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Synthesis of electrically conductive polypyrrole–polystyrene composites using supercritical carbon dioxide

II. Effects of the doping conditions

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Abstract

A polymer composite of polypyrrole (PPy) and polystyrene (PS) was synthesized in this study. Pyrrole was firstly impregnated within the PS substrate where supercritical carbon dioxide ($SCCO_2$) at 40 °C and 10.5 MPa was used as the solvent. The resulting polymer composite was then soaked in a solution of metallic salt to form an electrically conductive product. Thermal analyses were carried out in this study. Glass transition temperatures from the DSC curves and thermal decomposition temperatures from the TGA curves were observed. These temperatures rise gradually from pure PS, undoped blend to doped composite that indicates blending took place in $SCCO_2$, and polymerization was proceeding when the pyrrole/PS blend was soaking in the doping solution. Furthermore, various effects of the doping conditions on the conductivity of the PPy/PS composite were investigated. Water and acetonitrile were used as the solvents where the former yielded a higher conductivity of the product. Various doping temperatures were studied and a maximum conductivity was observed at 25 °C. The conductivity also depends on the nature of the oxidant. A bell-shaped profile of the conductivity with respect to the concentration of each oxidant was obtained. The maximum conductivity of the composites with iron compounds as oxidants decreases in the following order of anions: chloride > sulfate > perchloride > nitrate in aqueous solutions. Comparison of the scanning electron microscope results of the composite was presented where chloride and nitrate anions were used as the oxidant. It was found that the composite with higher conductivity has higher bulk density and less porous morphology.

Keywords: Polymer composites; Polypyrrole/polystyrene; Supercritical carbon dioxide; Doping conditions

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1. Introduction

Polypyrrole (PPy) is considered as one of the most promising conducting polymers for practical applications. This polymer, however, is hard, brittle, and insoluble in solvents. Efforts such as blending it with another polymer for the improvement of its mechanical properties received much attention in recent years. The polymer composite can be prepared in many ways. One of them is the mechanical mixing where the controlling factors for a good conductive composite are the sizes and uniformity of particles as well as the efficiency of mixing [1,2]. Another way to prepare the composite is the chemical or electrochemical synthesis in organic solvents [3–5]. The organic solvents may cause environmental pollution. One potential method for cleaner production is to replace the organic solvents by supercritical carbon

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dioxide ($SCCO_2$). Some investigators have used CO_2 as the solvent for free-radical polymerization [6], but very limited literature on the synthesis of polymer composite using $SCCO_2$ has been reported [7–9]. In our previous study [10], the effects of the blending conditions on the synthesis of electrically conductive polymer composite using $SCCO_2$ has been investigated.

In conventional processes, PPy is usually prepared by electrochemical or chemical polymerization in solution. Various factors that affect the conductivity of the polymer have been investigated for these methods [11–14]. For example, Machida et al. [11] have discussed the effects of various solvents, doping concentration, reaction temperature, and reaction time on the electrical conductivity. Some effects were explained by the change of the oxidation potential in their study. Laakso et al. [12] have found that doping with various oxidants resulted in different conductivity. Different doping anions showed different electron affinities in solvent as expressed by their redox potential. Oxidant with higher redox potential offered more driving force in the reaction. In this study, some affecting factors are investigated for the impregnation of the pyrrole monomer into a host polymer in $SCCO_2$, and a systematic discussion of the doping conditions for these composites is presented.

In this experiment, polymer blending was carried out by impregnating the pyrrole within the substrate under the environment of $SCCO_2$. After the blending process, the pyrrole/polystyrene (PS) blend was soaked in a metallic salt solution to form an electrically conductive product. The time of blending in the column was 24 h, which was determined by the equilibrium sorption of CO_2 in the PS matrix. A doping period of 20 min was also determined when the conductivity of the PPy/PS composite was unchanged with doping time. The determination of both the blending time and the doping time were based on our previous work [10]. In this study, the thermal stability of composites was tested and the influences of the doping solvent, the doping temperature and the nature of oxidants were investigated. Acetonitrile and water were used as the doping solvents. Doping temperature ranged from 15 to 45 °C. Iron chloride, iron sulfate, iron perchlorate, and iron nitrate were selected as oxidants. The conductivity of the composite was measured with the four-point probe method. Scanning electron microscope (SEM) and elemental analyses were also investigated to study the effect of various oxidants on the conductivity of the composites.

