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

I. Effects of the blending conditions

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Abstract

The electrical conductivity for a polymer composite consisting of polypyrrole (PPy) and an insulating host polystyrene (PS) is reported in this study. The host polymer was blended with pyrrole monomer using either supercritical carbon dioxide ($SCCO_2$) or high-pressure liquid carbon dioxide ($HPLCO_2$) as the carrying solvent. After the blending process, the blended host polymer was soaked in an oxidant solution. This process is compared with that of oxidant impregnation. With the same processing conditions, a polymer composite with much higher conductivity was obtained when the blending process was carried out before doping in an oxidant agent. Scanning electron microscope (SEM) and elemental analysis reveal that polymerization proceeded when the blended host polymer was soaking in the oxidant solution. It is observed that $SCCO_2$ provides better conditions for blending the host polymer with pyrrole monomer than $HPLCO_2$ at the same density. The maximum conductivity of the polymer composites also increases with temperature and pressure at the same $SCCO_2$ density.

Keywords: Conducting polymer blend; Polypyrrole; Polystyrene; Supercritical carbon dioxide

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1. Introduction

The synthesis of conducting polymers has become an important research area since its discovery in the past 20 years [1,2]. Most conducting polymers, such as polypyrrole (PPy), poly(3-octylthiophene), polyaniline, were synthesized by oxidative or electro-chemical polymerization [3–5]. Oxidizing agents, such as iodine and $FeCl_3$, are convenient for oxidatively polymerizing monomers and to produce conductive polymers [4]. Most conducting polymers are hard, brittle, insoluble in most solvents, and nonfusible even by heating up to their decomposition temperatures. One way to overcome the poor mechanical properties is to blend it with another insulating polymer. Composites have been formed by either directly dispersing the conducting polymer into an insulating host polymer or by in situ polymerization [5–7]. It appears that the combination of electrical and mechanical properties of composites have great promise for many applications. The potential usage of conducting polymer blends includes electro-chromic and electro-optical devices, packaging materials, actuators, batteries, and catalysis [8,9].

The process for synthesizing electrically conducting polymer or composites thereof may require a large amount of organic solvents, and the disposal of the waste is a major economic and environmental concern.

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The problem may be eliminated when nontoxic supercritical fluids are used as solvents. Carbon dioxide is often used as a supercritical fluid because it is readily available, nonflammable, nontoxic, and inexpensive. Also it has a relatively low critical temperature ($T_C =$ 31.1 °C) and a moderate critical pressure ($P_C = 7.3$ MPa) [10]. It has been noted that liquid CO_2 behaves like a hydrocarbon solvent with respect to its capacity to dissolve small monomer molecules [11,12]. Moreover, carbon dioxide leaves no residue in the treated polymer. The use of supercritical carbon dioxide ($SCCO_2$) to blend pyrrole with an insulating polymer has been investigated recently [6,7,13]. In those studies, the host polymers were impregnated with oxidant in the $SCCO_2$ and then exposed to the pyrrole vapor [6,7]. Otherwise, the host polymers were first soaked in an oxidant solution and the composite of PPy and the host polymer was then synthesized in $SCCO_2$ [13]. In this study, the latter method is referred to oxidant impregnation.

In this study, blending of pyrrole with the host polystyrene (PS) was carried out using either $SCCO_2$ or high-pressure liquid carbon dioxide ($HPLCO_2$) near the supercritical condition as the solvent. The blended host polymer was then soaked in the oxidant solution after the blending process. Polymerization of pyrrole monomer is accomplished in this oxidation process. This procedure is called pyrrole impregnation in contrast to the other literature method of oxidant impregnation [13]. In our procedures, the time for blending in the $SCCO_2$ or $HPLCO_2$ was determined by the equilibrium absorption of CO_2 in the PS matrix. The time of doping in oxidant solution was determined when the conductivity of the PPy/PS composite is unchanged with doping time. The morphology and electrical conductivity of the composites prepared by this method are strongly affected by the operation conditions of the blending process in CO_2 and the doping process in the oxidant solution. Scanning electron microscope (SEM) and elemental analyses were conducted to investigate the morphology and compositions of the composites with or without the doping process. The effect of varying the iron(III) chloride oxidant concentration on the conductivity of the composite is also reported.

