

Supercritical Carbon Dioxide Assisted Preparation of Conductive Polypyrrole/Cellulose Diacetate Composites

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ABSTRACT: Supercritical carbon dioxide (SC-CO₂) has been used to assist the preparation of conductive polypyrrole/cellulose diacetate (PPy/CDA) composites by *in situ* chemical oxidative polymerization. The morphology and conductivity of resulted composites were investigated with scanning electron microscopy and four-probe method, respectively. With the assistance of strong swelling effect of SC-CO₂, composite films were obtained with a macroscopically homogeneous structure and conductivity up to 10⁻¹ S cm⁻¹ order of magnitude. Increasing the pressure of SC-CO₂

increased conductivity, while increasing the temperature decreased conductivity. For comparison, PPy/CDA composite was also prepared with conventional oxidative method in aqueous solution. From the viewpoint of conductivity and environmental protection, the SC-CO₂ method showed its superiority over the conventional one. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 4575–4580, 2006

Key words: supercritical carbon dioxide; polypyrroles; cellulose diacetate; conducting composites; morphology

INTRODUCTION

Electrically conductive polymers have drawn lots of attention because of their potential application in a variety of areas.^{1–3} Among them, polypyrrole (PPy) is considered as a most promising one for its relative high conductivity (~10² S cm⁻¹), facile preparation, and environmental stability.^{4,5} However, the poor mechanical property, infusibility, and insolubility of PPy prepared both electrochemically and chemically were proved to be the major obstacles to its technical application. One effective way to overcome these problems is to incorporate PPy with another insulating polymer to make conductive polymer composite.

PPy composite can also be prepared by using electrochemical or chemical methods. The electrochemical method usually results in conductive composites with good mechanical property and high conductivity,^{6–8} but ultra-thin films of the host polymers are necessary and only composites as large as electrode area can be produced, which greatly impedes its mass production. The chemical oxidative method can be carried out through different ways.^{9,10} Conductive composites have been made by sequentially immersing the matrix film into the monomer and oxidant solution, or dipping a preformed oxidant-impregnated matrix film

into the pyrrole vapor and solution. Apparently, this is a diffusion-controlled process and really time-consuming,^{11,12} usually it produces a surface-conducting composite with a sandwich structure.¹³

On the other hand, supercritical carbon dioxide (SC-CO₂, $T_c = 31.1^\circ\text{C}$ and $P_c = 7.37\text{ MPa}$) can be used for polymer synthesis and processing because of its peculiar properties.^{14–16} It is proved that SC-CO₂ possesses both high diffusion coefficient and near-zero surface tension, and so it can swell most polymers including those generally considered as solvent-resistant, and thus greatly enhances the infusion of penetrant. Additionally, simply changing temperature and pressure can tune the solvent strength of SC-CO₂ continuously over a wide range, thus adjusting the degree of polymer swelling and monomer partitioning. Therefore, the synthesis of conductive composites by using SC-CO₂ should have superiority over traditional methods mentioned earlier. Weiss and coworkers impregnated ferric triflate (oxidant) into polyurethane (PU) foam by using SC-CO₂, and obtained PPy/PU composite after pyrrole vapor phase polymerization.^{17,18} Tang et al. adopted a reverse process,^{19,20} where pyrrole was firstly impregnated into polystyrene matrix with SC-CO₂, and then the resulting matrix was soaked into FeCl₃ solution to fulfill the polymerization. However, in these studies, the formation of PPy composite was actually not accomplished in SC-CO₂, and the polymerization was still diffusion-controlled by either pyrrole vapor or FeCl₃ oxidant at atmospheric pressure. The composites obtained had a sandwich structure.

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In this article, cellulose diacetate (CDa), which as a good candidate for flexible conductive films, was chosen as the matrix of PPy/plastic composite. The PPy/CDa composites were *in situ* prepared in SC-CO₂ circumstance. For comparison, PPy/CDa was also made by using conventional chemical oxidation method. Here, the influence of temperature and pressure on the conductivity of the composite was investigated by correlating with the pyrrole adsorption process, the resultant PPy contents, and the morphology of the composite.

EXPERIMENTAL

Chemicals and materials

Pyrrole (purchased from Academy of Military Medicine Science, People's Republic of China) was distilled under vacuum and stored in a refrigerator at about 4°C before use. Anhydrous FeCl₃ (purchased from Beijing Chemical Reagent Company, People's Republic of China) and acetone (purchased from Beijing Chemical Factory, People's Republic of China) were used without further purification. CO₂ with purity of 99.95% was supplied by Beijing Huayuan Gas Inc., People's Republic of China and used as received. A commercial grade CDa was purchased from Shanghai Cellulose Acetate Factory, People's Republic of China, with the degree of substitution 2.45 determined by titration method.