2. Experimental

2.1. Chemical materials

Anhydrous iron (III) chloride, iron (III) sulfate pentahydrate, iron (III) nitrate nonahydrate (Acros), iron (III) perchlorate (Aldrich) of guaranteed grade were used as received. Acetonitrile was purchased from Merck Co. The purity of all chemicals was better than 99% and was used without further purification. Water was purified with NANO ultrapure water system. Pyrrole monomer (Acros) was purified by distillation under reduced pressure and stored at 4 °C in the absence of light. Pellet PS (Acros) was pressed as sheets with 2 mm in thickness at 250 °C. Carbon dioxide was purchased from San-Fu Chemical Co. (Taiwan) with purity better than 99.5 mol% and was also used as received.

2.2. Polymer composite syntheses

The experimental apparatus has been described in our previous publication [10]. PS specimen with dimensions of 30 mm × 8 mm × 2 mm was used as the substrate, and was placed into the column to perform the blending experiment. An amount of 0.05 cm^3 pyrrole monomer was injected on the surface of the PS matrix by glass syringe. The column was maintained at 40 °C where CO_2 was slowly charged into the cell until a pressure at 10.5 MPa was reached. A blending time of 24 h was employed, which was determined by the equilibrium sorption of CO_2 in the PS matrix [10]. CO_2 was slowly vented at the end of the blending, and the blend was removed from the column. After the blending process, the pyrrole/PS blend was doped with various oxidation agents. The doping time was taken as 20 min, which was also determined when the conductivity of the PPy/PS composite was unchanged with doping time [10]. The sample was then dried under the vacuum for 72 h.

2.3. Characterization

Electrical conductivity was measured by the four-point probe method with a Zentech 502BC micro-resistance meter. The morphologies of the polymer composites were determined using the PHILIPS XL30 SEM. Glass transition temperatures were measured using a differential scanning calorimeter (TA DSC-2010). Thermal decomposition temperatures were measured using a thermogravimetric analyzer (Perkin–Elmer TGA-7). Elemental analysis of C, H, N was also carried out with an elemental analyzer (Perkin–Elmer 2400). The element, Fe, of the composite was analyzed by ICP-AES (Jarrell-Ash, ICAP 9000).

3. Results and discussion

A pyrrole/PS blend was formed under the environment of $SCCO_2$ at 40 °C and 10.5 MPa. The blend was then immersed in a doping solution to yield a conducting product. Fig. 1 shows the photographs of various specimens. The pure PS substrate was transparent, the

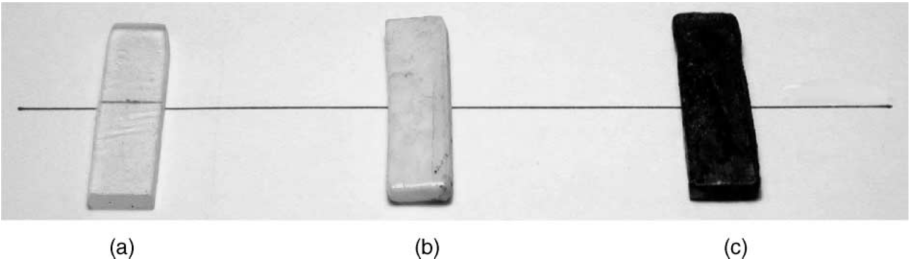

Fig. 1. Photograph of experimental specimens in this study: (a) pure PS substrate, (b) undoped pyrrole/PS blend and (c) doped PPy/PS composite.

undoped pyrrole/PS blend was milky white and the doped PPy/PS composite was black. The DSC analyses show that the glass transition temperatures are 101, 103 and 104 °C for the pure PS substrate, the undoped pyrrole/PS blend, and the doped PPy/PS composite, respectively. An increase in the glass transition temperature for blended PS substrate was observed. It is also found that the PPy/PS composite doped with iron chloride shows a higher glass transition temperature than the undoped pyrrole/PS blend. Fig. 2 shows the TGA curves under nitrogen atmosphere for the pure PS substrate as well as the undoped pyrrole/PS blend and doped PPy/PS composites. Their decomposition temperatures are 321, 350 and 390 °C, respectively. It shows that the decomposition temperature of the blended PS substrate is higher than the pure PS substrate, while that of the doped PPy/PS composite is much higher than the undoped pyrrole/PS blend. From these observations, it is inferred that the blending of pyrrole with PS matrix proceeded in the $SCCO_2$ phase. Polymerization occurred when the blend was soaking in the doping solution.

