

Preparation and Characterization of Electroconductive Polypyrrole–Thermoplastic Composites

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ABSTRACT: Polypyrrole–thermoplastic composite films were obtained by casting. Homogeneous films were prepared with dispersant poly(vinyl methyl ether) or poly(vinyl ethyl ether) by two methods. Electric conductivity, morphology, mechanical properties, and sensitivity to H₂O₂ in water were studied. Composites of polypyrrole with poly(vinyl chloride) carboxylated and poly(vinyl methyl ether) presented improved mechanical and electrical properties compared with other composites studied. These films were sensitive to H₂O₂ in water, showing a significant change in electric resistance. This change is discussed in relation to the H₂O₂ concentration and the exposure time. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 1498–1506, 2001

Key words: polypyrrole; composites; thermoplastics; electroconductive polymers; dispersant

INTRODUCTION

There has been a growing interest during the last few years for conductive polymers, mainly due to a large number of potential technological applications of these materials.¹ Polypyrrole (PPy) is one of the main polymers in this trend. Indeed, free-standing film of PPy with high conductivity and stability can be obtained by electrochemical oxidation and polymerization of pyrrole monomers. However, a serious problem for the technological application of free-standing polypyrrole films is their hardness and brittleness, making them difficult to process. Intensive studies have been carried out to improve the mechanical properties and processability of free-standing polypyrrole films.²

The improvement of the mechanical properties of electroconductive polypyrrole films has been attempted by different methods: for example, electrochemical polymerization^{1,3–5} polymerization of pyrrole in a matrix with good mechanical properties,^{2,6–8} and preparation of composite materials based on polypyrrole,^{9–12} and others. It also has been reported that poly(vinyl methyl ether) (PVME) and poly(vinyl ethyl ether) (PVEE) have been used as dispersants for the preparation of the films.^{13,14} Both polymers have been used in mixtures with polystyrene and poly(α -methyl styrene). The use of PVME as dispersant in the polymerization of aniline in water or aqueous alcohol media yields dispersions of submicronic conducting polyaniline particles.¹⁵ Pyrrole in absolute alcohol or a water–alcohol mixture and FeCl₃ as an initiator-dopant have also been reported.¹⁶ Most of these methods to prepare electroconductive materials are troublesome and pose difficulties in the control of electroconductive properties.

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In an attempt to overcome the poor mechanical properties of the films, we report here a simple method for the preparation of composite films of PPy with different thermoplastics. With this method, it is possible to control the electroconductive properties depending on the amount conductive phase in the composite. It was necessary to add a dispersant to the composite to improve the homogeneity of the films and to avoid the agglomeration of electroconductive phase. The effect of using different dispersants in the films preparation was studied. We also studied the electrical properties, the mechanical properties, and scanning electron micrographs (SEM) of films with an optimal ratio of PPy and PVME or PVEE. Finally, the sensitivity of films to hydrogen peroxide solution in water was studied.

EXPERIMENTAL

Composite films of PPy were prepared by mixing polypyrrole perchlorate powders with different thermoplastics; however, by visual inspection, the films were heterogeneous, showing regions in which PPy was not dispersed, and therefore had poor conductive behavior. To improve the homogeneity of the films we used the following two methods.

Method I

PPy was synthesized as follows: A solution of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in acetonitrile was added in a dropwise manner to the reactor that contained pyrrole and PVME in acetonitrile, and the solution was stirred under nitrogen atmosphere. A fine suspension was formed. To ensure a complete reaction, the mixture was stirred for 2 h. The PVME:pyrrole ratio was 0.32. Deionized water was added to precipitate the product, which was collected by a glass filter and dried under vacuum. All concentrations are weight percent or weight ratio. The films were prepared by casting, using tetrahydrofuran (THF) solutions of different thermoplastics with 13% polypyrrole, in which % polypyrrole = $100 \times \frac{\text{polypyrrole weight}}{\text{polypyrrole weight} + \text{thermoplastic weight}}$. The thermoplastics used were: poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA), poly(*n*-butyl methacrylate) (PBMA), poly(isobutyl methacrylate) (PIBMA), poly(vinyl acetate) (PVAc), poly(vinyl chloride) (PVC), and poly(vinyl chloride) carboxylated (PVCc).