2. Experimental

2.1. Chemical materials

Pyrrole monomer (Acros) was purified by distillation under a reduced pressure and was stored at 4 °C in the absence of light. Anhydrous iron(III) chloride of guaranteed grade was used as received. Pellet PS (Acros) was pressed as sheet with 2 mm in thickness at 250 °C. Carbon dioxide was purchased from San-Fu Chemical (Taiwan) with a purity better than 99.5 mol% and was also used as received.

2.2. Syntheses of the polymer composite

The host polymer of PS was cut into specimens with dimensions of 30 × 8 × 2 mm. They were soaked in $SCCO_2$, and the solubility of carbon dioxide was measured. In this study, pure CO_2 from a cylinder was liquefied through a cooler at −6.5 °C. To improve the fluid compression, each head of the pump was equipped with a cooling jacket in which aqueous alcohol at −6.5 °C was used. Liquid CO_2 was then compressed by a metering pump (ConstaMetric 3200 P/F, LCD Analytical Inc.), and was heated through a pre-heating coil immersing in a water bath before introducing into the equilibrium column. A 10 cm^3 supercritical fluid extraction column (Keystone Scientific, Inc.), which had been pressure tested to 69 MPa without flaw, was used in this study. The column made by stainless steel was immersed in a water bath. The experimental temperature and pressure were measured using a calibrated quartz thermometer (INS) and a calibrated pressure gauge (Heise). The accuracy for temperature measurement is ±0.1 K, and that for pressure measurement is ±0.02 MPa. The needle valves (Whitey) were also maintained at the experimental temperature to ensure an equilibrium condition. A schematic diagram of our experimental apparatus is shown in Fig. 1.

The time for blending pyrrole with the host polymer needs to be determined at first. Operation conditions of 40 °C and 10.5 MPa were chosen in this study, which were also used by previous investigators [13]. The host polymer was soaked in $SCCO_2$ for various time periods. CO_2 was vented after the host polymer was soaked for a certain time. The weight increases of the host polymer were then determined at various times and the results are

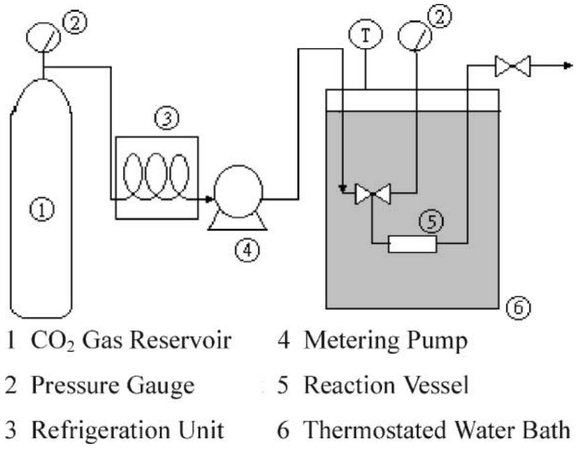

Fig. 1. Schematic diagram of the apparatus.

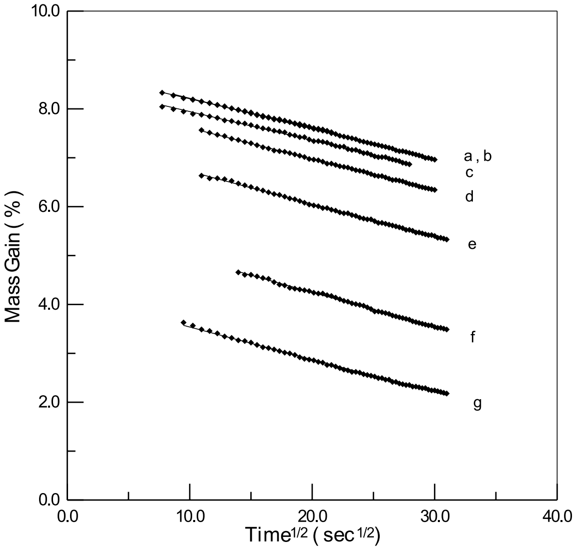

Fig. 2. Desorption curves of carbon dioxide from the PS matrix at various soaking times ($a = 24$ h, $b = 16$ h, $c = 9$ h, $d = 4$ h, $e = 3$ h, $f = 2$ h, $g = 1$ h).

shown in Fig. 2. The maximum amount of absorption of CO_2 in the host polymer after a specific soaking time is determined from the y-intercept as shown in Fig. 2 [14,15]. Fig. 3 illustrates the variation of the maximum amounts of sorption with various soaking times. The maximum amount of absorption levels off at a soaking time of 24 h, which indicates saturation was reached within this time period. This saturation point shows that the equilibrium solubility of CO_2 in PS is 8.79 mass% at 40 °C and 10.5 MPa. The equilibrium time of 24 h was taken as the blending time for PS matrix in $SCCO_2$.

