Highly Electrically Conducting Polyurethane-Based Composite

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The preparation of a new conducting composite based on a polyurethane (PU) membrane radiatively grafted with poly(acrylamide) (PAAm) is described. Polypyrrole (PPy) was inserted into the PU/PAAm composite using a new chemical–electrochemical catalytic method. The hydrophilicity of the host matrix is essential for the incorporation of the conducting phase throughout the film in aqueous solution, and also the interaction between the insulating host membrane and the PPy is important to achieve high conductivity. Conductivities as high as 100 S cm^{-1} were obtained. The environmental stability of these films was good: 97% of the initial conductivity retains after 100 days. Flexible, stretchable, and strong conducting films can be prepared. Films that exhibit conductivity of 70 S cm^{-1} could be stretched up to 24% of their original length. Thick transparent films having fairly high levels of conductivity were prepared in methanol–water solution. The mechanical and thermal properties and composition of the new conducting composite are reported.

Introduction

Mechanical quality of materials is important whenever their utilization is considered. The use of an organic polymer film usually requires properties such as stability, intractability, flexibility, and processability. Intrinsic conducting polymers (ICP) which were reported about a decade ago, lack these properties. Materials, such as polyacetylene, polythiophene and polypyrrole (PPy) are infusible, unmelt-able and unprocessible brittle materials.[1,2]

During the past years various efforts to improve the handling and the mechanical properties of ICP have been reported.[3] In some cases a bulky dopant played the role of the plastisizer in the film.[4] Recently we found that remarkably flexible and smooth PPy films can be electrochemically grown in aqueous solutions when the anodical reaction is carried out in a phthalate buffer. *In situ* electroforming of plastisizers derived from phthalic acid are accounted for the flexibility of these films.[5] The second, most investigated, method to enhance the mechanical properties is based on the implantation of a conducting polymer in an insulating host matrix.[6–8] In these cases the new composite is expected to gain both conductivity and good mechanical properties from its two components with some sacrifice of these qualities. Electrochemical and chemical processes were used to polymerize PPy in the host matrixes. The electrochemical processes involve polymerization of pyrrole on an electrode, precoated with an insulating swelled film.[6] Thus, the monomer has to diffuse throughout the insulating film in order to reach the electrode and the polymerization propagates from the electrode–film interface to the bulk of the film. Usually these reactions were carried out in organic solutions; however, the electrochemical impregnation in aqueous solution of polypyrrole into hydrophilic composite was also reported.[9] Chemical polymerization of pyrrole in aqueous solutions was intensively investigated. When insulating films are present in the reaction mixture, the polymerization takes place either throughout the film or on its surface, depending upon the swelling of the film.[7,8] Film swelling is necessary when bulk conductivity is desired. The use of aqueous solution as the polymerization solvent is obviously advantageous, but under these conditions low levels of conductivity (1–10 S cm^{-1}) are obtained.

Recently we developed a catalytic chemical–electrochemical (C–EC) process for the preparation of ICP.[10] The process is made of two steps: pyrrole is chemically polymerized using iron(III) chloride as the oxidizing reagent, and the formed iron(II) is electrochemically recycled. This catalytic process enables a more controlled reaction; consequently a higher level of conductivity can be achieved. The new process was used to prepare conducting ionomers.[11]

In this work the use of the C–EC technique is extended to insert conducting polymer into insulating nonionomeric films. Polyurethane grafted with poly(acrylamide) (PU/PAAm) is used as the host matrix and PPy is polymerized throughout the entire thickness of the film using iron(III)

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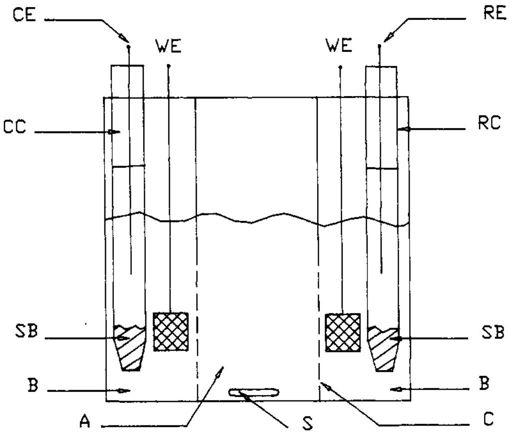