Preparation of PPy/CDa composite

FeCl₃-containing CDa film was prepared by casting 30 mL of acetone solution containing 1.2 g of CDa and 2.4 g of anhydrous FeCl₃ in a petridish. After being placed under ambient condition till acetone vaporized away, the dish was further kept at 40°C under vacuum for 72 h. The freestanding film with about 0.3 mm thick was then cut into 2 × 3 cm² strips for further preparation. Each piece of the film contained about 0.001 mol of FeCl₃.

Method I

A high-pressure reaction vessel was used for the polymerization in SC-CO₂. Pyrrole monomer of 0.01 mol, which was excessive when compared with oxidant FeCl₃, was placed in the vessel along with a FeCl₃-containing CDa strip hung over it. The vessel was purged with low pressure CO₂ three times to replace the air, and then filled with more CO₂ to the desired pressure. After the treatment at the desired pressure and temperature for a certain period of time, the vessel was depressurized slowly. The specimen was transferred into a desiccator under an inert atmo-

sphere to desorb CO₂. The mass of PPy incorporated into the matrix was determined gravimetrically.

Method II

A FeCl₃-containing CDa strip was immersed in 25 mL of aqueous solution of pyrrole with 1 mol/L concentration (about 0.025 mol) at 40°C under N₂ atmosphere for various intervals of time from 20 min to 12 h. Within a few minutes, the color of the film changed from yellow to black, indicating a quick occurrence of PPy polymerization.

For characterization, the strips after polymerization were soaked and washed in fresh methanol and deionized water, respectively, several times to remove unreacted FeCl₃ and other by-products till the solution became colorless. Then, the strips were dried at 40°C under vacuum for 48 h.

Pyrrole monomer absorption by CDa matrix in SC-CO₂

The pyrrole absorption by pure CDa matrix in SC-CO₂ circumstance was investigated according to the method adopted by Berens et al.²¹ The experimental procedure was almost the same as method I except that after desired absorption time, the vessel was quickly depressurized and the sample transferred to a high precision balance within 45 s. Then, the desorption process was recorded. When most CO₂ diffused away, the weight of the sample kept constant. Therefore, the remaining mass gain was identified as an approximation of pyrrole absorbed at the end of absorption.

PPy composite characterization

The conductivity was measured by a standard four-probe method. To obtain good surface contact, very smooth coating of silver paste to the touch point was performed. Fourier transform infrared (FTIR) spectroscopy experiments were performed by using a Perkin-Elmer 180 instrument with a resolution of 4 cm⁻¹. PPy composites were fractured in liquid nitrogen, coated with a ~10 nm thick layer of gold on the fractured surface, and observed with a Hitachi S-530 scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Comparison of polymerization methods

For both preparation methods, the formation of PPy was obvious because the color of the CDa film changed from yellow to black. Figure 1 shows the FTIR spectra in the region from 2000 to 800 cm⁻¹ for pure CDa (a) and PPy/CDa prepared with method I

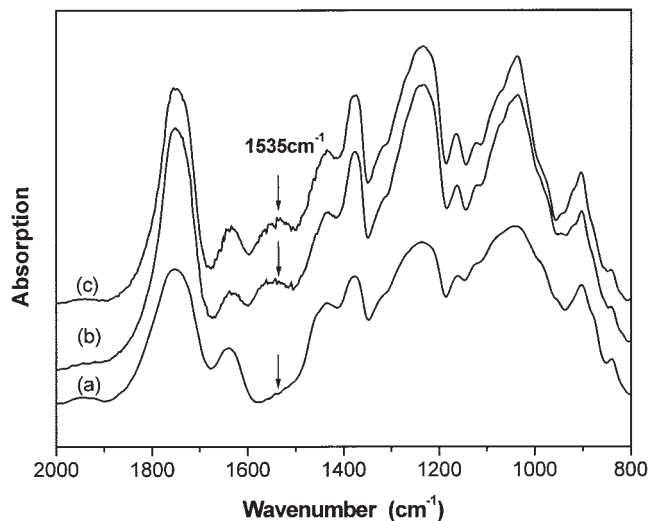


Figure 1 FTIR spectrum for pure CDA (a), PPy/CDA composites prepared in SC-CO₂ (b), and in aqueous solution (c).

