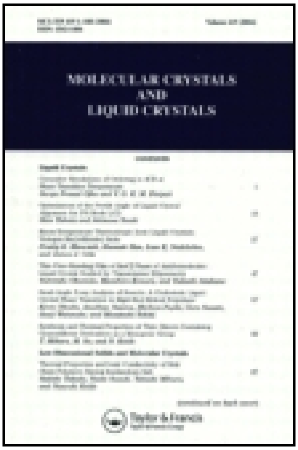

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CHARACTERISTICS OF ELECTRICALLY CONDUCTING POLYMER-COATED TEXTILES

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Intrinsically conducting polymer (ICP)/textile composites were prepared by coating polypyrrole (PPy) or poly (3,4-ethylenedioxythiopene) (PEDOT) on the fabrics through chemical and electrochemical oxidation of pyrrole or EDOT. We investigated the effects of the preparation conditions on the properties of the resulting composite such as ICP content, electrical conductivity, surface morphology, and electromagnetic interference shielding effectiveness (EMI SE). The specific volume resistivity of the composite was as low as 0.3 Ω-cm, giving rise to about 36 dB of EMI SE over the wide range of frequency up to 1.5 GHz. We also prepared the elastic textile composites, exhibiting a monotonic increase of the electrical resistance with the elongation up to 50%. We, therefore, propose the elastic textile composite can be used as a strain sensor for large deformation.

Keywords: electrically conducting textile composite; electromagnetic interference shielding; intrinsically conducting polymer; polypyrrole; poly (3,4-ethylenedioxythiophene); strain sensor

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1. INTRODUCTION

Electrically insulating or hydrophobic properties of the synthetic fibers for general uses bring about inevitable disadvantages such as the electrical shock caused by static charge accumulation and the electromagnetic interference (EMI) caused by transmission of detrimental electromagnetic waves. Therefore, a number of researchers have been carried out to provide the synthetic fibers with the electrical conductivity, including spinning of electrically conducting fibers [1,2] or coating fibers with electrically conducting materials such as metals [3,4] or intrinsically conducting polymers [5].

Intrinsically conducting polymers (ICP) such as polypyrrole (PPy) and poly(3,4-ethylenedioxythiophene) (PEDOT) have been considered as the key materials to many commercial applications [6,7] since they possess high electrical conductivity, ease of synthesis and good environmental stability. It has been reported that the electrically conducting PPy-coated textiles may be useful for many applications since the textiles may have not only excellent physical properties of the textiles such as mechanical strength and flexibility but also electrical and microwave properties of PPy [8–11]. The applications include static charge dissipation, EMI shielding, coatings or jackets for flexible conductors, broadband microwave absorbent. Recently, it was also reported that PPy-coated textiles could absorb some portion of microwave radiation [12,13]. This implies that electrically conducting polymer-coated textiles can be applied to the application fields such as military camouflage, where EMI shielding by absorption rather than reflection is more important.

In this study, we report the fabrication methods to achieve PPy/PET and PEDOT/PET composites with high electrical conductivity and EMI shielding effectiveness (EMI SE). We investigated the effects of preparation conditions on the properties of the resulting composites such as electrical conductivity, surface morphology, EMI SE, and relative EMI SE by absorbance and reflection. We also prepared an elastic PPy/textile composite using a PET/Spandex fabric as the substrate fabric and investigated the mechanical properties of the composites and the change of the electrical resistance with the mechanical strain. We propose the elastic composite may be used as a strain sensor for large deformation.

2. EXPERIMENTAL

PPy/textile and PEDOT/textile composites were prepared by the polymerization of PPy or PEDOT on the textiles through chemical and electrochemical oxidation of the monomer in sequence. A PET plain textile and an elastic PET/Spandex (97/3) were used as the substrate textiles for EMI shielding composite and for large deformation strain-sensor.