Method II

The PPy perchlorate used as a starting material was prepared with copper(II) perchlorate as an oxidative coupling agent at 25 °C and a Cu:pyrrole ratio of 1.5.^{17,18} The films were prepared by casting from THF solutions of different thermoplastics, with a concentration of 3% PPy and PVME: PPy ratio of 0.5. The same thermoplastics that were used in method I were also used in method II. The PVME:PPy and PVEE:PPy ratios were changed in the range 0.1–0.3 to study the effect on conductivity. Films of PVCc mixed with PVME or PVEE without PPy were prepared as references for mechanical testing. Conductivity was measured by the standard two-point probe method. The materials morphology was investigated using a JEOL 5410LV scanning electron microscope. The stress-strain measurements were performed in an Instron tensile tester model 4502 with a head speed of 10 mm/min. The sensitivity to H_2O_2 was studied by immersing the films with 13% PPy and PVME, prepared by method II, in the H_2O_2 solutions for different exposure times and also in the different H_2O_2 concentration with an exposure time of 1 h. After the exposure the films were dried at room temperature for 24 h, the change in electric resistance was measure.

RESULTS AND DISCUSSION

Electric Conductivity

Composites with all the thermoplastics, prepared by Method I, contained 13% PPy because their conductivity was small and lower concentrations of PPy were difficult to measure. Also, method I films in which PVEE was used as dispersant presented conductivity too low ($<10^{-10} \text{ S cm}^{-1}$) to measure. Method II films showed higher conductivity and were prepared with 3% PPy and the two dispersants; their conductivities were between 10^{-3} and $10^{-9} \text{ s cm}^{-1}$, depending on the nature of thermoplastic used and the quantity of PPy. Conductivity data for the films obtained with different preparation conditions are shown in Table I. These values were used as reference to study the effect of PVME and PVEE in the composites. Blends prepared by method I showed lower conductivities than those prepared by method II. In method I, when PVEE was used, we obtained material like very hard rock, which was difficult to grind to prepare films. Powder pellets

Table I Preparation Conditions of Composites Films and Conductivity (σ , S cm⁻¹)

Thermoplastic	Method I: 13% PPy		Method II: 3% PPy		
	Without Dispersant	With PVME	Without Dispersant	With PVME ^a	With PVEE
PMMA	8×10^{-5}	1×10^{-9}	5×10^{-5}	3×10^{-5}	3×10^{-5}
PEMA	3×10^{-4}	7×10^{-8}	2×10^{-5}	2×10^{-5}	4×10^{-5}
PBMA	5×10^{-4}	7×10^{-9}	2×10^{-9}	4×10^{-9}	8×10^{-9}
PIBMA	1×10^{-3}	1×10^{-7}	6×10^{-6}	2×10^{-5}	2×10^{-6}
PVAc	3×10^{-4}	6×10^{-9}	8×10^{-6}	3×10^{-7}	4×10^{-7}
PVC	6×10^{-5}	$<10^{-9}$	5×10^{-9}	5×10^{-7}	3×10^{-7}
PVCc	2×10^{-4}	$<10^{-9}$	4×10^{-6}	4×10^{-6}	7×10^{-7}

^a Dispersant: polypyrrole ratio in the sample preparation = 0.5.

of PPy synthesized with PVME presented an electrical conductivity of 1.2×10^{-1} s cm⁻¹, which was lower than those pellets of PPy synthesized without PVME (25 s cm⁻¹). The probable role of the dispersant is to modify the PPy particle formation processes; we suggest aggregative nucleation in which the dispersant participated in forming incipient nuclei and reduced interfacial tension, resulting in the formation of a smaller agglomerate. In method II, we found that PVCc was the best thermoplastic used in the composites prepared because its composite had good electrical properties and was not fragile. Films prepared at 3% PPy, with PVEE were more homogeneous than those prepared with PVME, but less electroconductive. Use of PVEE resulted in better dispersant activity and attachment of polymer molecules to the surface of a PPy particles. The formation of this PVEE layer stabilizes the PPy particles but reduces the conductivity.

To study the effect of the concentration of the dispersant on the conductivity, the dispersant: PPy ratio was decreased from 0.5 to 0.1 in composites prepared by method II with PVCc. The results are shown in Table II. With PVME, all composites showed conductivity values around 10^{-6} s cm⁻¹, independent of the PVME:PPy ratio, and all were homogeneous.