Figure 1. Electrochemical cell. (A) Space in the inner cylinder where the films were placed. (B) Space between the two cylinders. (C) Hole-full wall of the inner cylinder. WE, CE, RE: working, counter, and reference electrodes, respectively. CC, RC: counter and reference compartment, respectively. SB: salt bridge. S: stirrer.

chloride. The reaction is carried out in aqueous solution. Stable, flexible composite, denoted PU/PAAm/PPy, which exhibited conductivity as high as 100 S cm^{-1} are obtained. Electropolymerization of pyrrole into PU films in acetonitrile was reported previously.[12] In the present work we use different polymerization method and different host matrix that result in improved conducting films. In this paper the preparation and characterization of PU/PAAm/PPy films are described and their properties are compared to those of PU/PPy previously reported.

Experimental Section

Materials. Pyrrole (Aldrich) was distilled under reduced pressure and kept at 4 °C in dark. Hydrous ferric chloride (Bio-Lab, Israel), anhydrous Ferric chloride, and *p*-toluenesulfonic acid (Aldrich), were used without further purification. Polyurethane was grafted with poly(acrylamide) using an *in situ* grafting technique.[13] Monooriented (F type, 20 μm) ethylenevinyl alcohol (EVAL) copolymer (32:68 mol %) EF grade (Kuraray Inc., Japan) was used. Triple distilled water was used in all experiments.

Electrochemical Cell. A specially designed three-compartment electrochemical cell was used for the preparation of conducting films (Figure 1). It was constructed of two glass cylinders, the diameters of which were 3.5 and 7.0 cm, coaxially inserted one into the other. In this way two spaces, inside the inner cylinder and between the two cylinders (A and B in Figure 1, respectively) were formed. The wall of the inner cylinder (C in Figure 1) was full of discontinued holes (1–2-mm diameter) which ensured a free flux of substances between A and B but prevented physical contact between the films (in A) and the electrodes in B. The solution in A and B could be referred to as one working environment, the anolyte in this case. The anolyte was an aqueous solution containing 0.05 M *p*-toluenesulfonic acid as the supporting electrolyte and 30 mM iron(III) chloride. The counter and the reference electrode compartments (CC and RC in Figure 1) were made of hollow glass pipe, which were plugged in one side with a salt bridge (Agar/1 M NaCl). CC and CR compartments and two working platinum electrodes (WE) were inserted in B. The catholyte in the counter electrode compartment was 1 M iron(III) chloride, and the cathode was a carbon felt. A solution of 1 M NaCl was used in the reference electrode compartment, and a saturated calomel electrode (SCE) was used as a reference electrode.

The C–EC Process. The polymerization of pyrrole was carried out potentiostatically using bipotentiostat (Pine RDE 4). In a typical experiment the cell was cooled to 0 °C while stirring the anolyte in A (Figure 1). A constant potential of 600 mV (vs SCE) was applied to the working electrode, and the system was allowed to reach a steady state, which was characterized by a constant low current. Several pieces of PU/PAAm films (diameter 1.2 cm) were placed in A. After a steady state had been attained, pyrrole was injected into A to make a concentration of 80 mM. The molar ratio of iron(III)/pyrrole was usually 0.375, much lower than 4, which is the optimal ratio used in the chemical polymerization of pyrrole.[14] The progress of the reaction could be observed as the films darkened due to the formation of PU/PAAm/PPy. Samples of films were removed at different intervals, washed thoroughly with water, and dried.

Film thickness was measured with digimatic bench micrometer (Mitutoyo, Japan) having a resolution of 1 μm. Specific conductivity was measured using the four probes Van der Pauw technique.[15] In some cases two probe resistivity was measured using a Keithley 614 electrometer.

Film Stretching. Tensile properties of the conducting film were tested according to ASTM D638-71a. Stress–strain curves were obtained using Instron D1206-1 at room temperature at stretching rate of 5 mm min^{-1}.

Composition Analysis. Scanning electron microscopy (SEM) and energy-dispersive analysis X-rays (EDAX) experiments were carried out using a JEOL JXA-8600 superprobe. EDS (energy-dispersive spectrometry) and WDS (wavelength-dispersive spectrometry) techniques with defocused beam (20 μm) were employed for the surface analysis of the films.

