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Polypyrrole–polypropylene composite films: preparation and properties

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Polypyrrole–polypropylene conducting polymer composite films with good mechanical properties and high electrical conductivity were prepared using a two-direction permeation/diffusion polymerization method. The oxidant used was iron(III) chloride. Polypropylene microporous films prepared by the biaxial stretching technique were used as the matrix material. The maximum conductivity of these composite films, 6.0 S cm^{-1}, is of the same order of magnitude as that of pure polypyrrole, 4.5 S cm^{-1}, which was synthesized by chemical oxidation of pyrrole monomer in aqueous solution. The composite films exhibit quite uniform mechanical properties in the film plane. Young's modulus is in the range 0.4–0.8 GPa, tensile strength 40–85 MPa and elongation at break 90–200%, maintaining the mechanical properties of polypropylene in the composite. Polymerization conditions, including reaction time, reaction temperature and concentrations of the pyrrole and $FeCl_3$ solutions, have a great influence on the structure and properties of the composite films. The structure of the conducting polymer in the composite films was characterized by X-ray photoelectron spectroscopy and the surface morphology of the films was investigated using scanning electron microscopy. Two kinds of surface structure were observed, one is a loose particle structure and the other is a compacted surface structure.

(Keywords: conducting polymer; polypyrrole; polypropylene)

INTRODUCTION

Electrically conducting polymers have received a great deal of attention because of their potential applications, such as in rechargeable batteries, gas separation membranes, antistatic agents and electroluminescent diodes[1–4]. However, their poor mechanical properties and processability constitute major obstacles to their extensive applications[5]. To improve the mechanical properties and processability many kinds of method have been used, including the introduction of long alkyl groups into the main chain[6,7], the synthesis of soluble precursors[8,9], the preparation of conducting polymer composites[3], and so on[6–10]. Among these methods, the preparation of composites is the easier and more effective.

In recent years many kinds of conducting polymer composites based on polypyrrole (PPy) have been prepared. The matrix polymers that have been used include polyethylene[10,11], poly(vinyl chloride)[12,13], poly(ethylene oxide)[14,15], poly(vinyl alcohol)[16–18], poly(tetrahydrofuran)[19], polystyrene (PPy–PSt)[20] and polyurethane[21]. In our laboratory a new kind of isotactic polypropylene (PP) microporous film, prepared by the biaxial stretching technique, was developed[22]. These PP microporous films are characterized by good and uniform mechanical properties in the film plane, high porosity and high gas permeability. What is more, the pores in the films are connected with each other, resulting in the formation of a large pore network. This pore network is very useful for the formation of a continuous network of conducting polymer. In previous work the authors developed a method, using this PP microporous film as the matrix material, to prepare polyaniline-based conducting polymer composites with combined good mechanical properties and high conductivity[23,24]. Our results indicated that the biaxially stretched PP microporous film is an excellent matrix material for this purpose. In the present paper, the preparation and characterization of PPy/PP composite films are described.

EXPERIMENTAL

Materials and measurements

Pyrrole (Fluka), iron(III) chloride hexahydrate (AR grade) and dodecylbenzene sulfonic acid sodium salt (AR grade) used in this work were purchased from commercial sources and were used without further purification. PP microporous films were prepared by biaxial stretching in our laboratory. The average pore size in the obtained microporous films was ~ 0.05 μm,

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and the porosity was around 35%[22]. The thickness of the PP microporous films used in this work was ~ 25 μm.

X-ray photoelectron spectroscopy (X.p.s.) was performed using a PHI 53000 X-ray photoelectron spectrometer (Perkin–Elmer), with data acquisition and treatment being carried out by computer. Mechanical properties of the composite films were measured on an Instron 1122 testing machine. Morphological observation was carried out using a Hitachi S-540 scanning electron microscope. Electrical conductivities were determined by the conventional four-probe method. Before the conductivity measurement the loose particle layer was stripped off from the surfaces of composite films.

