

Polyaniline/Polypropylene Film Composites with High Electric Conductivity and Good Mechanical Properties

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SYNOPSIS

Polyaniline/polypropylene composites were prepared by oxidative polymerization of aniline in biaxially stretched polypropylene microporous films with ammonium persulfate as the oxidant. A continuous permeation/diffusion polymerization process was used in order to incorporate more polyaniline in the composite. The influence of reaction time and temperature and the concentration of monomer and oxidant aqueous solutions on the electric conductivity of the composites was investigated. The composites may exhibit a loose particulate surface morphology and a compact surface with a ring-shaped structure. The content and distribution of polyaniline in the composite and, hence, its electric conductivity and surface properties can be controlled over a wide range. Composites with the combination of high electric conductivity and good mechanical properties can be obtained under proper conditions. The composite films were flexible and strong enough and have electric conductivity as high as 5–6 S/cm. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Since the discovery of polyacetylene as an electrical conductive polymer, many conjugated double-bond polymers have been investigated, and studies of conducting polymers based on aromatic or heterocyclic monomers like aniline, pyrrole, thiophene, and their derivatives have attracted great attention in recent years due to their good environmental stability.¹ However, like most of the conductive polymers, they also have the disadvantage of poor processibility and/or poor mechanical properties. One of the important approaches to solve these problems is to formulate composites of conductive polymers with one or more conventional nonconductive polymers.¹

In preparing composites, the conducting polymer can be impregnated into a host polymer by chemical oxidation or electrochemical oxidation methods. The electrochemical polymerization of aniline^{2–4} and pyrrole^{5–7} in swollen or porous polymer films has been reported in some cases. However, this method is limited by the size, shape, and the nature of the electrodes involved and the difficulty in preparing uniform host film of large size.

The chemical oxidation method, although usually producing polymers of less electrical conductivity than does the electrochemical method, has the advantage of easier mass production and shorter reaction time. Conducting composites were prepared by exposing oxidant containing nonporous host polymers like poly(methyl methacrylate), poly(vinyl chloride), and poly(vinyl alcohol) to pyrrole vapor.⁸ Porous polymer films were also used as the host polymer of composites in order to reduce the reaction time. Bocchi et al.⁹ reported their results for conducting composites of polypyrrole/filter paper. Ruckenstein and co-workers^{10,11} prepared polypyrrole composites with crosslinked porous polystyrene films as the matrix obtained by employing the concentrated emulsion polymerization method. It was difficult for the composites to keep the high electrical conductivity of the pure conductive polymer. In this work, the preparation of polyaniline/polypropylene, (PANI/PP) composites with the combination of high electrical conductivity and good mechanical properties of the two constituent polymers was investigated.

EXPERIMENTAL

Aniline was distilled and stored in the dark before use. Ammonium persulfate and hydrochloric acid

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(Beijing Chemical Factory, China, analytical reagent grade) were used as received. Microporous polypropylene films¹² were used as the host films. Their thicknesses are about 25 microns.

The composites were prepared with a U-type reactor which is composed of two parts separated by a piece of the microporous film (Fig. 1). A monomer aqueous solution and oxidant aqueous solution were poured separately into the two parts of the reactor to start the polymerization process. A certain amount of hydrochloric acid was added in both solutions. After polymerization, usually at 10°C and in a period of 45 min in this work, the composite films were removed from the reactor, washed with distilled water, and imbibed in 1M HCl or 0.5M ammonium hydroxide for more than 6 h and then dried in vacuum at 50°C for 6 h. Polyaniline(SF)/polypropylene and polyaniline(BF)/polypropylene composite films were both obtained. Here, SF and BF stand for the salt form and the base form, respectively.

