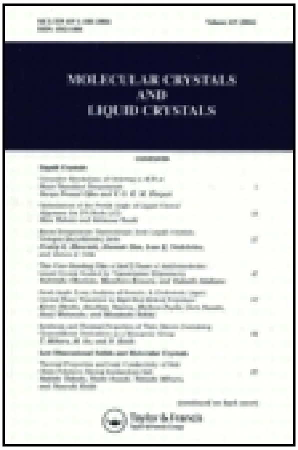

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Pet Fabric/Poly(3,4-Ethylenedioxythiophene) Composite with High Electrical Conductivity for EMI Shielding

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Highly electrically conducting fabrics were prepared by chemical polymerization of poly(3,4-ethylenedioxythiophene) (PEDOT) on a PET fabric. Monomer solution was prepared by dissolving EDOT and poly(vinyl pyrrolidone) (PVP) as a binder in 1-butanol. The oxidant solution was prepared by dissolving ferric p-toluene sulfonate (FTS) in 1-butanol. The mixture of the monomer and oxidant solutions was applied to PET fabric and polymerization was carried out under various conditions. We studied the effect of the chemical polymerization conditions on the properties of resulting composites such as electrical conductivity and surface morphology, environmental stability, electromagnetic interference shielding effectiveness (EMI SE). The specific volume resistivity, specific surface resistivity and EMI SE of the resulting composite were extremely low as 0.15 Ω·cm, 10 Ω/□ and quite high as 18 dB, respectively.

Keywords: electrically conducting fabric; electromagnetic interference shielding; PET fabric; poly(3,4-ethylenedioxythiophene)

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1. INTRODUCTION

Electromagnetic interference shielding effectiveness (EMI SE) of a material is the sum of shielding effectiveness (SE) resulting from the reflection, absorption and multiple reflection shielding mechanisms. EMI shielding by absorption rather than reflection is more important for many applications at the present time [1–3]. Traditional approach for EMI shielding relies on the use of metallic materials. Metals or materials coated with metals possess very high EMI SE ranging from 40 to 100 dB. However, they cannot be used as electromagnetic waves absorbent since their shallow skin depth makes them shield EMI mainly through the surface reflection. On the other hand, electrically conducting polymers are capable of not only reflecting but also absorbing the electromagnetic wave, exhibiting a significant advantage over the metallic shielding materials.

Poly(3,4-ethylendioxythiophene) (PEDOT) is the first example of a new class of polythiophenes with very high stability in oxidized states and a low band-gap [4,5]. Coating of PEDOT on the textiles may give rise to the electrically conducting textiles useful for many applications since the PEDOT-coated textiles may have not only excellent physical properties of the textiles such as mechanical strength and flexibility but also electrical and microwave properties of PEDOT. Textiles coated with PEDOT may have potential applications for static charge dissipation, EMI shielding as coatings or jackets of flexible conductors, broadband microwave absorbent.

In this study, we report a method to achieve PEDOT/PET fabric composite with extraordinarily high electrical conductivity and practically useful EMI SE. We studied the effects of the chemical polymerization conditions on the properties of resulting composites such as electrical conductivity, surface morphology, thermal stability and EMI SE. Effect of the composite conductivity on the relative shielding efficiency by absorption and reflection was also investigated.

2. EXPERIMENTAL

PET fabric/PEDOT composites were prepared by chemical polymerization of PEDOT on a PET fabric. PEDOT was coated on the PET fabric by applying the mixed solution of monomer and oxidant solution to the fabric, followed by polymerization of PEDOT on the surface of PET fiber. We changed various polymerization conditions such as concentrations of monomer, additive and oxidant solutions and the kind of additives.

EDOT (Bayer) was dissolved in 1-butanol containing 30 wt% poly (vinyl pyrrolidone) (PVP), (Aldrich, $Mw = 360{,}000\,g/mol$) to EDOT monomer as a binder. To investigate effect of reducing agent on the properties of the resulting PEDOT, monomer solutions were also prepared with 1-methyl-2-pyrrolidone (NMP) (Aldrich) or dimethylacetamide (DMAc) (Aldrich). Ferric p-toluene sulfonate (FTS) oxidant solution in 1-butanol was purchased from Bayer. Immediately after the monomer and the oxidant (mole ratio = 1:1.5) solutions were mixed, certain amount of the mixture solution was applied to the PET fabric. The fabric was placed at a desired polymerization temperature (70°C) for a certain time, resulting in polymerization of PEDOT on the surface of PET fiber. The fabric was washed with methanol and acetone and dried in an oven at 70°C for 1 hour. Chemical polymerization was repeatedly performed for desired times to obtain an electrical conductivity for a high EMI SE with desired absorption to reflection ratio.