Thermal Analysis. Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) were carried out with a Mettler DSC25 in conjunction to Mettler TC11 TA processor and du Pont Instruments 951 thermogravimetric analyzer with 990 thermal analyzer, respectively. Because of the hydrophilicity of the films the samples were preconditioned at 100 °C for 8 min. The experiments were carried out in an inert atmosphere.

UV–Vis Spectra were taken with a HP 8452A diode array spectrophotometer.

Results and Discussion

General Description of the Film Preparation. Although the induced chemical–electrochemical process (C–EC) was developed for polymerization of PPy inside ionomeric films, it was found that it is a convenient method to transform insulating films or fabric into conducting materials.[16] When the set of the experimental conditions described above was used, the polymerization of pyrrole takes place solely in the PU/PAAm film, while the working electrode and the solution remained clean.

The progress of the reaction, in terms of the change in film conductivity with reaction time, is shown in Figure 2. The conductivity increased with the reaction time: after one hour conductivity of 20–30 S cm^{-1} was obtained, reaching a constant value of $\approx$100 S cm^{-1} after 4–5 h. A similar behavior was observed with polyethylene grafted with poly(styrenesulfonic acid) (PE/PSSA). However, the maximal conductivity obtained with this ionomer was only $\approx$12 S cm^{-1} after 4–5 h of reaction. The reaction with anhydrous iron(III) chloride was somewhat faster than when hydrous iron(III) chloride was used (Figure 2). The final conductivity was found to depend upon reaction conditions, composition of the film, and the reaction mixture. For example, low conductivity was obtained when the reaction temperature was higher than 0 °C. Slightly lower conductivity ($\approx$70 S cm^{-1}) was also obtained when lower concentration of iron(III) chloride and *p*-toluenesulfonic acid (15 and 25 mM, respectively) were used. No polymerization of pyrrole was observed during 5 h of

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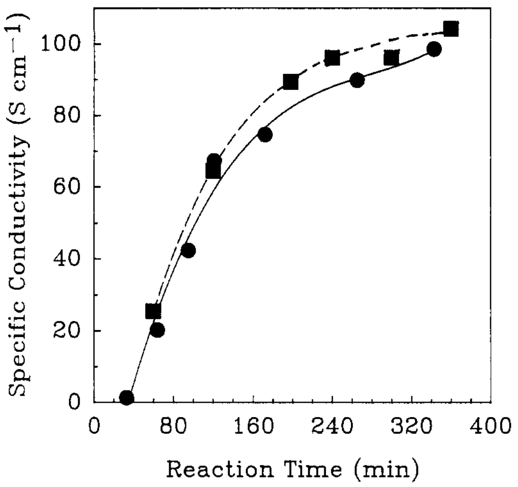

Figure 2. Variation of film conductivity with the reaction time. Concentration of reactants: 30 mM $FeCl_3$, 80 mM pyrrole, and 0.05 M *p*-toluenesulphonic acid. The polymerization was carried out at 0 °C. Filled circles: hydrous iron(III) chloride. Filled squares: anhydrous iron(III) chloride.

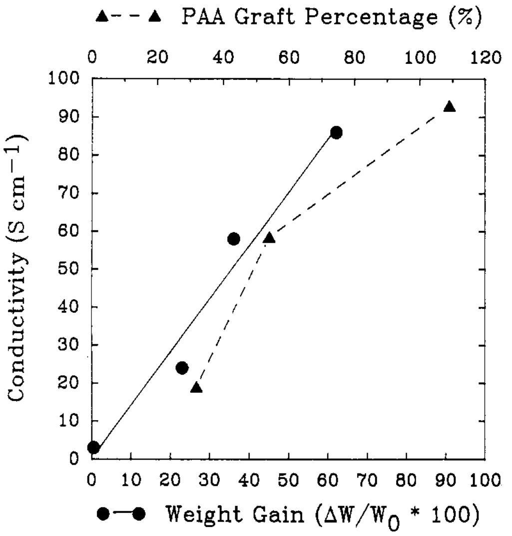

Figure 3. Variation of specific film conductivity with the weight gain of the membrane (filled circles), and the percentage of PAAm grafted in the PU (filled triangles).

reaction when methanol was used as a solvent, or when Tiron (4,5-dihydroxy-1,3-disulfonic acid, disodium salt) was used as the polymerization agent instead of iron(III) chloride. Tiron was used recently for a catalytic electroformation of PPy in aqueous solutions.[17] Two reasons can be accounted for the lack of pyrrole polymerization in the presence of Tiron as the oxidation agent: a thermodynamic reason, namely, low quinone concentration resulted from the low potential and the pH of the reaction mixture and/or a kinetic reason, viz., slow electron-transfer rate between pyrrole and the oxidized Tiron.