Preparation of composite films

PPy/PP composite films were prepared by chemical oxidative polymerization of pyrrole, which is similar to the procedure described elsewhere[23,24]. A typical procedure is described below. The polymerization was carried out at 10°C in a U-type reactor which consisted of two L-shaped tubes and a piece of PP microporous film fixed between the two tubes. A 0.2 M aqueous solution of pyrrole containing 3% (w/w) dodecylbenzene sulfonic acid sodium salt was poured into one of the L-shaped tubes and a 0.5 M aqueous solution of $FeCl_3$ was into the other. After reaction for 60 min, the film was removed from the reactor and imbibed in acetone for 8 h and then imbibed in distilled water for 8 h. Finally the film was dried in vacuum at 50°C for 24 h. By controlling the reaction time, reaction temperature and concentration of the pyrrole and $FeCl_3$ solutions, conductive PPy/PP composite films with different structures and properties can be obtained.

RESULTS AND DISCUSSION

Characterization of the structure of PPy/PP

Figures 1a and *b* show, respectively, the wide survey X.p.s. spectra of PPy/PP composite films on the $FeCl_3$

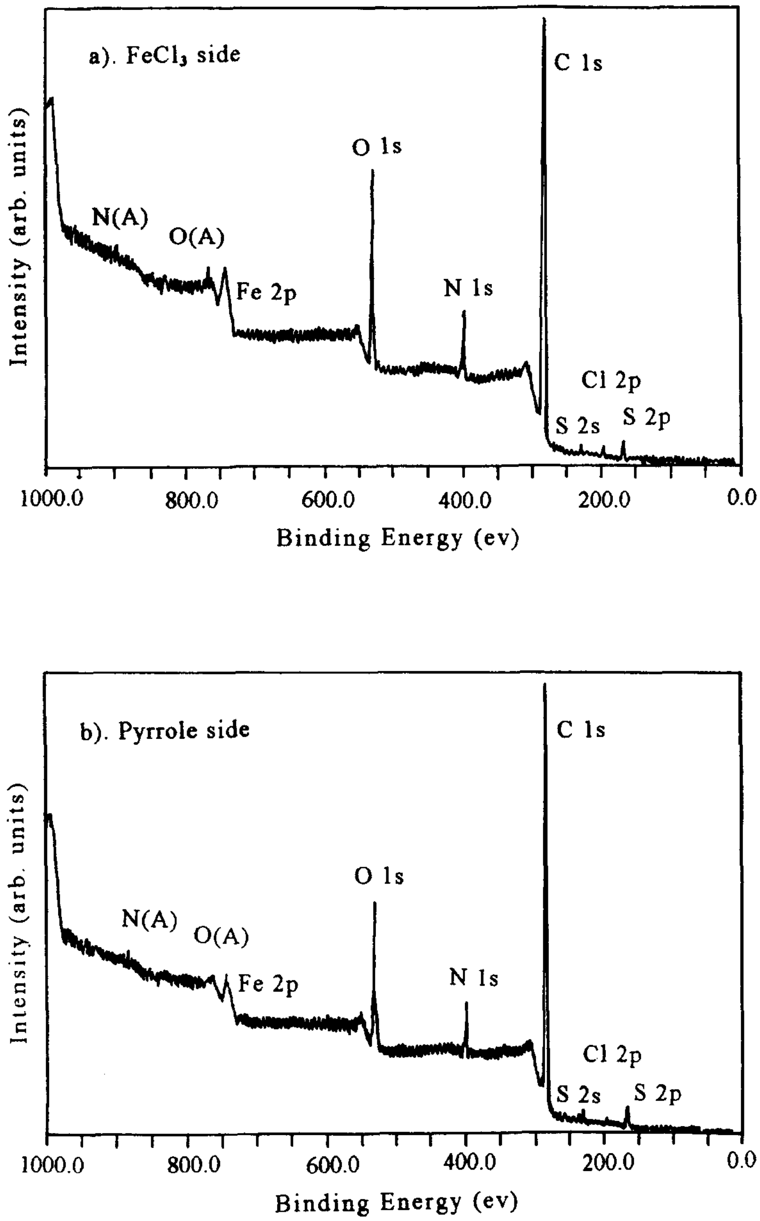

Figure 1 Wide survey X.p.s. spectra of PPy/PP composites: (a) $FeCl_3$ solution side; (b) pyrrole solution side