Various effects of the doping conditions were investigated in this study. Firstly, two kinds of doping solvent of acetonitrile and water were used. The conductivity of the composites doped with iron chloride in these solvents is shown in Fig. 3. Upon using acetonitrile as the doping solvent, precipitation was observed during the doping process. The PS matrix dissolved in acetonitrile after doping for a certain period. On the other hand, water was chosen as the doping solvent owing to its low corrosion and high solubility of oxidants. When water was taken as the solvent in the doping process, a higher peak conductivity value of 1.12×10^{-2} S/cm was observed. Comparisons of the maximum conductivity values and the corresponding concentrations of the doping solutions are shown in Table 1. It has been

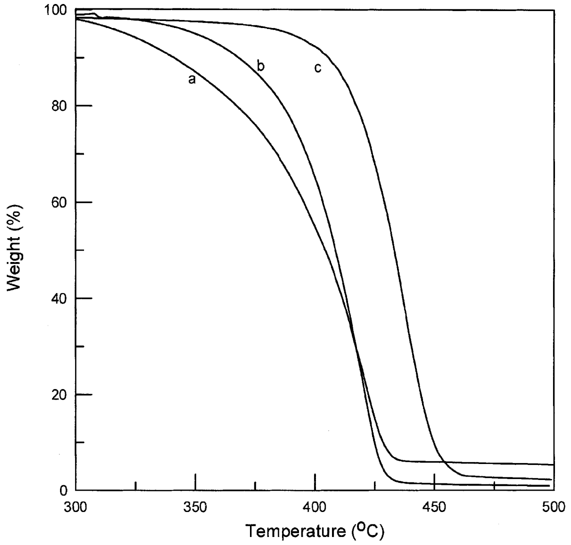

Fig. 2. TGA curves of (a) pure PS substrate, (b) undoped pyrrole/PS blend and (c) doped PPy/PS composite with 2.25 M $FeCl_3$. The blend and composite were prepared at 40 °C and 10.5 MPa.

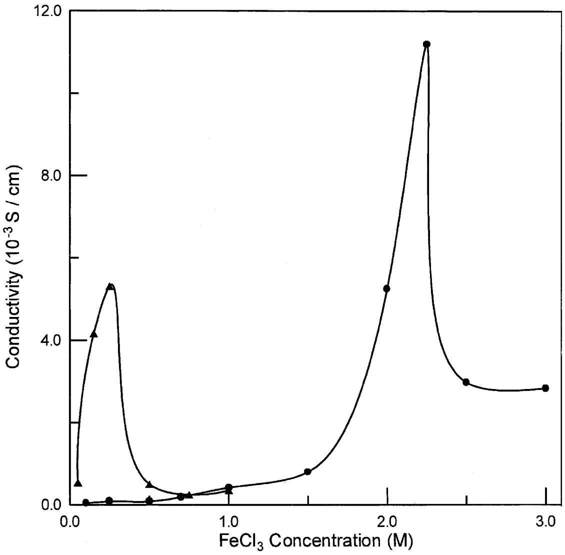

Fig. 3. Plots of the electrical conductivity against the doping concentration with various doping solvents [(●) water; (▲) acetonitrile].

Table 1
The electrical conductivity of the PPy/PS composites with different doping solvents

Doping solvent	Concentration of $FeCl_3$ (M)	Maximum conductivity (S/cm)
CH_3CN	0.25	5×10^{-3}
H_2O	2.25	1.12×10^{-2}

demonstrated that solvents possessing OH group such as methanol and water yielded higher conductivity [11], and a consistent result is also obtained in this study. Water was used as the doping solvent for the rest of this study because much higher peak conductivity was achieved.

Fig. 4 illustrates the effect of the doping temperature on the conductivity of the PPy/PS composite. The conductivity changed with various doping temperatures and concentrations of aqueous $FeCl_3$ solutions. For a fixed concentration of the doping solution, the conductivity has a maximum value at 25 °C. The conductivity decreased as the doping temperature deviates from this value. At room temperature, the maximum conductivity appeared at an oxidant concentration of 2.25 M.

Figs. 5 and 6 show the conductivity of composites when different iron (III) compounds of sulfate, perchlorate and nitrate were used as the oxidants. It is demonstrated in these figures that the conductivity increased to a peak value and then decreased promptly with increasing concentration of the doping solution. The maximum conductivities were observed at 2.25, 1.5, 1.0, and 0.5 M, respectively, when iron (III) chloride, sulfate, perchlorate, and nitrate were used. A similar bell-shaped profile of conductivity was also shown for the doping of interphase polymerization in previous researches [11,15]. The decrease in conductivity may be elucidated by the degradation of the conducting polymer as reported by other investigators [15–17]. The degradation reaction of the PPy/PS composite took place in the doping solution and it was attributed to the overoxidation in polymer. In aqueous solution or in the presence of trace of water,