Morphology

Scanning electron microphotographs of PPy powder, synthesized with and without PVME, are shown in Figure 1. When PVME is used (Method I), the resulting powder forms small agglomerates that have a solid rock shape and a size of ~ 50 μ m. It does not seem to be easy for the agglomerates to interconnect, and therefore percolation is hard to

achieve (Figure 1a). Powder utilized in method II (Figure 1b), shows larger agglomerates (100–200 μ m) that are easy to interconnect. This condition is favorable to percolation. This result is consistent with conductivity values because films prepared by method II had higher electrical conductivity.

SEM images of the surface and cross sections of the films are shown in Figures 2 and 3, respectively. Films without dispersant show agglomeration of PPy (Figure 2a), but in the macroscopic scale are highly heterogeneous because they show some transparent regions. In the macroscopic view, the films with PVME and PVEE are homogeneous and no difference is appreciated; in the SEM images, films with PVME (Figure 2b) show some scattered regions of PPy and the ones with PVEE (Figure 2c), show higher density of dark spots that should correspond to PPy. It is hard to see how the PPy is distributed within the bulk of the sample from the latter figures. The cross-section images of the samples shown in Figure 3 give a better idea of how PPy is distributed on the bulk of the sample. The images without dispersant

Table II Conductivity (σ) of Composites Films of PVCc-PPy-Dispersant Prepared by Method II with 3% PPy

Dispersant : PPy Ratio ^a	PVME σ , S cm ⁻¹	PVEE σ , S cm ⁻¹
0.0	4×10^{-6}	4×10^{-6}
0.5	4×10^{-6}	7×10^{-7}
0.3	6×10^{-6}	3×10^{-7}
0.1	5×10^{-6}	1×10^{-7}

^a Ratio in sample preparation.