PEDOT content in the composite was determined as the ratio of the weight of PEDOT in the composite to that of the pristine fabric. Specific surface resistivity ($\Omega/\square$) of PET fabric/PEDOT composite was measured by a two-probe method. Surface resistivity was obtained by measuring the resistance between two Pt wire electrodes pressed on the surface of the composite, where the distance between the electrodes and the length of the electrodes were 1 cm. Specific volume resistivity (ρ Ω-cm)of the composite specimen was obtained from the measured resistance (R) between two ends of the specimen using following Eq. (1):

$$\rho = R\frac{A}{l} \tag{1}$$

where A and l are the cross-sectional area of the end of the specimen and the distance between two ends, respectively.

Surface morphologies of the composites prepared by various conditions were observed by scanning electron microscopy (SEM, Hitachi). We examined thermal stability of the composite by monitoring the change of the specific volume resistivity upon isothermal heating at 70°C and 150°C in atmospheric condition.

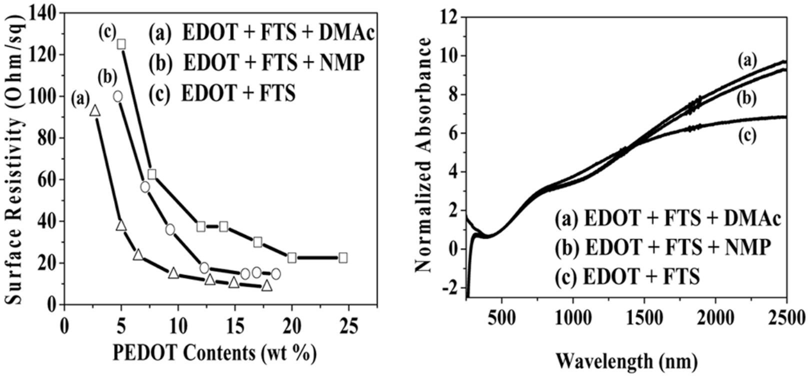
EMI SE was obtained by following ASTM D 4935–89 using a vector network analyzer (HP 8719 ES) equipped with an amplifier and a scattering parameter (S-parameter) test set over a frequency range of 50 MHz–13.5 GHz [6].

3. RESULTS AND DISCUSSION

PEDOT film was polymerized on glass substrate for various polymerization times from 5 to 60 minutes in order to optimize the polymerization time. In most polymerization conditions at 70°C, it was observed that the electrical conductivity of PEDOT increased with the polymerization time up to 20 minutes, but after 20 minutes the conductivity increased a little. We also monitored the change of the electrical conductivity of the composite with the polymerization time at 70°C, confirming that 20 minutes was long enough to produce the saturated conductivity. We, therefore, carried out the chemical polymerization for 20 minutes in most experiments.

PEDOT content and electrical conductivity of the composite increased with the number of polymerization as shown in Figures 1 and 2, irrespective of the preparation condition. PEDOT content in the composite kept increasing with the number of polymerization, while the surface resistivity decreased very steeply during the early stages of the polymerization, after which it decreased a little. We consider PEDOT coated on the fabric during the later stages cannot contribute to increase the conductivity of the composite, possibly because a conduction path of the composite was already saturated by PEDOT coated during the early stages.

Figure 1(a) displays the changes of PEDOT contents and surface resistivities of the composites prepared without and with DMAc or NMP as a function of the number of chemical polymerization. The composite prepared with DMAc or NMP exhibited steeper decrease in surface resistivity even at lower PEDOT content than the composite prepared without any additive as shown in Figure 1(a). We believe



(a) (b)

FIGURE 1 (a) Changes of PEDOT contents and surface resistivity of the composite prepared without and with NMP or DMAc (40 wt% to EDOT) as a function of the number of chemical polymerization and (b) UV-Vis-NIR spectra of the composites.