Pure polyaniline conductive films were prepared by solution cast of polyaniline solution in *N*-methylpyrrolidinone (NMP), followed by doping with HCl. The preparation procedure has been reported elsewhere.¹³

The electric conductivity of the composites was measured by the conventional four-point method. A two-point method with concentric ring-shaped electrodes was also used to measure the surface electric resistivity of the composite films. The surface resistivity of conductive pure polyaniline films was found to be in the range of 50–200 Ω/□. The morphology of the composites was investigated by a scanning electron microscope Hitachi S-530. IR spectroscopy experiments were performed by a Bruker IFS-113V instrument. UV-vis spectra were recorded by a Hitachi 340 instrument using the NMP solu-

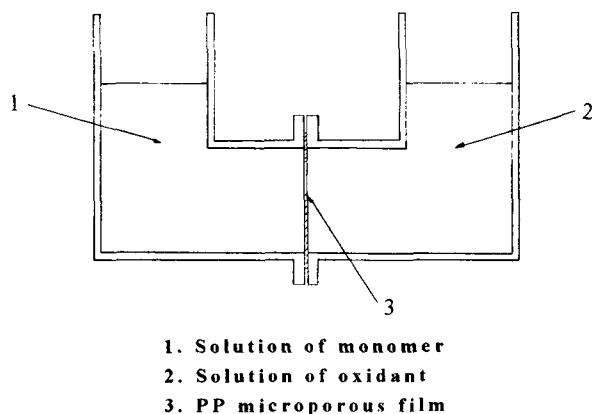


Figure 1 The U-type polymerization reactor.

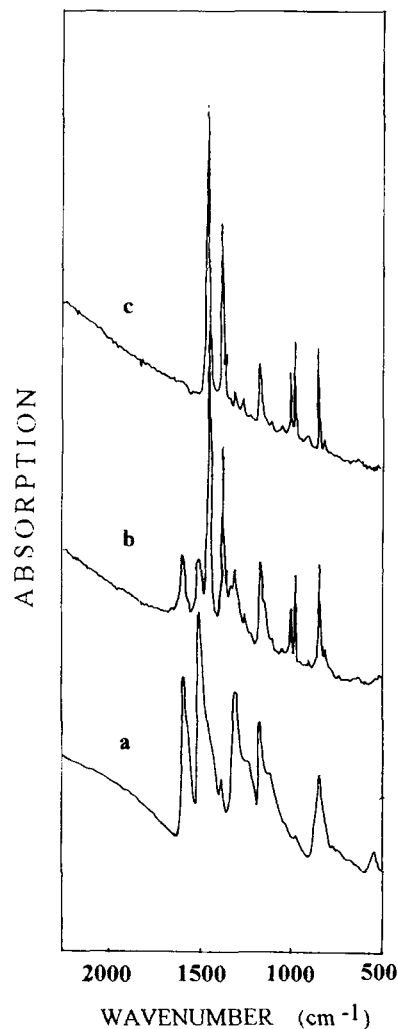


Figure 2 The IR spectra of (a) conventional polyaniline(BF), (b) polyaniline(BF)/polypropylene composite, and (c) polypropylene microporous film. BF stands for the base form.

tion of polyaniline(BF)/polypropylene and polyaniline(BF).

RESULTS AND DISCUSSION

The structure and properties of the host film are very important for composite preparation. A porous film matrix has the advantage of easy introduction of the conducting polymers or their monomers and other agents into the composites. Also, the porous structure of the film may also ensure the formation of a conducting polymer network within the host film at a lower content of the conducting polymer in the composite. However, when pores are formed in the host film, its mechanical properties will be lowered obviously. In this work, a special kind of

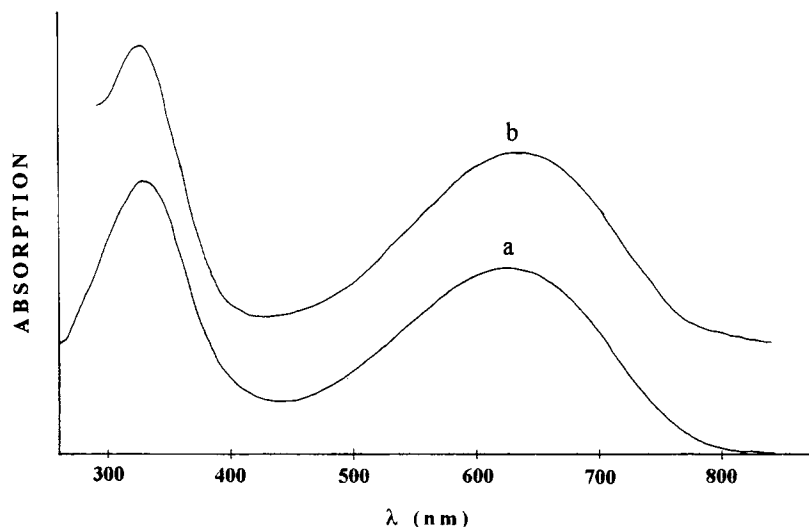


Figure 3 The UV-vis spectra of the NMP solution of (a) conventional PANI(BF) and (b) polyaniline(BF)/polypropylene composite. BF stands for the base form.