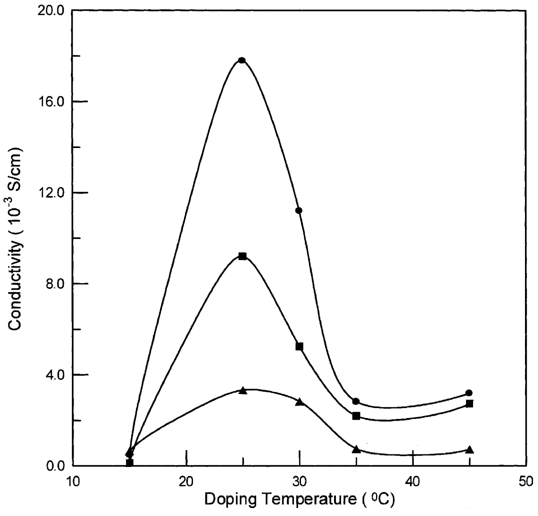

Fig. 4. The electrical conductivity of the PPy/PS composite at various doping temperatures ($FeCl_3$ concentration: (■) 2.0 M; (●) 2.25 M; (▲) 3.0 M).

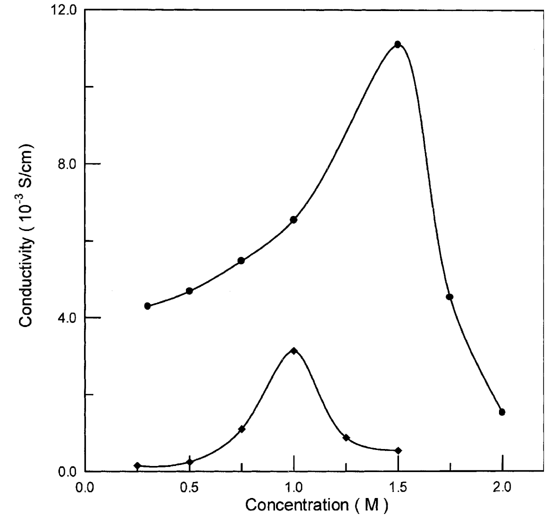

Fig. 5. Plots of the electrical conductivity of the composites against the doping concentration with various oxidants [(●) $Fe_2(SO_4)_3$; (◆) $Fe(ClO_4)_3$].

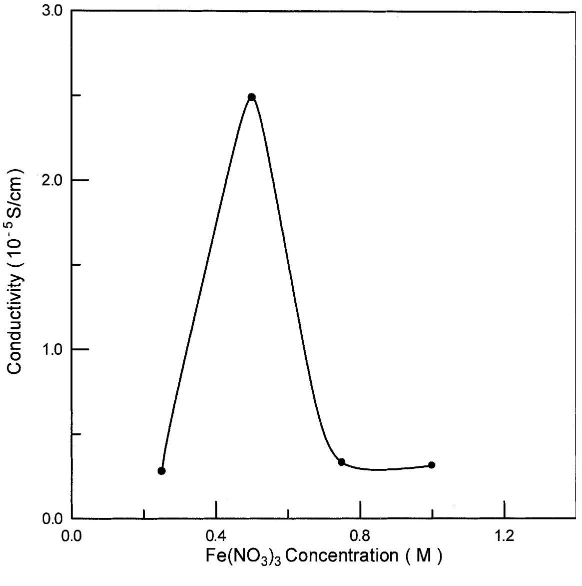

Fig. 6. Plots of the electrical conductivity of the composite against the doping concentration when $Fe(NO_3)_3$ was used as oxidant.

Table 2
Maximum conductivity and elemental analysis results of the PPy/PS composites with various oxidants

Doping agents	Oxidant concentration in aqueous solution (M)	Maximum conductivity (S/cm)	C (%)	H (%)	N (%)	Fe (%)
Undoped	–	$< 1 \times 10^{-7}$	91.93	7.78	0.06	–
$FeCl_3$	2.25	1.12×10^{-2}	88.56	6.61	0.54	1.18
$Fe_2(SO_4)_3$	1.50	1.11×10^{-2}	87.45	7.23	0.31	0.88
$Fe(ClO_4)_3$	1.00	3.14×10^{-3}	90.80	6.73	0.30	0.16
$Fe(NO_3)_3$	0.50	2.49×10^{-5}	89.05	7.43	0.28	0.14

excess oxygen has been observed in PPy samples and must be attributed to the covalently bound hydroxides and carbonyl defects. The presence of these defects leads to a degradation of the PPy properties [16].