During the polymerization of pyrrole an increase in the film thickness was observed while the other two dimensions remained almost unchanged. A typical change from 17 ± 1 to 28 ± 2 μm was found after 5 h of reaction. A linear correlation was found between the conductivity and the weight gain of the films (Figure 3). Bi and Pei found nonlinear increase of PU/PPy conductivity with the weight gain, and their maximal conductivity was only 16 S cm^{-1} [12] compare to 90 S cm^{-1} found for PU/PAAm/PPy. Homogeneous distribution of PPy inside the host matrix was visualized when cross sections of PU/PAAm/PPy were enlarged under an optical microscope.

The hydrophilic character of PU/PAAm is important because the diffusion of the reactants into the host matrix is a prominent condition for the formation of the conducting phase inside the insulating film. PU/PAAm films exhibit excellent swelling in aqueous solutions.[13] Polyacrylamide, being a water soluble polymer is the predominant factor in determining the membrane swellibility. The dependence of PU/PAAm/PPy maximal conductivity on the percentage of grafted PAAm[18] in the polyurethane film is shown in Figure 3. As seen in the figure the conductivity increases with increasing PAAm grafting similar to our previous observations that the conductivity of electrically conducting ionomers, based on PE/PSSA, increase with the film loading.[19] In PU/PAAm/PPy the dopant is not chemically bound to the polymer, thus, the three components, pyrrole, iron(III) chloride, and *p*-toluenesulfonic acid (the doping agent as will be shown later), must diffuse to the bulk of the membrane to form the doped conducting PPy. It is important to emphasize that the combination of both compounds PU and PAAm is essential to achieve a high level of conductivity. When PU was replaced by another substrate, lower conductivities were obtained. In a separate set of experiments PAAm was grafted on EVAL to produce EVAL/PAAm hydrophilic membranes. These membranes served as substrates for preparation of EVAL/PAAm/PPy conducting composites. Although the grafting percentage of PAAm in EVAL was high (up to 200%), the highest conductivity observed was about 30 S cm^{-1}.

Environmental Stability of the Films. The stability of the films, in terms of the change in their conductivity with time, is crucial whenever their utilization is considered. We have found that the conductivity of electrically conducting ionomers decreases quite rapidly with time, and the rate of the conductivity decrease was influenced by postprocess treatment, composition, and/or the amount of radiation dose used in the course of preparation of the ionomers.[10,16] In light of the limited stability found for the conducting ionomers, it was interesting to investigate the stability of PU/PAAm/PPy. The procedure included rinsing of the conducting membrane with water immediately after the end of the reaction (≈1 min), drying and determination of the initial conductivity (σ_0). The films were then subjected to different rinsing processes, and the conductivity was determined after each step and periodically during 100 days after their preparation. Figure 4 presents the results of the conductivity measured in air at room temperature (24 ± 2 °C). As seen in the figure three kinds of posttreatment were employed: rinsing with water, rinsing with HCl (1 M), and rinsing with sulfuric acid (0.1 and 1 M). When no posttreatment was carried out, the conductivity increased during the first week by ≈4% and then decreased slowly to 97% of σ_0 after 100 days (filled circles in Figure 4a). When the films were rinsed with acidic solution, about 20% increase of the conductivity was observed during the first 1–2 days and then it decreased gradually to $0.8\sigma_0$ after 100 days (filled and opened circles in Figure 4b,c, respectively). When posttreatment included rinsing with water for 24 h followed

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[18] The percentage of graft, %G, is defined as $100[(W_g - W_i)/W_i]$, where W_i and W_g are the weight of the film prior and after grafting, respectively.