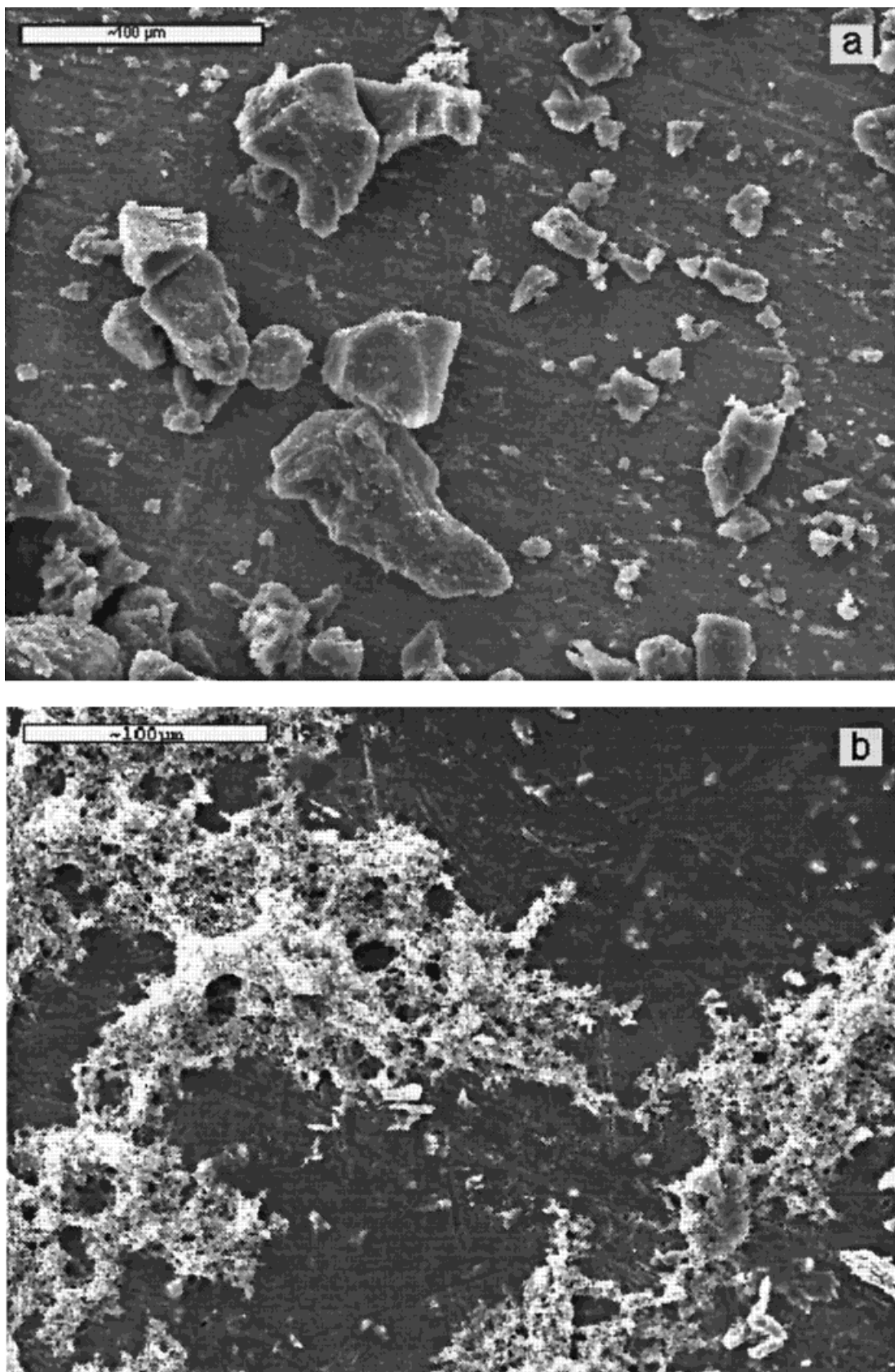


Figure 1 SEM micrographs of (a) polypyrrole synthesized by method I, and (b) polypyrrole powder without dispersant, used in method II film preparation.