porous polypropylene film developed in our laboratory was used as the matrix film of the composites. These microporous films are prepared by a biaxial stretching technique. They are characterized by a

combination of high gas permeability and good mechanical properties. The porosity of the films is around 35%, and the average pore size is about 0.05 micron. The high gas permeability implies that they are open-celled microporous films.

After polymerization, the white polypropylene film becomes a composite of greenish black color typical for conductive polyaniline specimens. The products of polymerization were characterized by IR and UV-vis spectroscopies. The spectra are given in Figures 2 and 3. No obvious difference was found between the polyaniline prepared by the conventional chemical oxidation procedure and samples of this work.

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

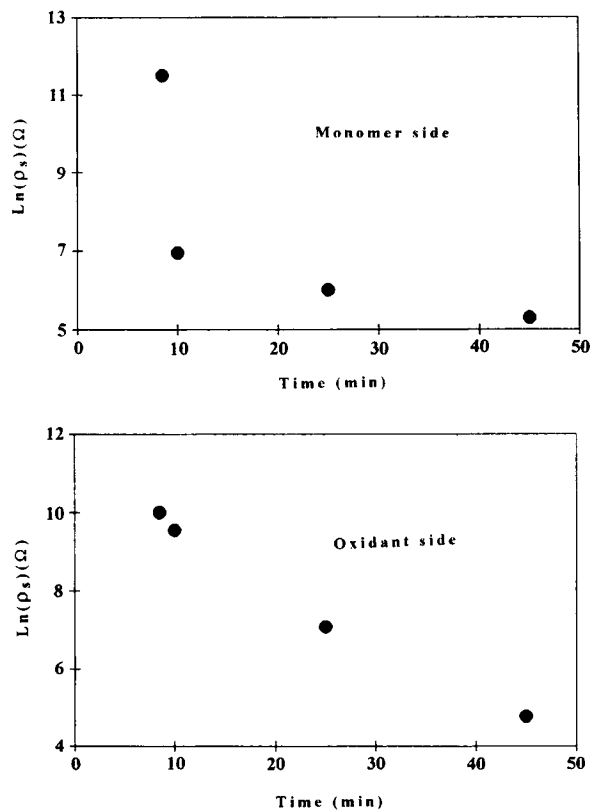


Figure 4 Time-dependence of electric resistivity during polymerization of a composite film at surface of the (a) monomer solution side and (b) oxidant solution side.

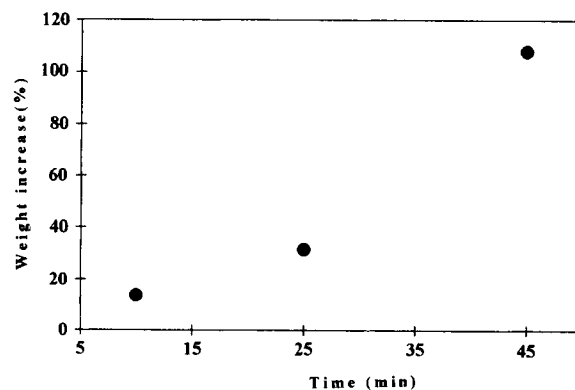


Figure 5 Time-dependence of weight increase for a composite film during polymerization.

Table I Influence of the Concentration of the Oxidant Solution on the Surface Electric Resistivity of the Composites

Oxidant Concentration (M)	Surface Resistivity (Ω/\square), Monomer Side	Surface Resistivity (Ω/\square), Oxidant Side	Weight Increase (%)
2.0	35	1290	402
0.20	125	188	106
0.10	600	570	19
0.04	1.6×10^4	1986	8.5

due to molecular diffusion may result in the oxidation polymerization of the monomers. The microporous matrix will be filled and then coated by the conducting polymer and becomes a conductive composite. The advantage of this continuous permeation/diffusion method is the ease to introduce more polyaniline into the composite and, hence, to obtain high conductive products.