(b) and II (c). Though most absorption bands of PPy are overlapped with CDA, the 1535 cm⁻¹ peak assigned to the pyrrole ring stretching vibration appears in both Figures 1(b) and 1(c), which also indicates the existence of PPy in the composites.

The surface and fracture SEM micrographs of PPy/CDA composites prepared with both methods are shown in Figure 2, the polymerization time was 6 h. It is evident that different polymerization route brings substantial difference to the morphology of composite. For composites prepared in aqueous solution, typical cauliflower-like mound²² of PPy layer is seen on the

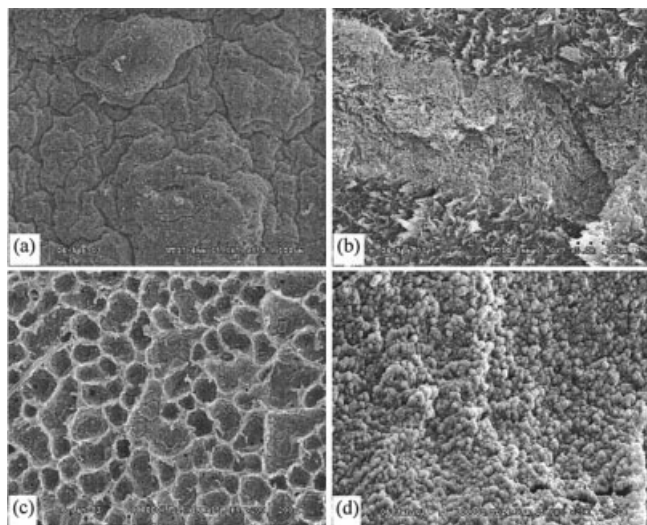


Figure 2 SEM micrographs of the PPy/CDA composites: surface (a) and cross section (b) morphology of the composite prepared in aqueous solution for 6 h; Surface (c) and cross section (d) morphology of the composites prepared in SC-CO₂ at 8 MPa/40°C/6 h.

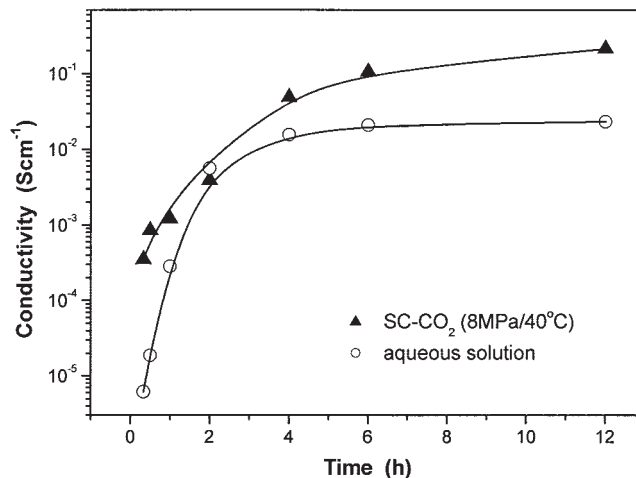


Figure 3 Conductivity of PPy/CDA composites prepared in SC-CO₂ and aqueous solution as a function of polymerization time.

surface of CDA films, as shown in Figure 2(a), and a sandwich structure within the inner section, as shown in Figure 2(b). Actually, for shorter immersing time, the sandwich structure of black PPy/CDA layer outside and gray CDA inside was observed directly. This was the result of the reaction occurring only at the place where pyrrole monomer contacted with the oxidant FeCl₃; therefore, the polymerization of pyrrole was confined to the outer layer of the matrix at first. Consequently, further diffusion of pyrrole into the film was prevented by the compact and rigid PPy layer formed on the surface. In the presence of SC-CO₂, the whole cross section of the macroscopically homogeneous PPy/CDA composite obtained with 6 h of polymerization was black [Fig. 2(d)]. The strong swelling effect of SC-CO₂ made it easier for pyrrole to penetrate into the core part of the matrix film, in comparison with aqueous solution method. But, CO₂ diffused out of the film rapidly by releasing the pressure at the end of polymerization. Subsequently, the de-swelling effect caused the shrinkage of the composite and induced the formation of net-like wrinkles on the film surface, as shown in Figure 2(c).