Chemical and electrochemical polymerizations of PPy on the PET and PET/Spandex fabrics with the thickness of about 0.5 mm were carried out by the reported procedure [12,13]. PEDOT was chemically polymerized on the PET fabric as the following procedure. EDOT and poly (vinyl pyrrolidone) (PVP) (10 wt% of EDOT) as a binder were dissolved in organic solvents such as n-butanol, acetonitrile (ACN) or methanol. Ferric p-toluenesulfonate (FTS) as an oxidant was dissolved in organic solvents such as methanol or n-butanol. Monomer and the oxidant solutions were mixed to give various mole ratios of oxidants to monomer and a certain amount of the mixed solution was immediately sprayed on the fabric. The fabric was placed in ambient condition for a few minutes and polymerization proceeded in a convection oven at 70°C for 20 minutes. The fabric coated with PEDOT was then washed with methanol and acetone and dried in a convection oven 70°C for 20 minutes. The chemical polymerization of PEDOT was repeated until a required electrical conductivity was obtained. The surface morphology of the composite was observed by SEM.

Electrical conductivity of the composite was measured by the two-probe method and expressed as the specific volume resistivity (Ω-cm). EMI SE was obtained 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 to 1.5 GHz [14]. EMI SE value expressed in dB was obtained from the ratio of the incident to transmitted power of the electromagnetic wave. We also measured the reflectance and the transmittance of the composite and calculated the absorbance.

We investigated the effect of PPy polymerization on the mechanical properties of the elastic PET/Spandex (97/3) composite by a tensile tester. We also studied the effect of the mechanical strain on the electrical property of the composite. The electrical resistance of the composite was measured by two probe method during extension of the composite at an elongation rate of 5 mm/minute, where we used the specimen with the width, length, and thickness of 1 inch, 3 inches, and 0.356 mm, respectively.

3. RESULTS AND DISCUSSION

PEDOT powders were synthesized for various polymerization times from 5 to 120 minutes in order to determine a proper chemical polymerization time of PEDOT on the fabric. We monitored the electrical conductivity of PEDOT increased with the polymerization time up to 20 minutes, after which the electrical conductivity showed little change. We, therefore, carried out all the chemical polymerization of PEDOT for 20 minutes, resulting in the electrical conductivity of about 30 S/cm.

Figures 1 and 2 display the changes of PEDOT contents and specific resistivities of the composites prepared under various conditions as a function of the number of chemical polymerization. Specific volume resistivity gradually decreased with the number of polymerization, which must be due to more incorporation of PEDOT in the composite with the repeated polymerization.

We observed the solvents of the monomer and the oxidant solutions affected the properties of the composite as shown in Figure 1. We found the chemical polymerization was best carried out using EDOT and FTS solutions in methanol and n-butanol, respectively. As shown in Figure 1, the oxidant solution in n-butanol gave rise to much lower specific volume resistivity than the oxidant solution in methanol at the same content of PEDOT.

We also investigated the effect of the ratio of the oxidant to the monomer on the conductivity of the composite. Specific volume resistivity significantly decreased with increase of the mole ratio at the same PEDOT content. We believe the more oxidant provides PEDOT with the more enhanced electronic structure and then the higher electrical conductivity. PEDOT/PET composite prepared with the mole ratio of the FTS to EDOT of 3 : 1 possessed a low specific volume resistivity of approximately 3 Ω-cm at the PEDOT content of about 35 weight percent.

Figure 2 shows specific volume resistivities of the composites prepared using various concentrations of the monomer solutions at a fixed mole ratio of the oxidant to the monomer of 3 : 1. We figured out the concentrations of

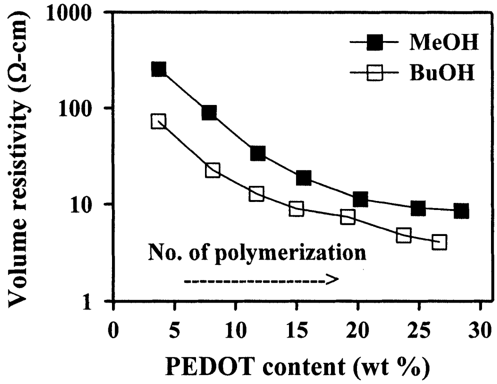

FIGURE 1 Changes of PEDOT content and specific volume resistivity of PEDOT/PET composites prepared with oxidant solutions in methanol and n-butanol.