As expected, the maximum conductivity was strongly dependent on the nature of the oxidant. The maximum conductivity of the composites doped with iron (III) compounds decreased in the following order of anion: chloride > sulfate > perchlorate > nitrate, as shown in Table 2. The conductivity of the PPy/PS composite doped with iron nitrate is lower than those doped with other oxidants by up to three orders of magnitude. As reported by previous investigations [14,18], the rate of polymerization was the lowest when chloride was used as doping anion. A lower rate of polymerization brought a higher bulk density and less porous morphology, which resulted in a higher conductivity. In contrary, a lower bulk density and more porous morphology will result in lower conductivity. Fig. 7 demonstrates the SEM results when $FeCl_3$ and $Fe(NO_3)_3$ were used as the oxidants. The difference in the morphology of the composites agrees reasonably with the feature in the above explanation.

The result of elemental analysis of the scraped composite surface with various doping oxidants is summarized in Table 2. The amount of PPy present in the composite was determined by nitrogen microanalysis, and the amount of oxidant was estimated by iron elemental analysis. With the same operating conditions for the blending process using $SCCO_2$, the composition of the pyrrole/PS blends was the same before doping. The pyrrole or pyrrole oligomers may be carried out from the blend by CO_2 as it desorbed gradually from the blend. Table 2 shows that the doped composites contained higher percentage of nitrogen than the undoped blend. This indicates that the polymerization of PPy proceeded during the doping process. The differences in compositions among the doped composites shown in Table 2 are owing to the different oxidizing abilities of various oxidants. From elemental analysis, it is found that the composite doped with iron chloride contained a higher percentage of both nitrogen and iron. It is indicated that when CO_2 desorbed from the blend and met the oxidant at the surface of the blend, more PPy was obtained using iron chloride as an oxidant.

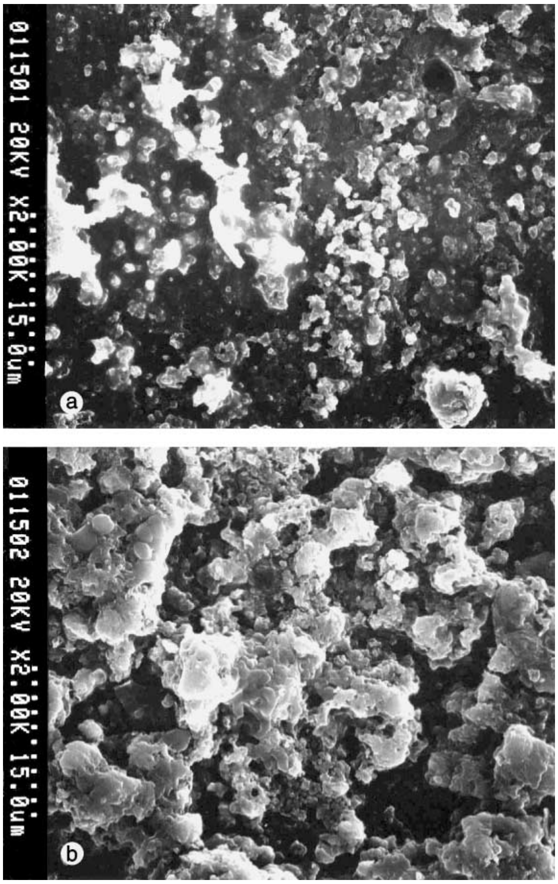

Fig. 7. Scanning electron micrograph of composites doped with (a) $FeCl_3$ (b) $Fe(NO_3)_3$ (2000×).

4. Conclusion

Various effects of the doping conditions for the conductivity of the PPy/PS composite, which was blended in $SCCO_2$, are discussed in this study. These factors included the doping solvent, the doping temperature, the concentration of the doping solution, and the nature of oxidants. Thermal analyses show that the formation of PPy enhances the thermal stability of composites. Two solvents, water and acetonitrile, were used and the former gave much higher composite conductivities. Various doping temperatures were employed, and a maximum value of the conductivity of the composite appeared at about 25 °C. The conductivity also changed with the concentration of the doping solution and a bell-shape profile was obtained. It was observed that the maximum conductivity of the composites doped with iron (III) compounds decreased in the following order of anion: chloride > sulfate > perchlorate > nitrate. The SEM results showed that the composite with higher conductivity has higher bulk density and a less porous surface. From elemental analyses, higher nitrogen and iron contents were also observed in the composite with higher conductivity.

Acknowledgements

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