The polymerization process can be characterized by the time-dependence of the electric resistance of the composites. Figure 4 shows a typical result of experimental data with ammonium persulfate as the oxidant. The surface resistivity of the composites decreases rapidly with reaction time in the initial stage and then exhibits a slow decrease, approaching a limit value. The transition region is around 10–20 min. Measurements on both sides of the composites show the same tendency. The time-dependence of the weight increase during the polymerization process is given in Figure 5. The weight increase at 10 min is only about 15%. At this stage, the electrical resistivity of the composite has become quite low as compared to that of pure polypropylene. It may imply the first formation of a continuous polyaniline network within the composite and on its surface. In the range of 30–40 min, the weight increase is around 60–80%, which is estimated to be the amount of polyaniline needed to fill the pore volume of the microporous film and to form thin layers at surfaces of both sides.

Besides the reaction time, there are many factors or conditions which may influence the electrical properties of the composites. The effects of the concentration of the monomer and oxidant solutions and the reaction temperature were studied and are discussed below.

Table I gives the data for specimens obtained in experiments with different concentrations of the oxidant solution. The concentration of the monomer solution used was 1.5M. The surface resistivity of the composites at the monomer solution side decreases rapidly with the oxidant concentration first and approaches a low value close to that of the conductive pure polyaniline films, when the oxidant concentration is about 0.1–0.2M. At the opposite side of the composites, the surface resistivity also decreases rapidly with increasing the concentration of the oxidant solution, but not monotonically, having a minimum in the oxidant concentration range around 0.2M. The weight increase of the composite is given in the last column of Table I. It increases, obviously, with the oxidant introduced into the composite, and the higher value of surface resistivity at the oxidant solution side might be related to the deviation of polyaniline from its emeraldine oxidation state.

Similar experiments were conducted to study the influence of the concentration of the monomer solution. The concentration of ammonium persulfate solutions used was 0.2M. With increasing monomer

Table II Influence of the Concentration of the Monomer Solution on the Surface Electric Resistivity of the Composites

Monomer Concentration (M)	Surface Resistivity (Ω/\square), Monomer Side	Surface Resistivity (Ω/\square), Oxidant Side	Weight Increase (%)
2.5	18	25	—
1.5	48	174	380
0.5	760	6.1×10^6	234
0.05	6.1×10^4	$> 2.7 \times 10^8$	10

Table III Influence of Reaction Temperature on the Surface Electric Resistivity of the Composites

T ($^{\circ}\text{C}$)	Reaction Time (min)	Surface Resistivity (Ω/\square), Monomer Side	Surface Resistivity (Ω/\square), Oxidant Side	Weight Increase (%)
2	45	80	1.2×10^6	271
10	45	48	175	250
32	25	27	47	244
57	45	25	5	590

concentration, the weight of the composites increases steadily first and then remains almost constant, when the monomer concentration was higher than 0.5–1.0M. The surface resistivity of the composites at both sides decreases with monomer concentration and approaches limit values in the monomer concentration range above 1.0–1.5M (Table II). These limit values of the composites are comparable with the surface resistivity of high-conductive solution-cast polyaniline films measured in our laboratory.

The reaction temperature was also found to have its influence on the electric properties of the composites. Table III gives the results obtained in the temperature range of 2–57°C. A 1.5M aniline solution and a 0.2M ammonium persulfate solution were used in these experiments. A slight decrease of resistivity with temperature was observed at the surface of the monomer solution side, while the resistivity at the surface of the oxidant solution side decreases with temperature significantly in the experimental range. These results indicate that the composites prepared at temperatures above 10°C may exhibit electric conductivity close to that of the solution-cast polyaniline specimens.

The electric and mechanical properties of these highly conductive composites are summarized in Table IV. The data of polypropylene host films and solution-cast conductive polyaniline films are also listed for comparison. It is clear that the composites may retain the good mechanical properties of the host polypropylene films, and the electrical conduc-

tivity of the composites has the same order of magnitude as that of the pure polyaniline film specimens prepared by the chemical oxidation method. The high electric conductivity value of the composites implies that the surfaces of the microporous film are well coated by high-conductive polyaniline layers and a continuous polyaniline network is established within the microporous film. The strength and modulus of the composites are comparable with those of pure polyaniline films. However, the latter is extremely brittle, having an elongation at break of only about 8%, while the composites are quite flexible films of versatile applicability in various areas.