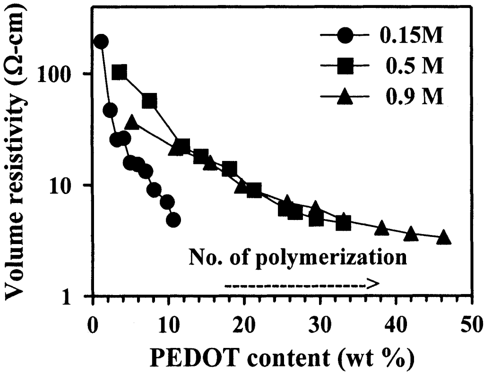

FIGURE 2 Changes of PEDOT content and specific volume resistivity of PEDOT/PET composites prepared with various concentrations of EDOT solutions.

monomer and oxidant solutions were very important factor to produce highly conducting composite with less content of PEDOT as shown Figure 2. The composite prepared using 0.9 M EDOT solution showed much faster increase of PEDOT content but much slower decrease of the specific volume resistivity than the composites prepared using 0.15 M solution. We, therefore, concluded the chemical polymerization with less concentrated monomer solution and the oxidant solution in n-butanol produced PEDOT/PET composite with higher conductivity at lower PEDOT content.

Nevertheless, we observed PPy produced the electrically conducting textile composite with better characteristics than PEDOT did. Figure 3 compares the changes of ICP contents and specific volume resistivities of

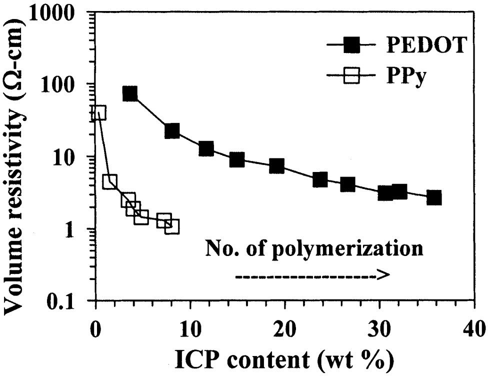

FIGURE 3 Changes of ICP content and specific volume resistivity of the textile composites prepared with PPy and PEDOT.

PPy and PEDOT composites with the number of the chemical polymerization. As shown in Fig. 3, PPy gave rise to much lower specific volume resistivity at the same ICP content than PEDOT. PPy/PET composite showed a very low specific volume resistivity of about 1 Ω-cm at only 8 wt%, while PEDOT/PET composite exhibited 3 Ω-cm even at 35 wt%. We also found the surface of PPy composite was much smoother than that of PEDOT composite. As shown in Figure 4, PPy produced very uniform film-like dense coating, while PEDOT produced not only the surface coating but also globular powders in the space between the fibers. This indicates PPy was more effectively coated to give the composite with higher conductivity at lower content than PEDOT. We, therefore, concluded PPy had to be coated on the textiles to produce the textile composite with higher conductivity and lower ICP content.

We confirmed the composites prepared in this study possessed practically applicable EMI SE. It is interesting that EMI shielding behaviors of the composites prepared in this study follow the same trend, irrespective of the kind of ICP. This indicates EMI shielding properties of the electrically conducting polymers depend little on the nature of the polymer but mainly on the conductivity of the polymer. EMI SE gradually increased from 10 to 15 dB with decrease of specific volume resistivity in the region from 7 to 3 Ω-cm and then more steeply increased to 36 dB. The steep increase of EMI SE must be due to the increase of the conductivity toward a metallic conductivity. We also noticed that the increase of EMI SE with the electrical conductivity resulted dominantly from the shielding by reflection. The shielding efficiency by absorption decreased with increase of the specific volume resistivity, while shielding efficiency by reflection increased. We believe the increase of reflectance must be due to shallower skin depth of the composite with high metallic conductivity. The composite with the

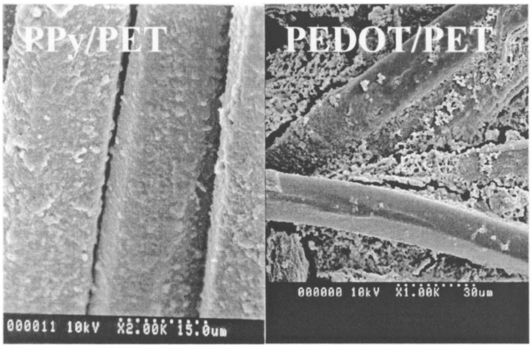

FIGURE 4 Surface morphologies of PPy and PEDOT textile composites prepared by chemical polymerization for 6 times.