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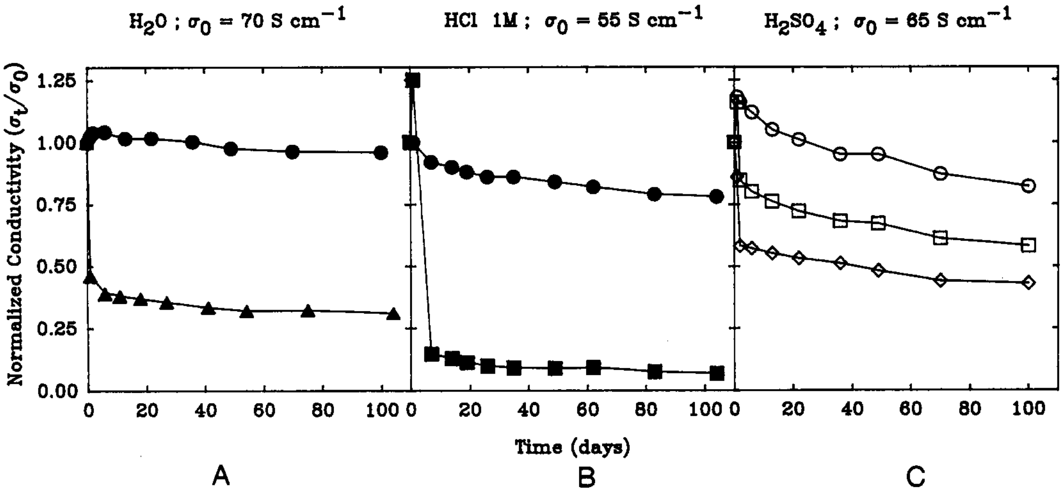

Figure 4. Environmental stability of the conducting membrane. (A) Posttreatment with water. Filled circles: rinsing with water for 1 min. Filled triangles: rinsing with water for 24 h. (B) Posttreatment with 1 M HCl. Filled circles: rinsing with HCl for 24 h. Filled squares: rinsing with HCl for 24 and then with water for 24 h. (C) Posttreatment with sulfuric acid. Open circles: rinsing with H_2SO_4 (0.1 M) for 24 h. Open squares: rinsing with H_2SO_4 (0.1 M) for 24 h and then with water (24 h). Open diamonds: rinsing with H_2SO_4 (1 M) for 24 h and then with water (24 h).

by treatment with acidic solution, a dramatic decrease in the conductivity was observed. The final conductivity was $0.3\sigma_0$ in the absence of acidic treatment (filled triangles in Figures 4a), about $0.6\sigma_0$ and about $0.4\sigma_0$ when 0.1 and 1 M sulfuric acid were used (squares and diamonds in Figure 4c, respectively). When HCl was used, a steep decline in the conductivity took place after 7 days and the final conductivity leveled off at $0.07\sigma_0$ (filled squares in Figure 4b). The dependence of the conductivity on the rinsing treatment may be rationalized by assuming leaching out of antioxidants from the conducting composite films. The deterioration of the conductivity in air is well documented[20] and organic antioxidants were recently used successfully to enhance the stability of PPy–paper composites.[21] Rinsing with water for a long period of time might cause leaching out of antioxidation species, such as iron(II) derivatives, which are trapped in the composite during the polymerization process, and hence the environmental stability of the composite decreased. Due to the low concentration of iron species in the films this hypothesis was not confirmed. Another possible explanation for the decrease of the film conductivity after the posttreatments is the reaction of the PPy with oxygen in the worm, humid atmosphere.

Thermal stability of PU/PAAm/PPy was also tested by placing a sample in air at 94 °C for different periods of time. The initial conductivity of 91 S cm^{-1} dropped to 86, 73, 56, and 41 S cm^{-1} after 6, 24, 96, and 296 h, respectively. On the other hand, the conductivity of the same film when kept in air at room temperature was unchanged for 2 months. A 25% decrease in the conductivity of this film was found after 26 months.

Mechanical Properties of the Conducting Films. Dog-bone specimens were cut from a large sheet of PU/PAAm and pyrrole was polymerized inside the film using C-EC technique. The polymerization time was varied so that films possessing different conductivities could be obtained. Results of the stress–strain mechanical measurements of PU/PAAm/PPy composites are shown in Figure 5. The calculated tensile strength, elongation and Young modulus of the films are presented in Table I.