Table 1 X.p.s. binding energies for Cl_{2p} and N_{1s}

Element	Binding energy[a] (eV)	Content (%)	$N^+/(N^+ + N)$	$-Cl/(N^+ + N)$
Monomer side				
N	399.7	4.65	0.21	
	401.5	1.27		
-Cl	201.6	0.11		0.019
Cl^-	198.8	0.2		
Oxidant side				
N	399.6	5.34	0.22	
	401.4	1.54		
-Cl	201.4	0.34		0.049
Cl^-	198.5	0.47		

[a] For chlorine, the binding energy is the value of $Cl_{2p_{3/2}}$

solution side and the pyrrole solution side. The peak position of different elements (i.e. the binding energies) obtained from *Figure 1* are summarized in *Table 1*. The data in *Figure 1* show that, besides carbon and nitrogen, chloride, *iron* and *sulfur* are also present in the surfaces of composite films, both on the $FeCl_3$ solution side and on the pyrrole solution side of the film.

Figure 2 shows the X.p.s. core-level spectra of Cl_{2p}. The Cl_{2p} peak can be decomposed into two spin-orbit split doublets ($Cl_{2p_{3/2}}$ and $Cl_{2p_{1/2}}$), with binding energy for $Cl_{2p_{3/2}}$ peaks located at 198.8 and 201.6 eV. This reasonably indicates that the chlorine incorporated exists in two distinct states. The former corresponds to Cl bonding with iron and the latter corresponds to Cl covalently bonding with the pyrrole rings[18]. Therefore, in PPy, Cl has been introduced into some of the pyrrole rings. The amount of chloro-substituted rings can be calculated from the results of X.p.s. and is listed in the last column of *Table 1*. The results indicate that the chloro-substitution on the surface is twice as high on the $FeCl_3$ solution side than on the pyrrole solution side. It has been reported[3,25–27] that the conductivity of polyaniline or polypyrrole will decrease when substituents are introduced on phenyl or pyrrole rings. For example, the conductivities of polyaniline, polytoluidine and polychloroaniline are $\sim 10^0$, $\sim 10^{-2}$ and $\sim 10^{-4}$ S cm^{-1}, respectively[25–27]. This can be explained by the torsional and electronic effects (electron-donating and electron-withdrawing) of the substituents[27,28]. This is the main