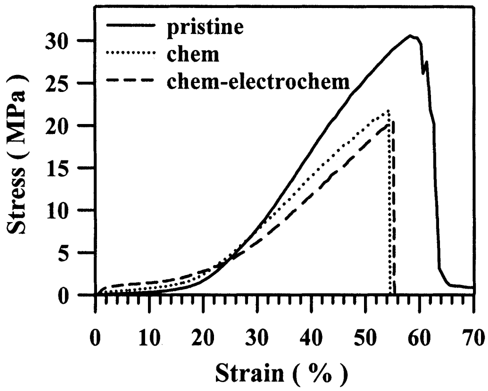

FIGURE 5 Stress-strain curves of a pristine elastic fabric and the textile composites prepared by chemical or chemical-electrochemical polymerizations.

specific volume resistivity of 0.2 ohm-cm showed EMI SE of about 36 dB, where 7% of the power of the incident electromagnetic wave was absorbed by the composite.

The mechanical properties of the elastic PPy/PET/Spandex composites were shown in Figure 5 and listed in Table 1. We found the elastic textile became stiffer and stiffer after chemical and electrochemical polymerizations, certainly due to coating of less flexible PPy coating and decrease of the free space for stretching. We also observed the mechanical properties of the composites became worse as listed in Table 1. Breaking elongation of the composites prepared by chemical and chemical-electrochemical polymerizations decreased a little from 58 to about 55%, while breaking stress decreased significantly from 30.6 to about 20 MPa. We believe the decrease of the breaking stress must result from the hydrolysis of the fiber surface by the strong oxidant solution during the repeated chemical polymerization. Nevertheless, We confirmed the elastic composite prepared in this study possessed practically applicable mechanoelectrical property as shown in Figure 6, exhibiting the monotonic increase of the composite

TABLE 1 Mechanical Properties of the Elastic T/PPy Composite

Preparation method	PPy content (wt %)	Specific volume resistivity (Ω-cm)	Breaking stress (MPa)	Breaking elongation (%)
Pristine	–	–	30.6	58.3
Chemical polymerization	4.3	1.5	21.8	54.4
Electrochemical polymerization	9.5	0.5	20.5	55.2

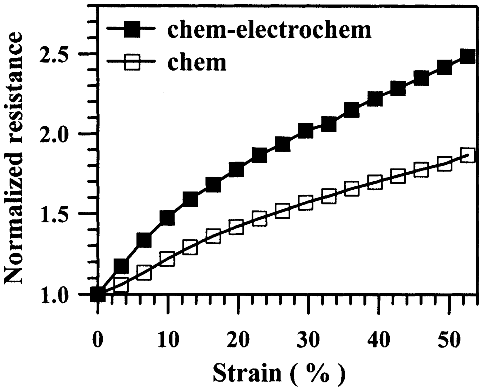

FIGURE 6 Electrical resistance changes of the elastic textile composite with the elongation.

resistance with the elongation up to about 50%. We, therefore, propose the elastic textile composite can be used as a strain sensor for large deformation.

4. CONCLUSION

Using chemical and electrochemical polymerizations of PPy or PEDOT, we prepared ICP/textile composites with high electrical conductivity and practically useful EMI SE. We studied the effects of the preparation conditions on the properties of the resulting composite. We figured out EMI SE increased with decrease of the specific volume resistivity and some portion of the electromagnetic power was absorbed by the composite. We believe the composite prepared in this study may be used in the application where EMI shielding by absorption rather than reflection is more important. We also prepared the elastic textile composites with high electrical conductivity. The composites exhibit a monotonic increase of the electrical resistance with the elongation up to 50%. We, therefore, propose the elastic textile composite can be used as a strain sensor for large deformation.

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