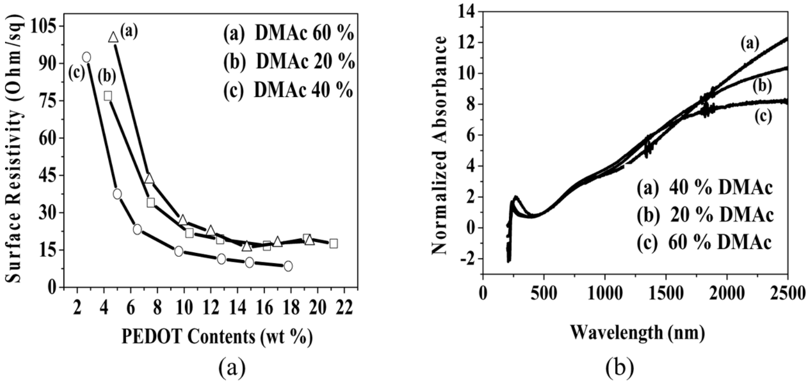


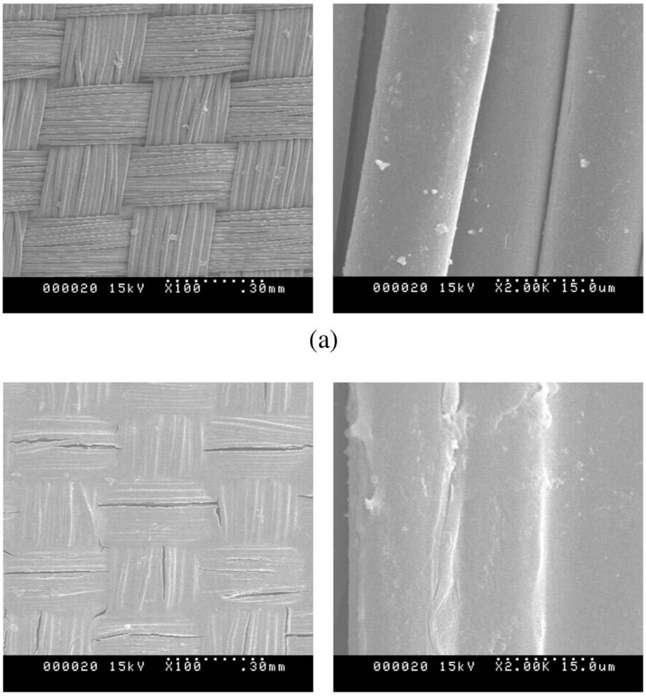
FIGURE 2 (a) Changes of PEDOT contents and surface resistivity of the composite prepared with different amounts of DMAc as a function of the number of chemical polymerization and (b) UV-Vis-NIR spectra of the composites.

that DMAc or NMP make polymerization proceed slowly, producing the electronic structure of PEDOT for higher electrical conductivity as shown in Figure 1(b). PEDOT polymerized with NMP or DMAc (40 wt% to EDOT) showed much stronger free carrier tail absorption in near IR region than PEDOT prepared without them. It was also observed that DMAc gave rise to lower surface resistivity at lower PEDOT content than NMP, resulting in remarkably low surface resistivity of about 10 Ω/□ at 18.4 wt% PEDOT content.

In Figure 2(a), the effect of the DMAc content on surface resistivity of the composite is shown, where the 40 wt% of the DMAc gave rise to the lowest resistivity among the conditions carried out in this study. This implies that amount of reducing agent is one of the important factors to produce PEDOT with high electrical conductivity. It is considered that polymerization proceed too fast and too slowly when DMAc less than and more than 40% was used, respectively. This was confirmed from UV-Vis-NIR spectra as shown in Figure 2(b), where PEDOT prepared with 40% DMAc showed the strongest absorption in NIR region.

We confirmed the role of PVP from the surface morphologies as shown in Figure 3. While the previously studied conducting polymer/textile composite had a random globular porous morphology [7], the composite prepared with PVP showed very uniform film-like dense morphology as shown in Figure 3 (b).

Environmental stability of the electrically conducting composite is of utmost importance for any practical applications. When the



(a)

(b)

FIGURE 3 (a) SEM photographs of (a) the surface of pristine PET fabric and (b) the surface of PET fabric/PEDOT composite prepared by six times chemical polymerization with DMAc.

composite was heated isothermally at 70°C for 120 minutes, little change in surface resistivity was observed in the both composites prepared without and with DMAc. However, when the composite was heated isothermally at 150°C for 120 minutes, the composite prepared with DMAc showed much less increase in surface resistivity than the composite prepared without DMAc as shown in Figure 4. The composite prepared with DMAc possessed excellent thermal stability, showing only about 2% increase in the resistivity even after heating at 150°C for 120 minutes as shown in Figure 4.

