE comparison of two stacked 15- μm composites (with and without a glue layer)

Enhanced peaks and dips in the EMI SE have been reported by others for polymers having gaps in between the conducting layers due to reflection losses,¹⁵ and the position and intensity of the peaks are sensitive to the thickness. To experimentally determine the effects of a gap, we conveniently stacked one sample on top of another from Fig. 5. The thickness of the Mylar was used to simulated a 50- μm gap between the two conducting composite layers. The measured results were the same

no matter on the staking order of the samples because the gap from the substrates are constant. The overall EMI SE improves to approximately 17 dB, but the advantage of a 50- μm gap is that it accentuates the EMI SE to a peak value of 21 dB at a narrow band near 17 GHz, as shown in Fig. 6.

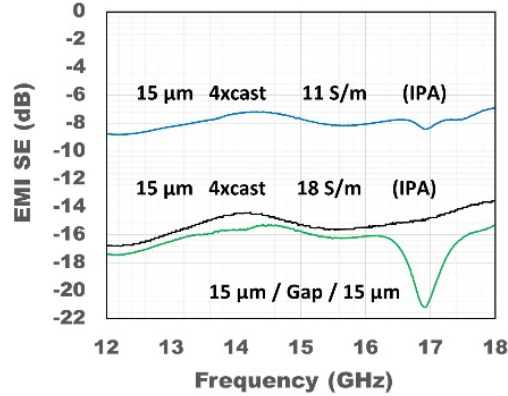


Fig. 6 EMI SE of two stacked 15- μm composites separated by a 50- μm Mylar gap

4. Conclusions

Spin-coated composite films composed of 2-wt% MWCNT/PEDOT:PSS on Mylar substrates have a variation of optical transmittance in the UV-vis spectra from high (90%) to low (20%) with a film thickness of 0.05 and 0.45 μm , respectively. Drop-cast composite films, on the other hand, have a greater starting thickness of 4.4 μm and a 0% optical transmittance. The EMI SE increases with the thickness of the sample. This study shows that the cumulative effects of composite layering are additive, but the EMI SE does not scale in the same way. A significant increase in the EMI SE is mainly attributed to the enhanced electrical conductivity of the composite. We demonstrated a 50- μm gap in between the two composite layers significantly accentuates the shielding properties of our composite to a peak value of 21 dB in the Ku-band.

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List of Symbols, Abbreviations, and Acronyms

CVD	chemical vapor deposition
dB	decibel
DMSO	dimethyl sulfoxide
EG	ethylene glycol
EMI	electromagnetic interference
GHz	gigahertz
IPA	isopropyl alcohol
MWCNT	multiwalled carbon nanotube
PDMS	polydimethylsiloxane
PEDOT:PSS	poly (3,4-ethylenedioxythiophene): poly (styrenesulfonic acid)
PMMA	polymethyl methacrylate
SE	shielding effectiveness

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