Figure 3 compares the influence of polymerization time on the electrical conductivity for the different preparation methods. For method I, the experimental condition (8 MPa/40°C) was just above the critical point of CO₂. However, the strong swelling effect of SC-CO₂ made pyrrole diffuse into and react within the matrix easily, resulting in a conductivity of 3.6×10^{-4} S cm⁻¹ with only 20 min of polymerization, about 2 orders of magnitude higher than that of method II. Obviously, both composites are only surface conductive at this stage. With the progressing of polymerization, more PPy penetrates further into the core part of the films. Consequently, both composites gradually

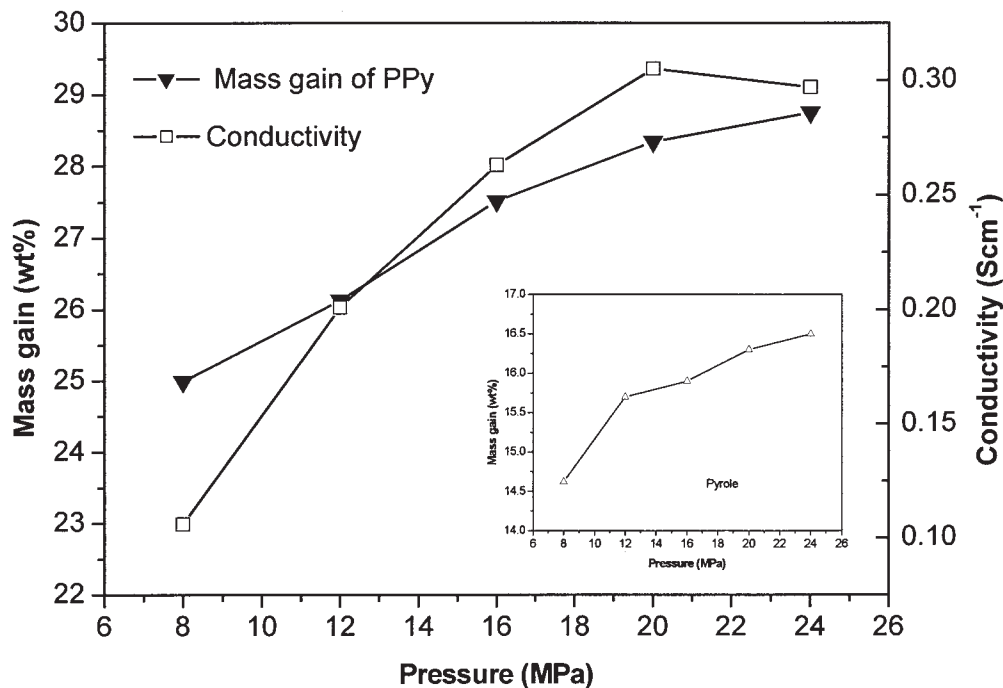


Figure 4 PPy contents and the conductivity of the PPy/CDa composites as a function of SC-CO₂ pressures for 40°C/6 h. Inset: pyrrole absorption versus pressure of SC-CO₂ for 40°C/6 h.

change from surface conductive to bulk conductive, and both conductivity curves level off with the increase of time. At the end of polymerization, the difference in conductivity is not so significant as at the beginning. Nevertheless, the conductivity of composite prepared in SC-CO₂ reaches 0.21 S cm⁻¹ after 12 h of polymerization, which is about 1 order of magnitude higher than that of composite prepared in aqueous solution. SC-CO₂ played a positive role in the formation of conductive path such as the unique net-like PPy layer on the surface.

Effects of temperature and pressure of SC-CO₂ on PPy/CDa composites

The polymerization of PPy/CDa composites under SC-CO₂ included two steps: (1) pyrrole monomers dissolved in CO₂ diffused into the matrix; (2) pyrrole polymerized chemically with oxidant FeCl₃ to form PPy as soon as they contacted within the matrix. It is widely recognized that the diffusion process of monomer is the controlling step during the oxidative polymerization of pyrrole. The temperature and pressure of SC-CO₂ have remarkable influence on the solvent strength, which in turn affect diffusion process of oxidative polymerization and the properties of the resultant PPy/CDa composites.

The inset of Figure 4 shows the absorption of pyrrole by CDa matrix at different pressure in SC-CO₂ at 40°C for 6 h. It is evident that with the increase of pressure, the pyrrole content had a continuous in-

crease, namely, from 14.6 to 16.5 wt % while the pressure increased from 8 to 24 MPa. The solvent strength of CO₂ increased with increasing pressure, resulting in higher degree of swelling effect on CDa and higher solvent capacity on pyrrole monomer. Both factors favored the impregnation of pyrrole into CDa matrix. On the other hand, the antiplasticization effect caused by the static pressure of CO₂ fluid impeded the diffusion of pyrrole in the CDa matrix at elevated pressures. Therefore, it was observed that the pyrrole absorption increased initially and then leveled off at higher pressures.