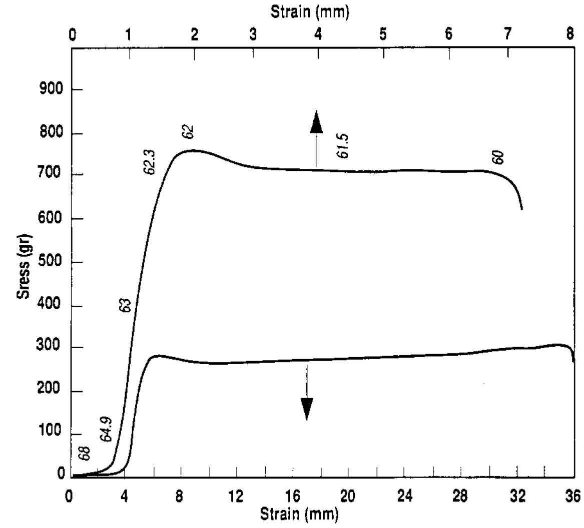

Figure 5. Stress–strain curves of polyurethane based films. Lower curve: PU/PAAm, grafting percentage 109%. Upper curve: PU/PAAm/PPy, σ = 68 S cm^{-1}. The inserted numbers are the *in situ* measured conductivities.

Table I. Mechanical Properties of PU/PAAm/PPy[a]

conductivity, S cm^{-1}	elongation at break, %	tensile strength, MPa	modulus of elasticity, GPa
[b]	94.81 ± 37	41.34 ± 2.70	1.10 ± 0.42
0.73	98.42 ± 31	37.03 ± 3.53	1.24 ± 0.35
19.00	56.69 ± 29	46.81 ± 3.43	1.48 ± 0.28
73.00	24.57 ± 8.8	52.68 ± 4.41	1.25 ± 0.44

[a] PU/PAAm film containing 109% PAAm. Pyrrole was inserted into the membrane using C–EC technique under the conditions: $FeCl_3$ 0.03 M; pyrrole 0.08 M; *p*-toluenesulfonic acid 0.05 M, applied potential 600 mV (vs SCE), reaction temperature 0 °C. Values are an average of at least 5 measurements. [b] Data for PU/PAAm (insulating host matrix) before polymerization of pyrrole.

The stress–strain curves of pure PPy is typical of a hard brittle material having high tensile strength, high Young modulus, and no yield stress.[22,6c] Conversely, a PU/PAAm film is a flexible, stretchable material. The stress–strain curve of PU/PAAm/PPy resembles more the PU/PAAm curve rather than the pure PPy; its yield stress point and

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Young modulus is very similar to that of PU/PAAm, showing no dependence on the amount of PPy inserted in the membrane (see Table I). The tensile strength of pure PPy depends, to a large extent, on the reaction medium; previous publication shows that when pure PPy was electrodeposited in acetonitrile the tensile strength of the film was ≈60 MPa, but in the presence of 25% water the film became significantly weaker and the tensile strength dropped to 8 MPa.[22] The tensile strength of PU/PAAm/PPy film increased as the quantity of PPy in the composite increased (third column in Table I). Thus, highly conducting flexible and tough films could be prepared. As the conductivity of the films increased they became less stretchable (second column in Table I), nevertheless, relative to other reported composites excellent elongation and conductivity properties were achieved. Elongation of 25% for films having a conductivity of 73 S cm^{-1} (Table I) is compared to elongation of only 4–7% for pure PPy/tosylate having a conductivity of ≈60 S cm^{-1}, when prepared in acetonitrile.[22,23]

At this stage it will be appropriate to compare the properties of our PU/PAAm/PPy to the previously published PU/PPy composite.[12] First it should be emphasized that the substrate material used in our study, namely, PU/PAAm, is completely different from pure PU. The physical and chemical properties of PU are dramatically changed after PAAm is grafted into the film. The grafted membrane becomes hydrophilic, as a result the elongation and modulus of elasticity reduced by about one order of magnitude. Second, when PU/PPy was prepared using the electropolymerization method, inhomogeneous films were obtained, since under their experimental condition the inner surface, close to the electrode, is more conducting than the outer one. On the other hand, the conductivity of our membrane and the distribution of PPy were the same in the two faces of PU/PAAm. It is noteworthy that upon introducing the PPy into the PU film the tensile strength *decreased*[12] as compared to the PU substrate. On the other hand when PPy is introduced into PU/PAAm the tensile strength of the newly formed composite *increased*. It is hard to rationalize the difference between ours and Bi and Pei's results because while we can see a trend in the dependency of the mechanical properties on the composite conductivity, the mechanical properties of only one sample of PU/PPy were reported.