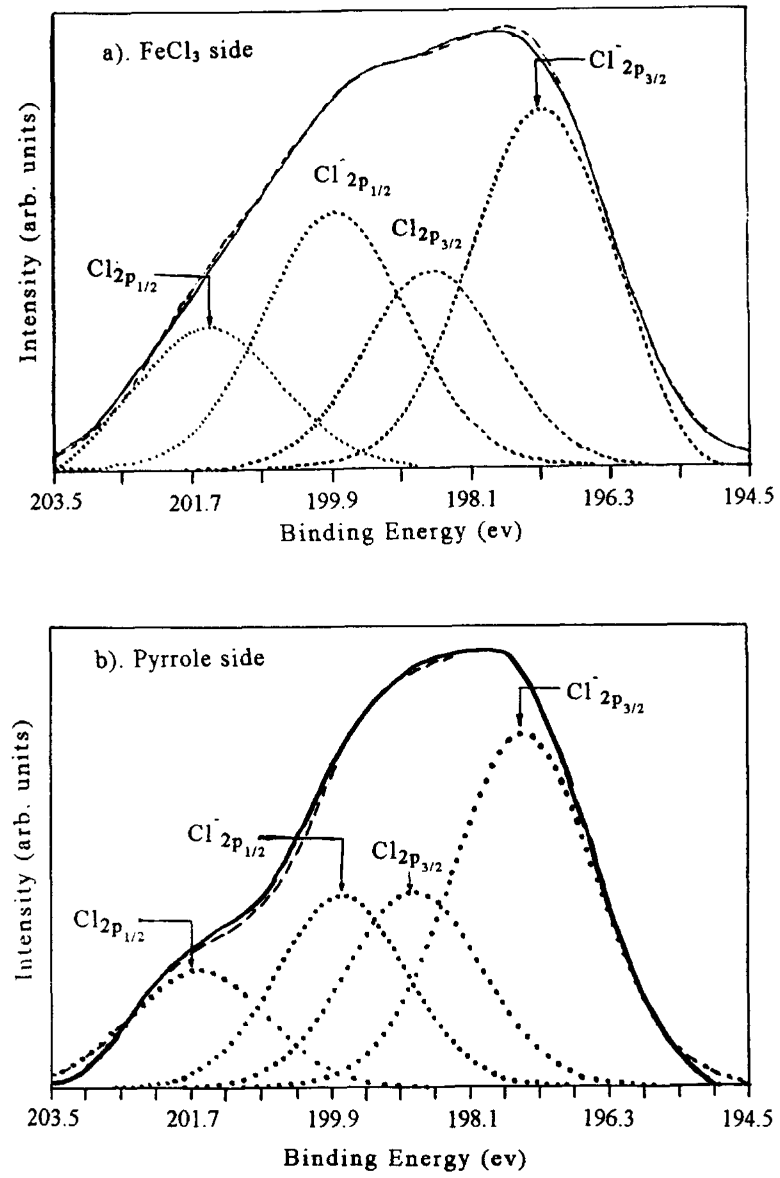

Figure 2 Cl_{2p} X.p.s. core-level spectra of PPY/PP composites: (a) $FeCl_3$ solution side; (b) pyrrole solution side

reason why the conductivity of the PPy/PP composite film on the $FeCl_3$ solution side is lower than that on the pyrrole solution side as shown in *Figures 5* and *6*.

The N_{1s} peak can be decomposed into two peaks (*Figure 3*), indicating that there are two nitrogen species in the PPy. The peak located at 399.7 eV corresponds to the nitrogen in neutral pyrrole rings, and the peak located at 401.5 eV corresponds to the nitrogen in positively charged pyrrole rings. The doping extent, $N^+/(N + N^+)$, can be calculated according to the area of the two peaks. The results (*Table 1*) show that there is almost no difference in doping extent (21% and 22%) between the two sides of the film; the doping extent on the $FeCl_3$ solution side is only 1% higher than that on the pyrrole solution side. During the polymerization process the monomer solution and the oxidant solution permeate into the host film along the tortuous pore network from two sides of the film. The mixing of monomer and oxidant in the boundary regions of the two solutions due to molecular diffusion may result in oxidation polymerization of the monomers. The concentrations of $FeCl_3$ on the two sides of the PP film might therefore be greatly different during polymerization. However, the difference of oxidation state (i.e. doping extent) on the two sides of the film is very small. This means that in the preparation of PPy/PP using $FeCl_3$ as oxidant, the concentration of the $FeCl_3$ solution has very little influence on the doping extent under these conditions. This is different from the results of Martin and co-workers[29].

Figure 4 shows scanning electron micrographs of the composite films. Variant morphologies on the two sides of the films were observed. On the $FeCl_3$ solution side the composites exhibited a compacted surface structure, whereas on the pyrrole solution side a loose particle structure was formed with many pores on each particle. The average diameters of the particles and pores are ~ 3 and 0.1 μm, respectively.

Influence of polymerization conditions on room temperature conductivities

The polymerization process can be characterized by the time dependence of the electrical conductivity of the composites. *Figure 5* shows typical experimental data with $FeCl_3$ as the oxidant. The conductivity of the