The host polymer was then placed into the column and prepared for the formation of a polymer composite. An amount of pyrrole monomer (0.05 cm^3) was injected on the surface of host polymer by glass syringe. The column was heated to 40 °C and CO_2 was then slowly added to the system until the desired pressure was reached. The blending condition was 40 °C and 10.5 MPa for 24 h. This blending time was determined because the maximum amount of absorption of $SCCO_2$ was reached at a soaking time of 24 h. At the end of the process, CO_2 was slowly vented and the blended host polymer was removed from the column. Other operating temperatures and pressures were also investigated in this study. Comparisons of the conductivity of the composites were made on the same basis of blending time of 24 h.

The blended host polymer was then doped with an oxidizing agent. Fig. 4 shows the electrical conductivity of the polymer composite as a function of the doping time where a 2.25 M $FeCl_3$ aqueous solution was used as an oxidizing agent. A *rapidly* increasing curve is observed at the beginning of doping period. It is observed that, for doping times longer than 20 min, the conductivity curve shown in Fig. 4 becomes flat. Hence a doping time of 20 min was used in our experiment in order to obtain maximum electrical conductivity for the composites. The doping time for other concentrations of iron chloride was also taken as 20 min. Comparisons of the conductivity of composites were made at the same doping time. After the doping process, the sample was dried under vacuum for 72 h.

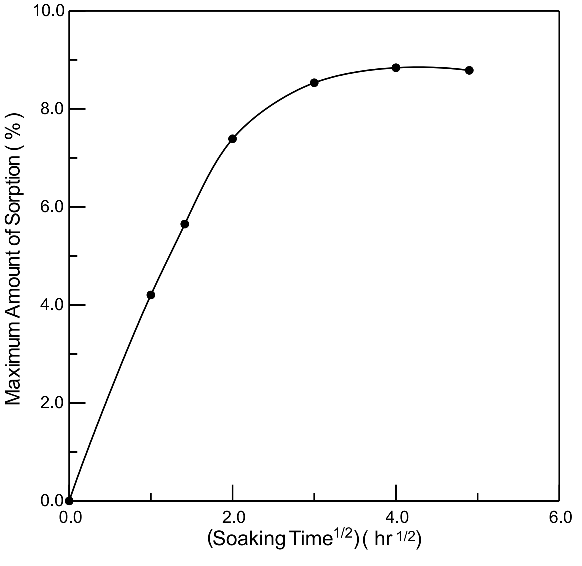

Fig. 3. Maximum amount of absorption of carbon dioxide into the PS matrix at various soaking times.

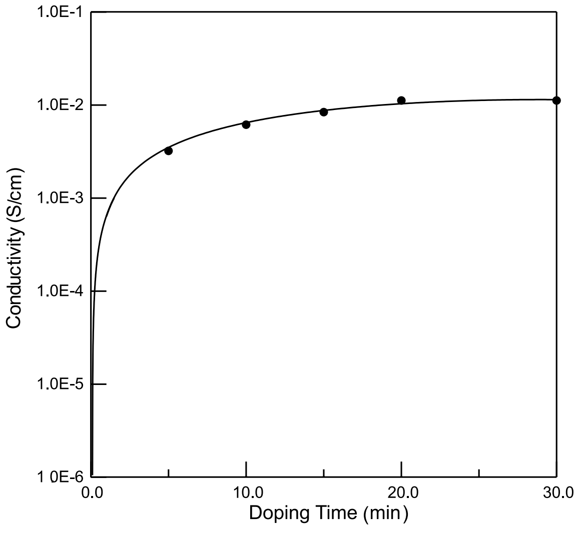

Fig. 4. Plot of the electrical conductivity of the PPy/PS composite against the doping time.