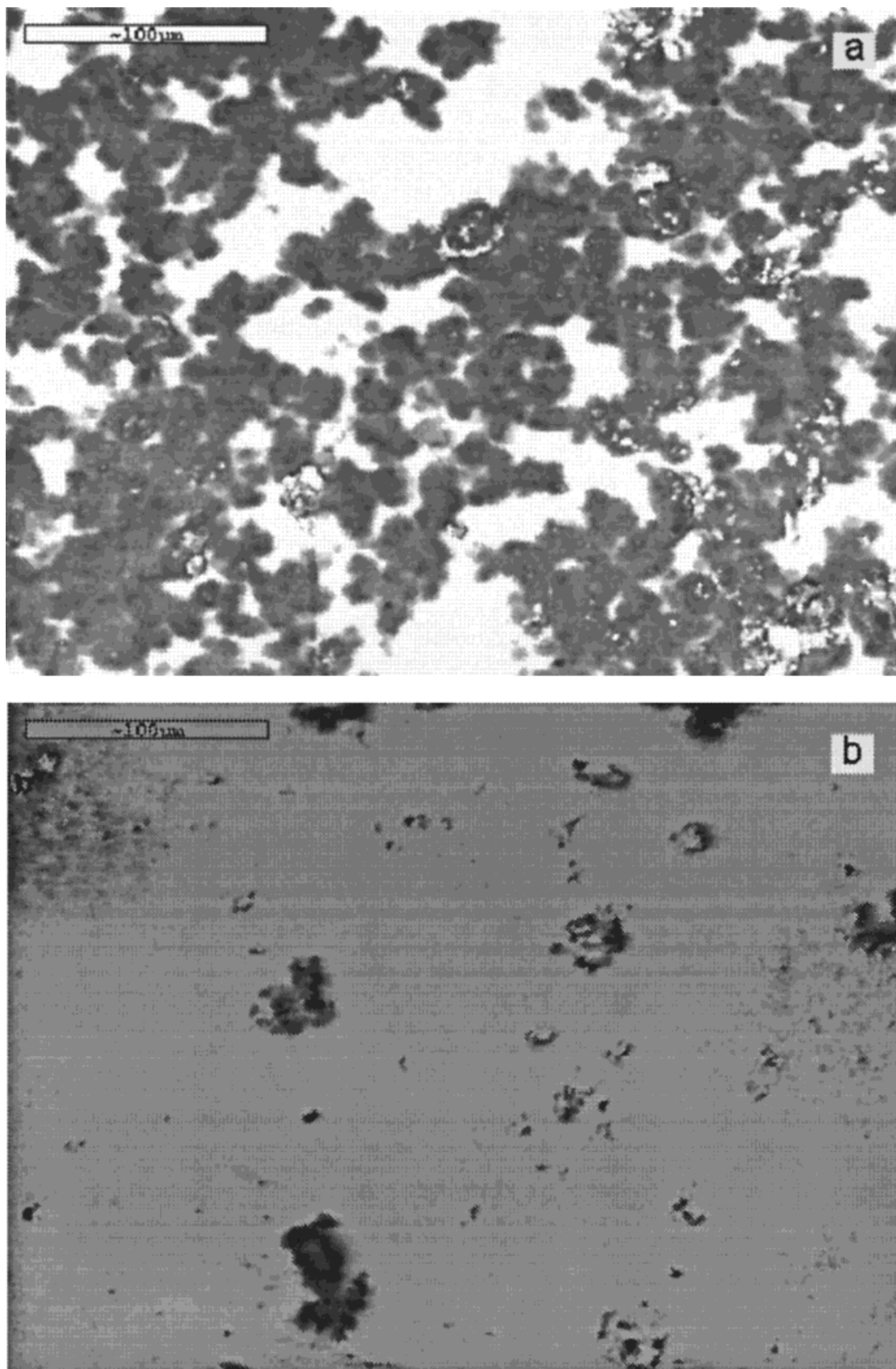


Figure 2 SEM micrographs of (a) films obtained by method II, without dispersant and 13% PPy; (b) films obtained by method II, with a PVME:PPy ratio of 0.1 and 13% PPy; and (c) films obtained by method II, with a PVEE:PPy ratio of 0.1 and 13% PPy.

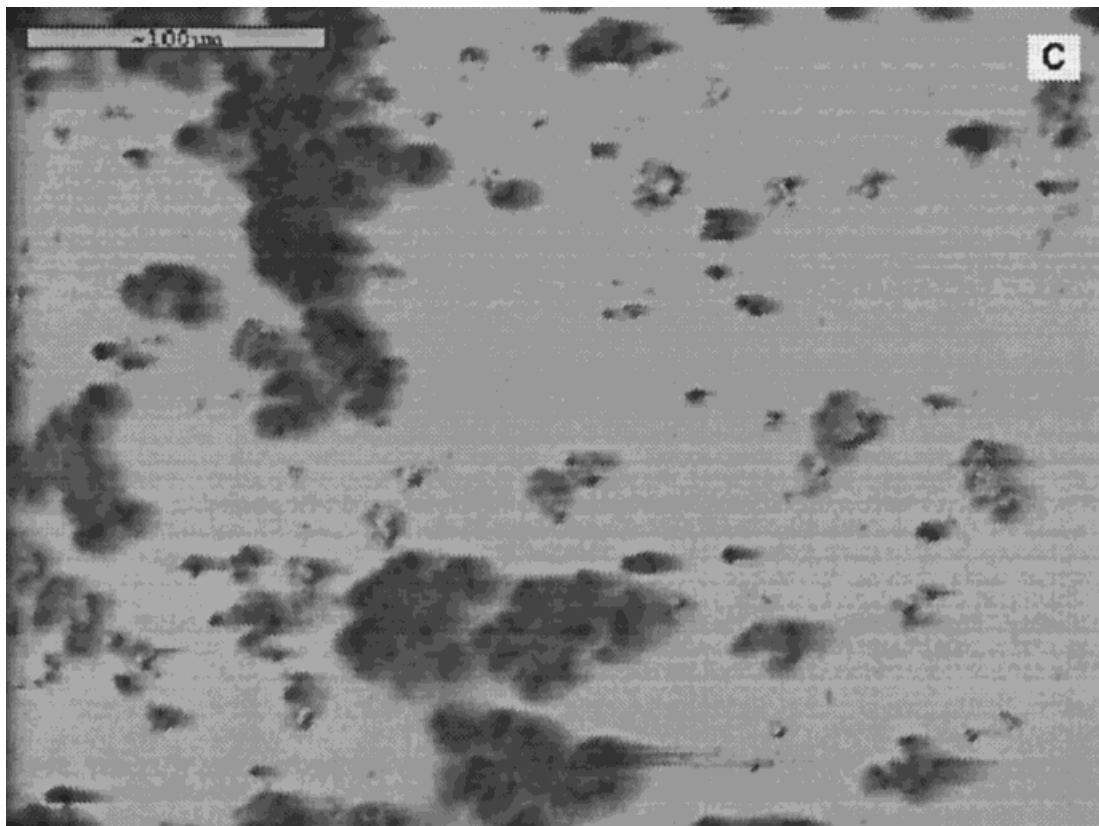


Figure 2 (Continued from the previous page)

(Figure 3a) and with PVME (Figure 3b) show large agglomerates that percolate throughout the sample; but the images also show that PPy domains are rather large, and large zones without PPy can be easily detected. Samples with PVVEE (Figure 3c) are completely different because the PPy domains are smaller than in the other two samples and the distribution is homogeneous. In this last sample, the dispersant helps to give a homogeneous film that has the same average properties in all the volume.