The average value of EMI SE, reflectance and absorbance over the frequency range from 50 MHz to 13.5 GHz are plotted as a function of the specific volume resistivity in Figure 5. As expected, EMI SE gradually increased from 8 to 18 dB with decrease of the specific volume resistivity from 0.56 to 0.15 Ω·cm. The relationship between EMI SE and

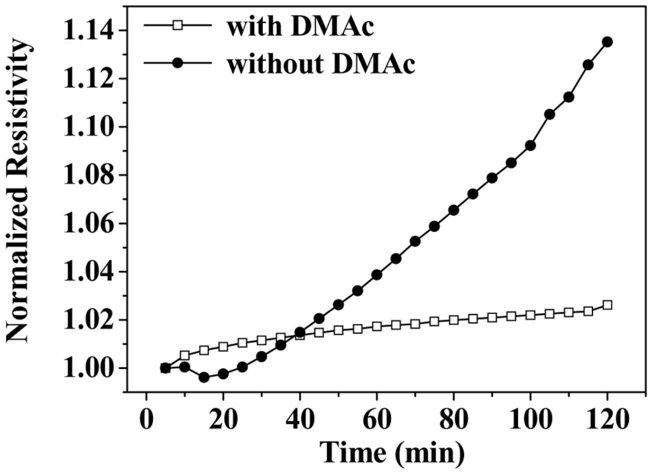


FIGURE 4 Normalized specific volume resistivity of the composite prepared without and with DMAc (40 wt% to EDOT) as a function of isothermal heating time at 150°C.

electrical conductivity of the PEDOT composite obtained in this study coincides with the relationships reported for other conducting polymer systems such as polyaniline film [8,9], polyaniline/polymer composite [10–13] or other conducting polymers [14]. In most of the systems

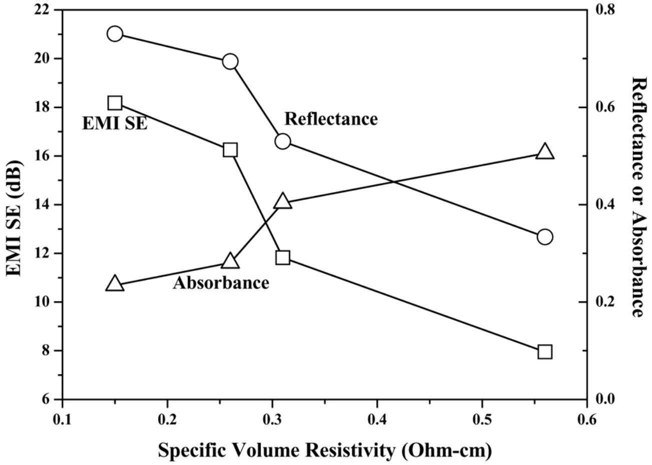


FIGURE 5 EMI SE, absorbance, and reflectance of PET fabric/PEDOT composites with various specific volume resistivity.

reported earlier, EMI SE increased slowly with electrical conductivity in relatively low conductivity region, while it increased rapidly in high conductivity region.

We believe that increase of EMI SE with the electrical conductivity results dominantly from shielding by reflection rather than absorption. As shown in Figure 5, shielding efficiency by reflection increased with decrease of specific volume resistivity, while shielding efficiency by absorption decreased. The increase of reflectance must be due to shallower skin depth of the composite with higher electrical conductivity. The composite with the specific volume resistivity of 0.15 Ω·cm showed EMI SE of about 18 dB, where 23% of the power of the incident electromagnetic wave was absorbed by the composite. We, therefore, expect that the PET fabric/PEDOT composite is practically useful for many applications requiring not only a high EMI SE but EMI shielding by absorption of the wave.

4. CONCLUSIONS

PET fabric/PEDOT composites with high electrical conductivity were prepared by polymerization of PEDOT on PET fabric, where polymerization was carried out by chemical oxidation of EDOT monomer. We prepared the composites under various conditions and investigated the properties of composite. As a result, the specific volume resistivity of the composite was as low as about 0.15 Ω·cm, giving rise to EMI SE of about 18 dB over the wide range of frequency, where 23% of the power of the incident wave was absorbed by the composite. We, therefore, expect that the PET fabric/PEDOT composite is practically useful for many applications requiring not only a high EMI SE but shielding by absorption of the wave.

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