The morphology of the composite surface has been observed by SEM. There are two kinds of morphological features. In some cases, a loose and particulate surface structure was observed [Fig. 6(a)]. The size of these particles is around 0.2–1.0 micron. Figure 6(b) shows another type of morphological features: The surface seems compact and has a ring-shaped structure. Usually, the compact surface structure was obtained at a shorter reaction time or with a lower weight increase of the film, and the particulates were observed on surfaces of composites after a longer reaction time. So, the loose layers are formed upon the compact layers. The two polyaniline layers are stacked on the surfaces of the host film and form a composite as a whole. The loose layers still can be taken away mechanically from the composite surfaces, but the compact layers are very tightly combined with the matrix. Usually, only

Table IV Properties of PANI/PP Composites

Properties	PP Host Film	PANI/PP Composite	Pure PANI Film
Tensile strength (MPa)	60–120	60–100	110
Young's modulus (GPa)	0.4–1.2	0.7–1.0	2.2
Elongation at break (%)	50–200	60–180	8
Electric conductivity (S/cm)	—	10^0 ^a	10^0 ^a

^a The high values of electric conductivity were found to be 5–6 S/cm and around 10 S/cm for PANI/PP composites and pure polyaniline films, respectively.

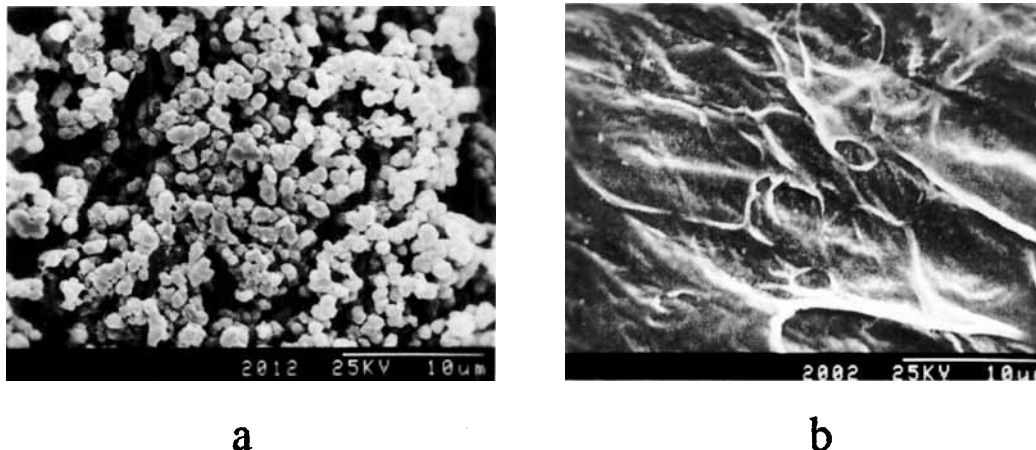


Figure 6 SEM micrographs of composites: (a) surface with loose particulate structure; (b) compact surface with ring-shaped structure.

powders are obtained during chemical oxidation polymerization of aniline in solution. Our results indicate that in the polymerization process described in this article compact polyaniline films can be formed under the influence of the microporous host film, and this influence decreases with increasing distance from the microporous film surface, and, finally, particulate polyaniline is obtained similar to polymerization of aniline in solution conditions without any substrate or host matrix.

The polymerization of polyaniline in preparing these composites is a permeation/diffusion-controlled process. The monomer solution and the oxidant solution permeate into and meet with each other within the host film. The mixing of monomer and oxidant and polymerization occur as a result of molecular diffusion at the boundary regions of the solutions. By proper controlling of the permeation process of the two solutions, it is possible to establish the boundary plane at different locations or depths within the film and to prepare electrically asymmetric composites.

CONCLUSIONS

It is shown that polyaniline/polypropylene composites with the combination of high electric conductivity and good mechanical properties can be prepared by the oxidation polymerization of aniline in a biaxially stretched polypropylene microporous film in a continuous permeation/diffusion process. The content and distribution of polyaniline in the composite and, hence, the electric conductivity and sur-

face properties can be controlled over a wide range. The composites are flexible and may have electric conductivity as high as 5–6 S/cm.

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