Mechanical Properties

Films prepared with PVCc as the thermoplastic and with PPy at concentrations of 13 and 3% were studied by stress-strain measurements. Films of PVCc were used as a reference. Samples with the two dispersants were prepared by method II with a dispersant:PPy ratio of 0.1. The results obtained are shown in Table III. Samples without PPy established the effect of the dispersants. The sample with PVME (1.5% w/w PVME in relation to PVCc) is affected in the final properties (at break) but has almost the same Young Modulus (YM) as the sample with PVCc. Moreover, samples with PVVEE

(1.5% w/w PVVEE in relation to PVCc) showed almost the same final properties as PVCc and a decrement in the YM. The PVVEE shows higher compatibility with PVCc, and does not change the response to large deformations but reduces the YM. PVME is less compatible and gives a reverse effect. The presence of the PPy drastically affects the film final properties, especially those films without the dispersants. Samples with PVME and PPy show a decrement in the final properties and in YM. As the SEM images show, the PPy domains are large, which is reflected in the stress and strain at break, because the PPy domains are brittle and are weak points in the sample. Compared with the other samples, those with PVVEE give better dispersion; therefore, their composites show better mechanical properties but lower electrical conductivity. Therefore, appropriate dispersants should be selected depending on the use of the resulting materials.

Practical Applicability

Composites prepared by method II, with 13% PPy and a PVME:PPy ratio of 0.1 (Table III), were