2.3. Characterization

Electrical conductivity was measured by four point probe method with a Zentech 502BC conductivity meter. The morphologies of the polymer composites were observed using a PHILIPS XL30 SEM. The atomic compositions of the composites were determined using an elemental analyzer (Perkin-Elmer 2400). Samplings of the analysis were prepared by scraping the surfaces of composites.

3. Results and discussion

Comparison of the electrical conductivity and EA analyses of the PPy/PS composites, resulting from two kinds of supercritical process with either oxidant impregnation or pyrrole impregnation is shown in Table 1. The first procedure was the same as described by Webb and Teja [13] where the host polymer PS was doped with oxidant before polymerizing with pyrrole monomer in $SCCO_2$. In the later procedure, the host polymer PS was blended with pyrrole monomer in $SCCO_2$ before doping and polymerizing in the oxidant solution. For comparison purposes, identical oxidizing agent of 0.15 M $FeCl_3$ in acetonitrile was used in both procedures. A lower conductivity about 2.09×10^{-6} S/cm was obtained for composites using oxidant impregnation. Applying the latter procedure in this study, however, much higher conductivities as well as nitrogen and hence PPy content were achieved, as shown in Table 1. Several experimental results can be used to explain the low electrical conductivity with procedures of oxidant impregnation as shown in Table 1. Firstly, the EA analysis shows less nitrogen content and hence fewer PPy resulting from this procedure. Secondly, the SEM image in Fig. 5(a) shows that the composite surface was only partially covered with PPy granule and the morphology exhibits a lot of pores caused by the desorption of CO_2 when it was vented. These factors could be eliminated by blending the host polymer with pyrrole in $SCCO_2$ before polymerizing in an oxidant solution, as we have done in this study to increase the conductivity.

Effects of the doping process are presented in this study. Fig. 5(b) and (c) show the comparison of the SEM images of composites with and without the doping process, respectively. The host polymer PS was transparent initially. Its color became milky white after blending with pyrrole in $SCCO_2$. During the doping process, the color of the blended host polymer finally changed to black. From the comparison of Fig. 5(b) and (c), it is shown obviously that the pyrrole molecules have been polymerized on the blend surface. A further investigation with elemental analysis has been made and the results are shown in Table 2. The smaller nitrogen content of the composite without doping, as shown in Table 2, indicates that the pyrrole or pyrrole oligomers may be carried out by CO_2 as it desorbed gradually from the blended host polymer. On the other hand, higher nitrogen content suggests that polymerization of pyrrole within the PS matrix proceeds when the blended host polymer was soaked in the oxidant solution. The amount of PPy in the composite was estimated from its nitrogen content. Less than 3 wt.% of PPy was observed in the composite that yields a conductive product. As cited in the literature [16], it needs about 15 wt.% of PPy in a PPy/polymer composite to reach a conductivity of 10^{-2} S/cm. The explanation for resulting a high conductivity with a low PPy content in this study might be owing to that PPy is concentrating on the surface of the composite [17]. As mentioned above, polymerization proceeded when the blended host polymer was soaking in the oxidant solution. At the same time, CO_2 was exuding together with the pyrrole monomer or oligomer from the blended host polymer. Polymerization occurred on the surface of the blend in presence of the oxidant solution.

Table 1
Electrical conductivity and elemental analysis of the polymer composites with different methods of preparation

Method of preparation	Conductivity (S/cm)	C (%)	H (%)	N (%)
Oxidant impregnation	2.09×10^{-6}	89.57	8.00	0.12
Pyrrole impregnation	1.21×10^{-3}	85.34	7.33	0.21

In this study, the operating temperature at 40 °C and pressure at 10.5 MPa were chosen as the blending condition, which was also used by previous investigators [13,18]. Density of CO_2 at this operating condition was estimated to be 14.17 kg mol/m^3 from the tables of thermodynamic properties of carbon dioxide [10]. The effects of temperature and pressure on the composite properties were investigated in this study where the density of carbon dioxide was kept constant. Two other temperatures at 30 and 50 °C were also chosen as the blending conditions. The corresponding pressures at these two temperatures are 7.95 and 13.14 MPa, which are evaluated from the Peng–Robinson equation of state [19] for CO_2 at the fixed density of 14.17 kg mol/m^3. The operation condition at 30 °C and 7.95 MPa is a state of $HPLCO_2$, whereas 50 °C and 13.14 MPa is in the supercritical region. Fig. 6 shows the dependence of the electrical conductivity of the composite on oxidant concentration. In this study, the blending process was operated at three temperature and pressure conditions with the same density of CO_2. Various concentrations of the oxidizing agent were used in the doping process. The conductivities of the composites formed at different operating conditions were measured, and the results are shown in Fig. 6. It is observed that the electrical con-