The relationship between pressure and pyrrole absorption would consequently affect the contents of PPy in the resulting composites after polymerization. A comparison of pyrrole absorption with mass gain of PPy in the CDa matrix indicated that the incorporation of pyrrole was a dynamic process during the polymerization in SC-CO₂, i.e., pyrrole diffused into the matrix was consumed immediately when it contacted with FeCl₃ and the gradient of concentration driving the diffusion of more pyrrole was maintained. In fact, the mass gain of PPy in PPy/CDa composite was about twice absorption of pyrrole in the CDa film under the same condition. Meanwhile, the PPy content had an increase about 4 wt % with increasing pressure from 8 to 24 MPa, as shown in Figure 4, due to the higher swelling effect of SC-CO₂ at higher pressure. Coupling with the effect that higher pressure favored the even distribution of conductive PPy component within the

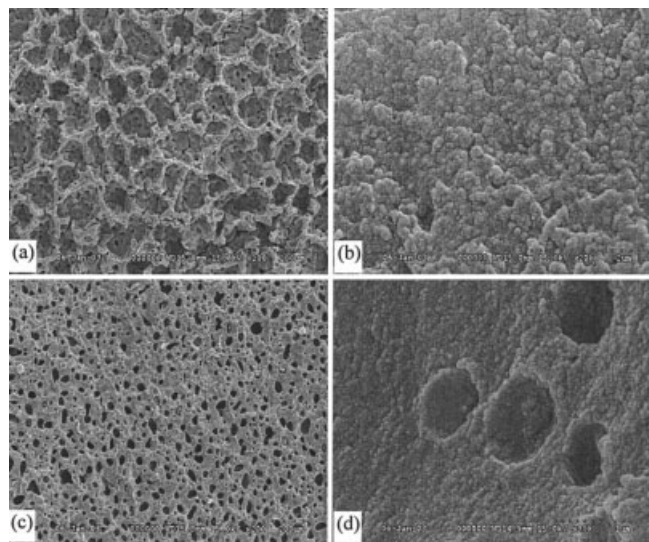


Figure 5 SEM micrographs of the PPy/CDA composites made under different conditions: surface (a) and cross section (b) morphology of the composites prepared in SC-CO₂ at 24 MPa/40°C/6 h; Surface (c) and cross section (d) morphology of the composites prepared in SC-CO₂ at 8 MPa/80°C/6 h.

composite, the conductivity showed a notable increase with the pressure, and at 20 MPa it reached a maximum value, 0.31 S cm⁻¹, triple the value at 8 MPa. The little drop of conductivity at 24 MPa was due to the worsened surface morphology as shown in Figure

5(a). Comparing with the surface morphology for the composite prepared under 8 MPa/40°C shown in Figure 2(a), there are some cracks appearing on the surface of PPy/CDA composite when the pressure was increased to 24 MPa, which could impair the conducting path and thus lead to a lower conductivity. In general, the conductivity increases as the percentage of PPy increases in the composite.

The polymerization temperature played a negative role on the absorption of pyrrole. Figure 6 gives the results of polymerization under different temperatures at 8 MPa/6 h. The density of CO₂ gets smaller and thus leads to weaker solvent strength at elevated temperatures. In correspondence with the pyrrole absorption process, PPy contents in PPy/CDA composites show a steady decrease with the increase of temperature, but the mass gain of PPy is still larger than the pyrrole absorption because of the dynamic diffusion during pyrrole polymerization. Figure 6 also gives the influence of temperature on the conductivity of PPy/CDA composites. Here, the experiments were not conducted above 80°C because of the serious deformation of the CDA film under those conditions, because of the dramatic plasticization effect of SC-CO₂. With the increase of temperature, conductivity decreases obviously from the order of 10⁻¹ to 10⁻³ S cm⁻¹. There were two key factors to decrease the conductivity: first, the PPy content in the composite, which decreased with increasing temperature, as