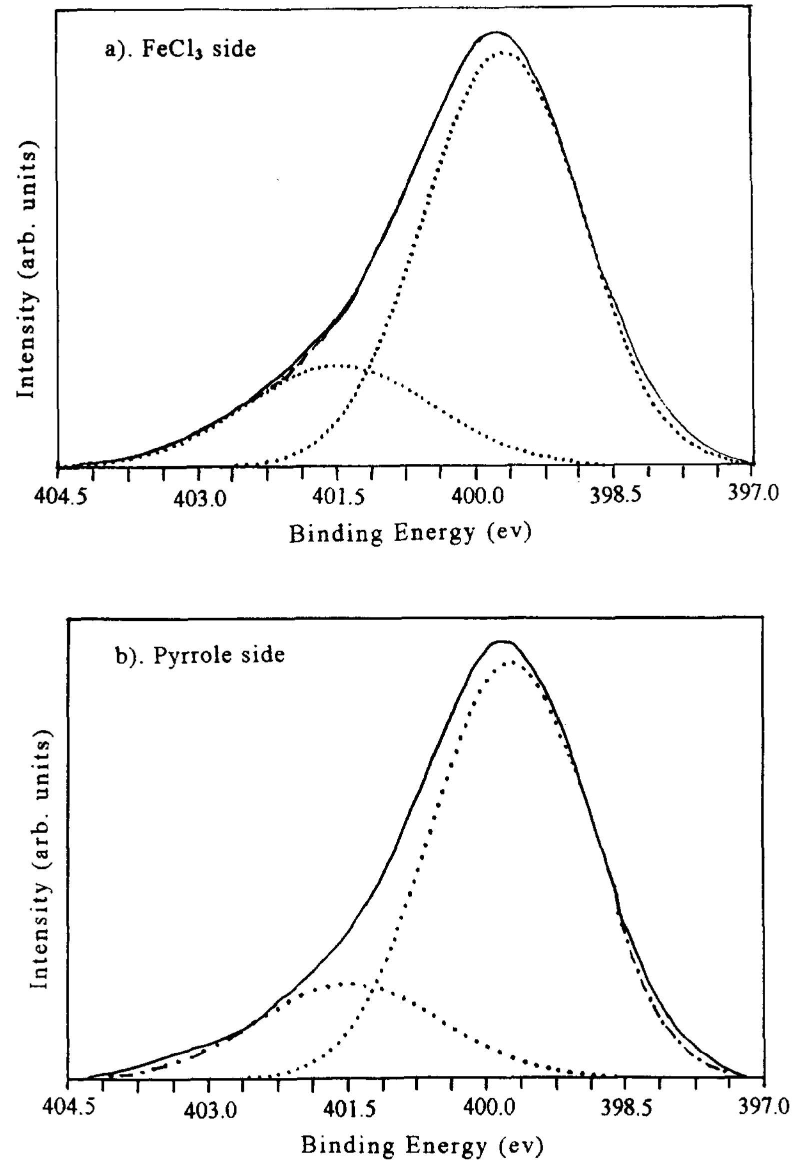

Figure 3 N_{1s} core-level spectra of PPy/PP composites: (a) $FeCl_3$ solution side; (b) pyrrole solution side

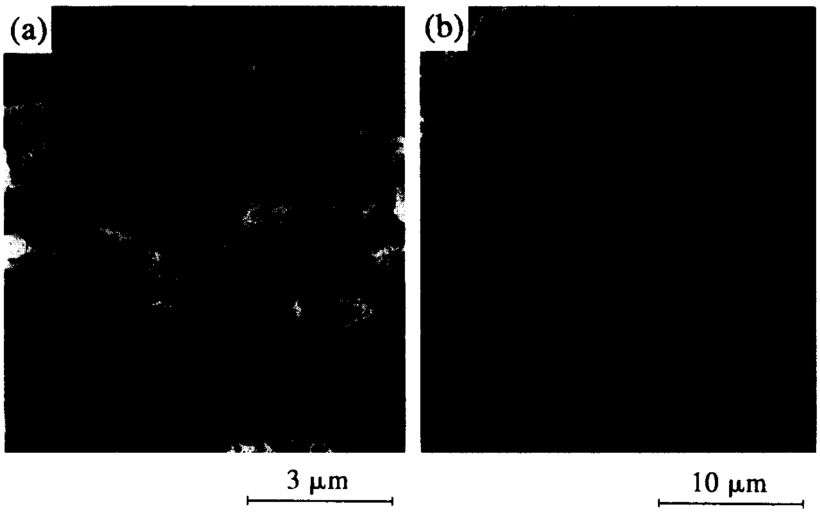

Figure 4 Scanning electron microphotographs of PPy/PP composite films: (a) $FeCl_3$ solution side; (b) pyrrole solution side