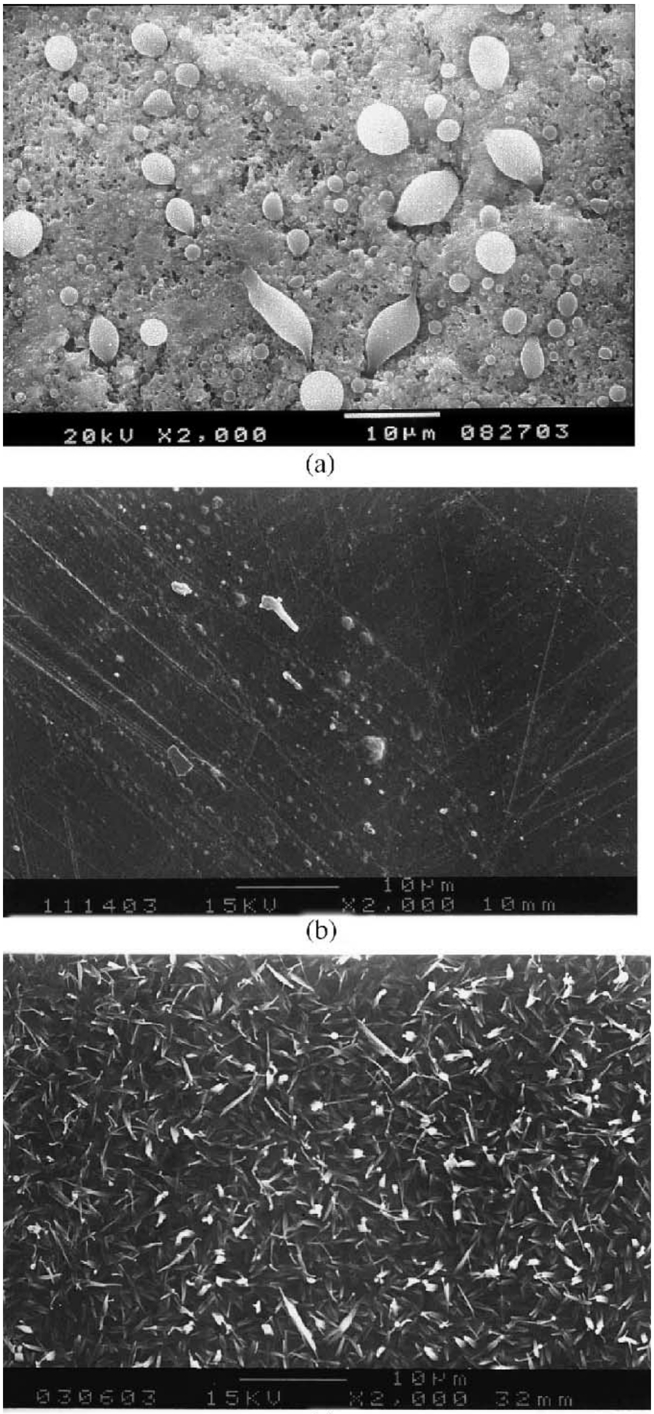

Fig. 5. SEM images of the host polymer (a) oxidant impregnation in 0.15 M $FeCl_3$ acetonitrile solution and polymerization in $SCCO_2$, (b) pyrrole impregnation in $SCCO_2$ without polymerization, (c) pyrrole impregnation in $SCCO_2$ and polymerization in 2.25 M $FeCl_3$ aqueous solution.

ductivity increases significantly when CO_2 changes from the high pressure liquid state to the supercritical fluid state. This result can be explained by the swelling efficiency in the blending period, which is a controlling

Table 2
Elemental analysis of the polymer composite

Method of preparation	C (%)	H (%)	N (%)
Blended host polymer without doping	91.93	7.78	0.06
Blended host polymer with doping in a 2.25 M $FeCl_3$ aqueous solution	88.56	6.61	0.54