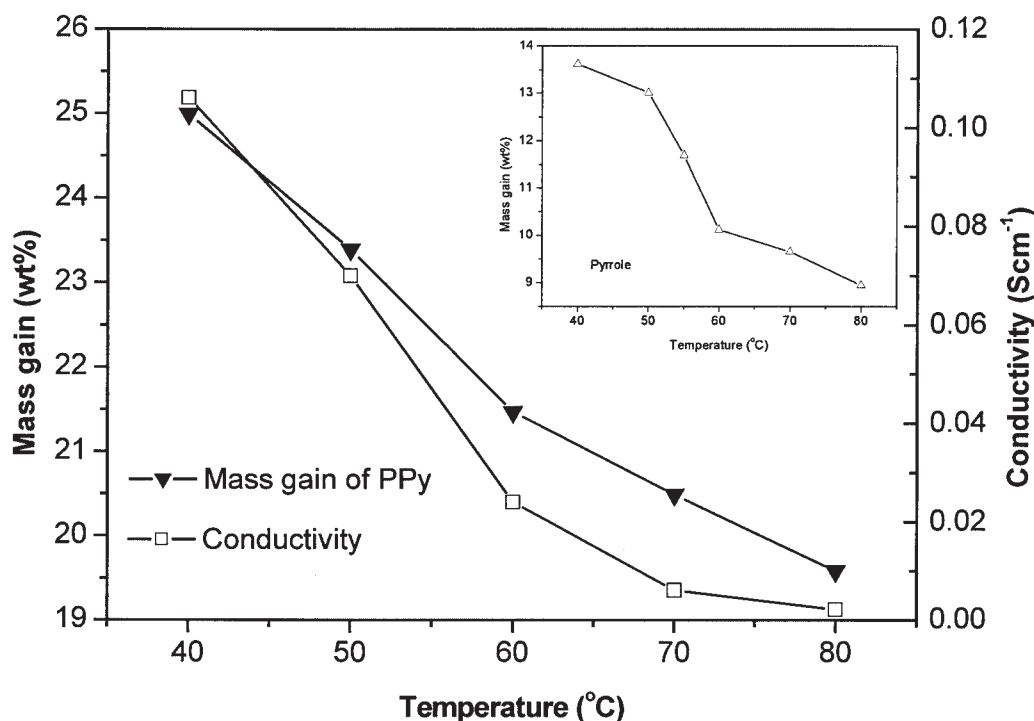


Figure 6 PPy contents and the conductivity of the PPy/CDA composites as a function of SC-CO₂ temperatures for 8 MPa/6 h. Inset: pyrrole absorption versus temperature of SC-CO₂ for 8 MPa/6 h.

shown in Figure 5; second, both the surface and cross section morphology, which impaired the conductivity of the composite prepared at higher temperatures. For the composites shown in Figures 2(c) and 5(c), the temperature was the only difference in the polymerization conditions. It is obvious that there are large amounts of cavities with the diameter in the range of 10–30 μm scattered on the surface, and microcells with diameter about 1 μm uniquely scattered in the cross section, respectively, of the sample obtained under 80°C [Fig. 5(c)]. Cavities and microcells were developed upon the release of pressure after the formation of PPy conductive paths within the matrix during the polymerization process; therefore, the growing of cavities and microcells cut off part of the conductive paths and resulted in a lower conductivity.

CONCLUSIONS

The PPy/CDA composites were prepared by *in situ* polymerization in the presence of SC-CO₂. With the assistance of strong swelling effect of SC-CO₂, pyrrole monomer efficiently penetrated into the FeCl₃-containing CDA film; thus, the obtained composite had a homogeneous structure and high conductivity. Comparison experiments proved that this method has advantages over traditional chemical oxidative polymerization in aqueous solution: (1) because of the strong swelling effect of SC-CO₂, more pyrrole monomers effectively penetrated into the CDA matrix and a higher conductivity could be expected within a shorter polymerization time; (2) SC-CO₂ brought a substantial influence on the morphology of PPy/CDA composite with net-like wrinkles of PPy layer appearing on the surface and macroscopically homogeneous structure within the film; (3) CO₂ is not toxic, not flammable, consequently environmentally friendly and cheap.

The influence of pressure and temperature of SC-CO₂ on the conductivity were correlated with the pyrrole absorption process and the morphology of the resultant composite film. With the increase of pressure from 8 to 20 MPa, the content of PPy in the PPy/CDA composites was increased, indicating that more monomers were absorbed by the matrix, resulting in a higher conductivity. However, the conductivity of

composite decreased by further increasing pressure to 24 MPa because of the cracks induced at higher pressure on the surface of the matrix. The temperature played a negative role on the pyrrole absorption process, together with microcells formed within the composite and cavities on the surface under higher temperature. Both factors lowered the conductivity of PPy/CDA composites with the increase of temperature.

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