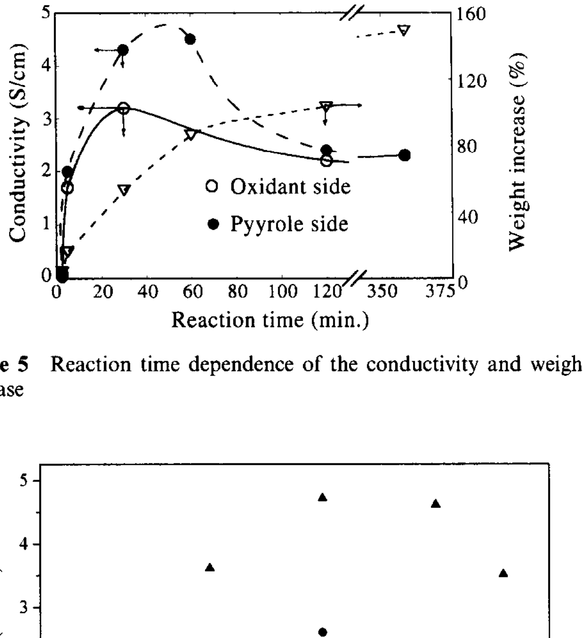

Figure 5 Reaction time dependence of the conductivity and weight increase

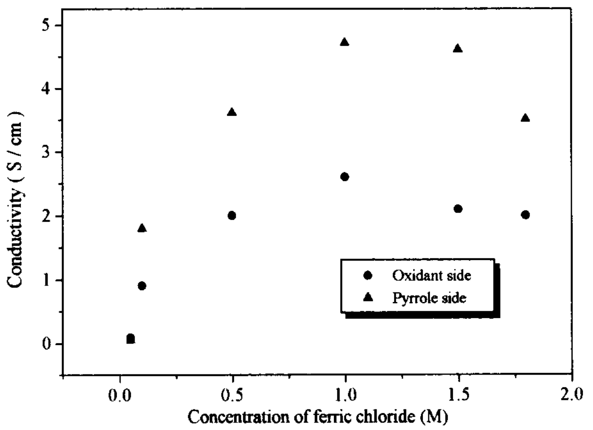

Figure 6 Influence of $FeCl_3$ concentration on the conductivity of composite films

composites increases rapidly with reaction time in the initial stage, and then exhibits a maximum at about 50 min. Measurements on both sides of the composites show the same tendency. However, the conductivity measured on the $FeCl_3$ solution side is lower than that on the pyrrole solution side and has a maximum at about 30 min. The time dependence of the weight increase during the polymerization process is given in *Figure 5*. The weight increase at 2.5 min is only about $\sim 4.0\%$, whereas at this stage the electrical conductivity of the composite has become quite high compared with that of the PP microporous film. This may imply that a continuous polypyrrole network is first formed on the surface of the PP microporous film, including the inner surface and the outer surface. At times of 20–60 min the weight increase is around 30–80%, the thickness increase is $> 14\%$ and the conductivity is of the same order of magnitude as that of pure PPy powder ($4.5\,\mathrm{S\,cm^{-1}}$ synthesized by chemical oxidative polymerization of pyrrole. The density of PPy powder is $\sim 1.4\,\mathrm{g\,cm^{-3}}$ (ref. 29) and the porosity of the PP microporous film is $\sim 35\%$. Therefore, at reaction times above 20 min, the surfaces of the microporous film are well coated by highly conductive PPy layers and a continuous PPy network is established within the microporous film.

The concentration of $FeCl_3$ and pyrrole solutions has great influence on the conductivities of the composite films. *Figure 6* shows the relationship between conductivity on both sides of the composite film and concentration of the $FeCl_3$ solution. The concentration of pyrrole solution used here was 0.2 M. The conductivity has a low value at low $FeCl_3$ concentration and increases with increasing $FeCl_3$ concentration. When the concentration of the $FeCl_3$ solution is > 0.05 M the conductivity of the specimen is $> 10^{-1}\,\mathrm{S\,cm^{-1}}$, implying that the conductive network has formed in this case; when $FeCl_3$ concentration > 0.5 M the conductivity of the specimen becomes $> 2\,\mathrm{S\,cm^{-1}}$ and does not vary obviously with further increases of $FeCl_3$ concentration.