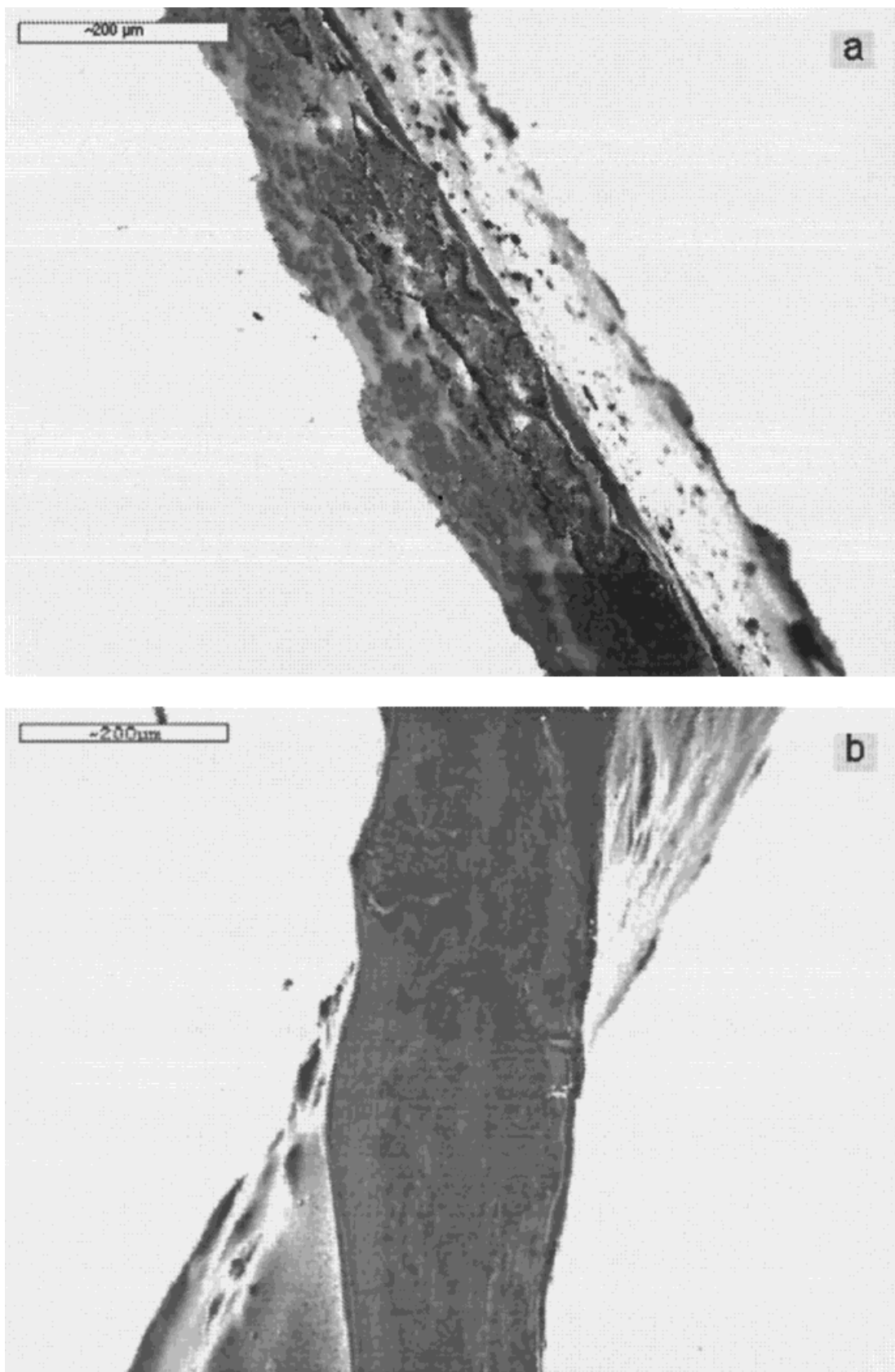


Figure 3 SEM micrographs of (a) the cross section of films obtained by method II, without dispersant and 13% PPy; (b) the cross section of films obtained by method II, with a PVME:PPy ratio of 0.1 and 13% PPy; and (c) the cross section of films obtained by method II, with a PVEE:PPy ratio of 0.1 and 13% PPy.

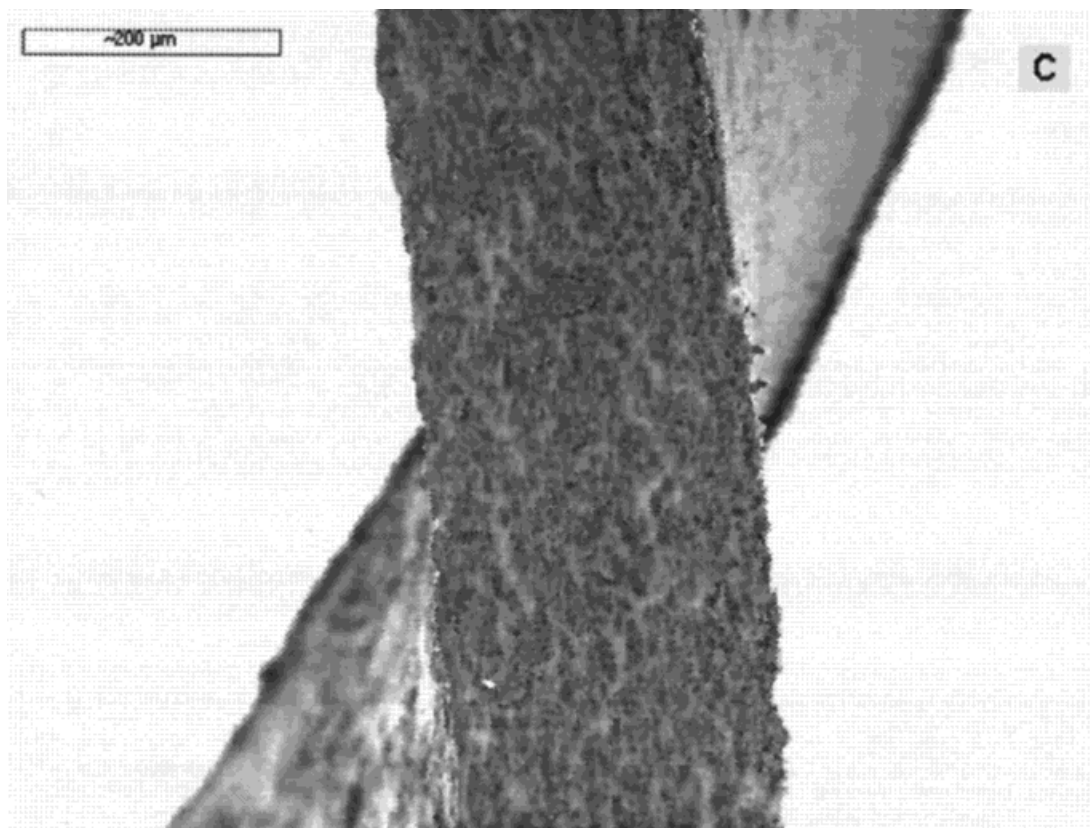


Figure 3 (Continued from the previous page)

sensitive to H₂O₂ solution with a concentration >10% and an immersion time of 60 min, as shown in Figure 4a. Using a 30% H₂O₂ solution led to a considerable increase in electric resistance after

an immersion time of 45 min (Figure 4b). The oxidant H₂O₂ causes degradation of PPy in the composite, decreasing electric conductivity with increasing H₂O₂ concentration in solution. This