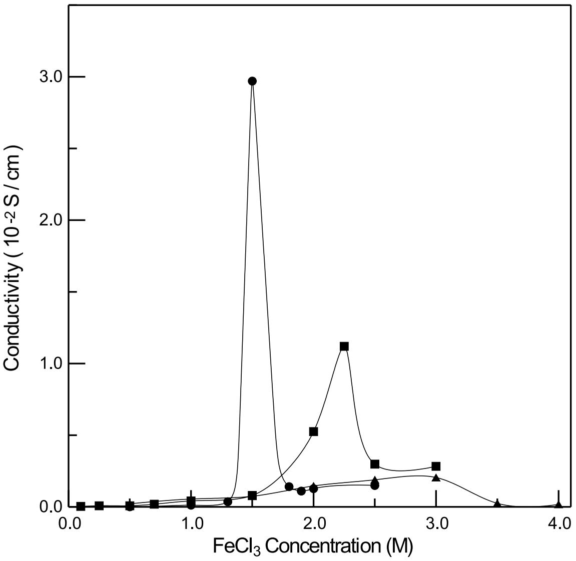

Fig. 6. Plots of the electrical conductivity against the concentration of $FeCl_3$. The blending conditions in CO_2 are at (a) (▲): 30 °C and 7.95 MPa, (b) (■): 40 °C and 10.5 MPa, (c) (●): 50 °C and 13.14 MPa.

factor for the structure and conductivity of the resulting composites. It is known that the polymer matrix can be swollen in carbon dioxide. The swelling effect, which is defined as the percentage change in volume of the polymer matrix, increases linearly with pressure until it reaches a limiting value [20]. On blending the host polymer with pyrrole in $SCCO_2$, a temperature above 40 °C should be employed to ensure a satisfactory rate of swelling [19]. The peak values of the measured conductivity at various operating conditions are listed in Table 3. The results confirm that the $SCCO_2$ is a suitable medium for the blending process. For the same density of CO_2 in the supercritical region, the result in Table 3 shows that the maximum electrical conductivity increases by increasing temperature and pressure from 40 °C and 10.5 MPa to 50 °C and 13.14 MPa. This phenomenon can be explained by the temperature effect on polymers. For most polymers, the glass transition temperature covers an interval about 10 to 20 °C. It was proved that the glass transition temperature would be lowered at a higher pressure due to the increasing solubility of CO_2 in the polymer [21,22]. The glass transition temperature of PS is 100 °C at normal pressure, and this value would be lower in our high pressure operation conditions. When a higher temperature is employed, the PS matrix will be closer to its glass transition state. In such a state, a number of voids in the polymer matrix will disappear and the accommodation of the PPy particles to form a conductive network becomes easier [23]. It is shown in Table 3 that the maximum electrical conductivity is about one order of magnitude greater in $SCCO_2$ than that in $HPLCO_2$. In the $SCCO_2$ region, a higher temperature and pressure condition favors the electrical conductivity. The maximum conductivity increases from 1.12×10^{-2} to 2.97×10^{-2} S/cm as the blending conditions change from 40 °C and 10.5 MPa to 50 °C and 13.14 MPa.

Table 3
Maximum electrical conductivity under various blending conditions

State	Temperature (°C)	Pressure (MPa)	$[FeCl_3]_{aq}$ (M)	Maximum conductivity (S/cm)
$HPLCO_2$	30	7.95	3.0	2.1×10^{-3}
$SCCO_2$	40	10.50	2.25	1.12×10^{-2}
$SCCO_2$	50	13.14	1.5	2.97×10^{-2}

Density of carbon dioxide is fixed at 14.17 kg mol/m^3.

4. Conclusion

An improvement of the operating procedures to synthesize a polymer composite of PPy and PS is presented in this study. It is shown that a much higher conductivity value is obtained by carrying out the blending in $SCCO_2$ and then treating the blended host polymers with an oxidizing agent. Elemental analysis indicates that polymerization proceeded when the blended host polymer was immersed in the oxidant solution. $SCCO_2$ has better swelling ability than $HPLCO_2$, which results in an increase in the conductivity of composites obtained using the supercritical fluid. The conductivity of the polymer composites is affected by the operating conditions in $SCCO_2$. For the same density of $SCCO_2$, an operation condition at higher temperature and pressure yields an increase in the conductivity of the composite.

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