Figure 7 shows the influence of PPy concentration on the conductivity of the composites. Here the concentration of $FeCl_3$ solution was 0.5 M. The maximum value of conductivity is $6.8\,\mathrm{S\,cm^{-1}}$.

The reaction temperature was also found to have an influence on the electrical properties of the composites. *Table 2* gives the results obtained in the temperature range of 1.5–50°C; a 0.2 M pyrrole solution and a 0.5 M $FeCl_3$ solution were used in these experiments. The conductivity of the composites increased with decreasing temperature, which is in contrast with the results observed in the preparation of polyaniline/polypropylene (PANI/PP)[23]. This difference in reaction temperature dependence of conductivity between PANI/PP and PPy/PP composites corresponds to the difference

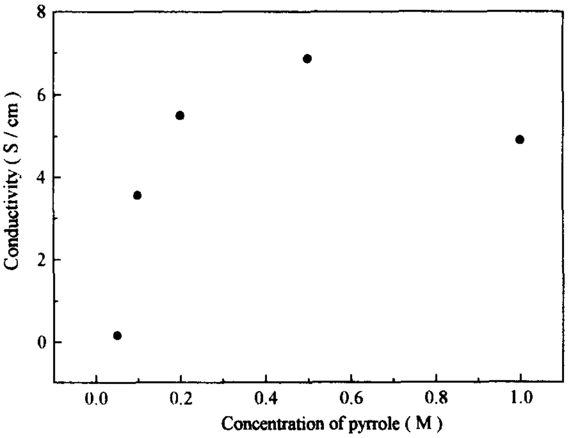

Figure 7 Pyrrole concentration dependence of the composite conductivity

Table 2 Influence of polymerization temperature on conductivity of the composite films[a]

Polymerization temperature (°C)	Conductivity ($S\,cm^{-1}$)	Weight increase (%)	Thickness increase (%)
1.5	6.7	54.3	44
10	5.7	85.9	159
30	3.8	86.7	63
50	0.6	68.5	58

[a] Reaction time, 60 min; concentration of pyrrole, 0.2 M; concentration of oxidant, 0.5 M

Table 3 Mechanical properties of PPy/PP composite films

	PP microporous films	PPy/PP composite films[a]	Pure PPy films[30]
Young's modulus (GPa)	0.4–1.2	0.4–0.8	—
Tensile strength (MPa)	60–120	40–85	23.6
Elongation at break (%)	50–200	90–200	3

[a] Reaction time, 5 min; concentration of pyrrole, 0.2 M; concentration of oxidant, 0.5 M; temperature, 10°C

in particle structure between the two specimens. On the monomer solution side both PPy/PP and PANI/PP films exhibit particulate features (*Figure 4* and ref. 23). The particles on PANI/PP composites are compact, whereas those on PPy/PP composites are loose with many pores on them. This pore structure ensures continuous polymerization even at lower temperature.

The mechanical properties of these highly conductive composites are summarized in *Table 3*. Data for the PP host films and for PPy films synthesized by the electrochemical polymerization method are also listed for comparison. It is clear that the composites retain the good mechanical properties of the host PP films. The strength and elongation at break of the composite films are larger than the corresponding values for the electrochemically polymerized PPy films.

CONCLUSIONS

A conducting polymer composite film, polypyrrole/polypropylene, was synthesized by chemically oxidative polymerization. Some pyrrole rings in the PPy chains were substituted by Cl. The doping extent was ~ 21% on both sides of the film. The conductivities of the films were of the same order of magnitude as that of PPy powder synthesized by chemically oxidative polymerization in water. The polymerization conditions, i.e. reaction time, reaction temperature and concentrations of pyrrole and $FeCl_3$, influence on the conductivity of the composite films. The mechanical properties of the composite films were better than those of PPy films synthesized by electrochemical polymerization in aqueous solution. Two kinds of surface structure were observed: one is a loose particle structure and the other is a compact structure.

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