Table III Mechanical Properties of Films PVCc-PPy and PVCc-PPy-Dispersant Prepared by Method II with a Dispersant: PPy Ratio of 0.1

% PPy	σ , S cm ⁻¹	Stress at Break, MPa	Strain at Break, %	Young Modulus, MPa × 10 ²
Without dispersant				
13	2 × 10 ⁻⁴	5.7 ± 5.6	3.4 ± 2.8	7.9 ± 5.9
3	4 × 10 ⁻⁶	9.5 ± 1.2	4.7 ± 1.2	12.4 ± 1.5
0	0	24.0 ± 6.1	403.3 ± 58.1	3.1 ± 0.9
With PVME				
13	2 × 10 ⁻⁶	8.5 ± 5.0	35.3 ± 27.6	3.1 ± 0.9
3	5 × 10 ⁻⁶	17.4 ± 5.3	266.4 ± 94.5	2.3 ± 0.4
0 ^a	0	20.7 ± 5.7	345.1 ± 123.6	3.1 ± 0.8
With PVEE				
13	1 × 10 ⁻⁸	19.6 ± 3.5	163.3 ± 84.0	2.9 ± 0.3
3	1 × 10 ⁻⁷	19.2 ± 5.4	244.3 ± 97.5	2.0 ± 1.2
0 ^a	0	21.0 ± 2.5	416.8 ± 29.1	2.6 ± 0.6

^a With 1.5% w/w dispersant.

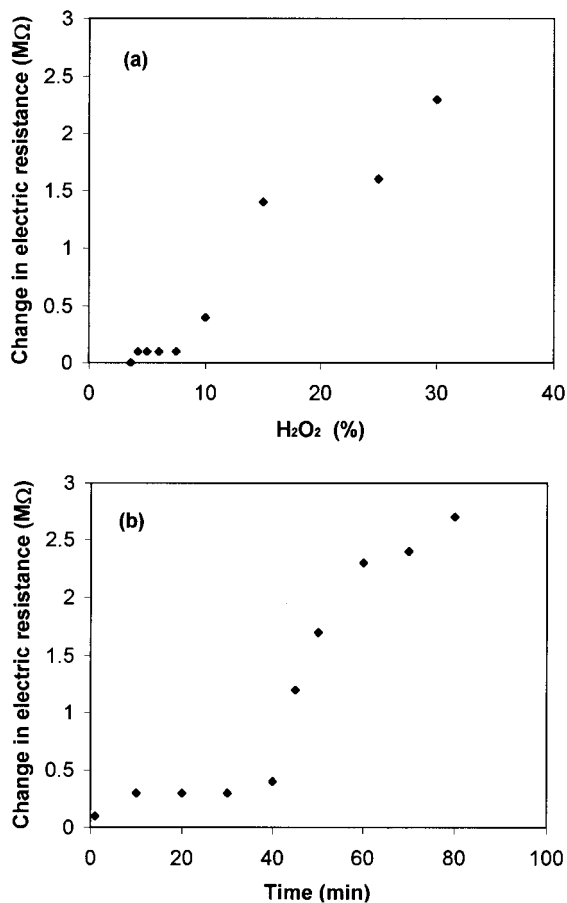


Figure 4 Change in electric resistance to (a) different concentration (%) of H_2O_2 solution in water of films obtained by method II, with a PVME:PPy ratio of 0.1 and 13% PPy; and (b) different exposure time into H_2O_2 30% solution in water of films obtained by method II, with a PVME:PPy ratio of 0.1 and 13% PPy.

effect suggests that the films obtained have potential application as chemical sensors.

CONCLUSIONS

Two simple methods to prepare electroconductive composites were used and the resulting films were compared. The results showed that using method II with PVCc and a PVME:PPy ratio of 0.1, we obtained homogeneous films with a con-

ductivity of $10^{-6} \text{ s cm}^{-1}$ and improved mechanical properties. Therefore, method II is recommended to obtain films with better electric and mechanical properties than those obtained by method I. Films with 13% PPy were sensitive to H_2O_2 , therefore they are useful materials for building a H_2O_2 sensor.

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