The effect of stretching on the conductivity was studied by *in situ* determination of the conductivity during the stretching experiment. Four thin gold wires (ϕ = 40 μm) were glued with conductive silver glue to the narrow central part of the dog-bone specimens. The initial distances between the wires were 4 mm. During the stretching a constant current of 1 mA was passed between the two outer wires while the potential was measured between the two inner wires. The calculated conductivities[24] are given in Figure 5. As seen the conductivity remained practically unchanged during the stretching experiment, contrary to expectation that it will increase.[5,25] This finding can be understood in light of the composite structure; PU/PAAm/PPy is composed of a ductile PU/PAAm matrix into which brittle PPy was polymerized. The stretching affects mostly the elastic matrix, leaving the brittle conducting filler and the conductivity unchanged. Similar results were obtained in the chemically prepared conducting ionomers.[19]

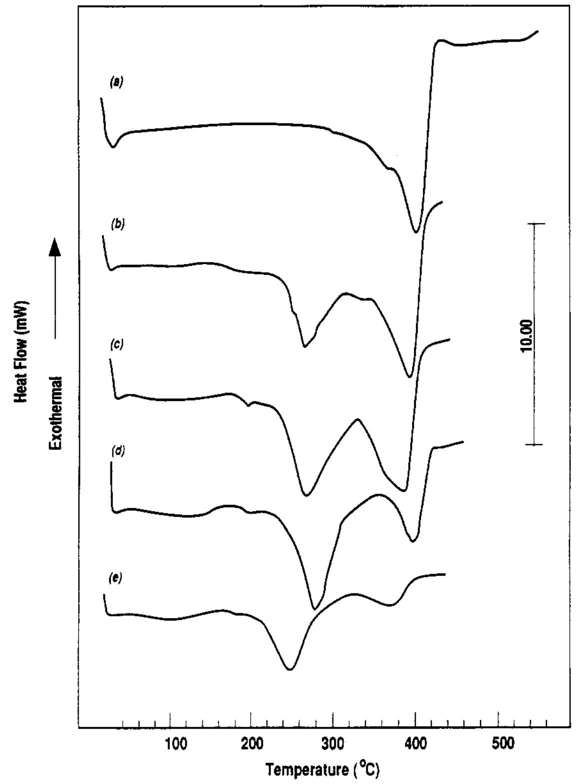

Figure 6. DSC of polyurethane films. (a) PU row material. (b) PU/PAAm. Grafting percentage 32%. (c) PU/PAAm. Grafting percentage 109%. (d) PU/PAAm/PPy. Grafting percentage 109%, conductivity 33 S cm^{-1}. (e) PU/PAAm/PPy. Grafting percentage 109%, conductivity 66 S cm^{-1}.

Thermal Analysis of the Films. To explore the stability and the interactions between the conducting and insulating building stones of the composite, thermal analysis was carried out.

TGA measurements of PU showed a smooth weight-loss in the temperature range 300–410 °C. PU/PAAm and PU/PAAm/PPy exhibited different thermogravimetric behavior: in both materials the weight loss began at 255 °C and the weight–temperature curves were split into two regions characterized by different slopes. No effect of PPy on the decomposition of the composite could be observed.

Further information concerning the thermal properties was obtained from DSC experiments. The effect of the PAAm graft percentage %G[18] and the amount of PPy in the composite on the DSC characteristics of the system is shown in Figure 6. PU had a single endothermic peak at 405 °C resulting from its decomposition in inert atmosphere (curve a). Grafted PU exhibited two endothermic peaks at 280 and 400 °C, attributed to the decomposition of PAAm and PU, respectively. The peak intensity assigned to PAAm at 280 °C increases with increasing PAAm graft percentage (curves b and c). The shape of the baseline around 187 °C is typical of a glass transition (T_g). The shape was reproducible using repetitive heating-and-cooling cycles of in the range 150–220 °C. No glass transition was observed for pure PU. The T_g observed at 187 °C is higher by 22 °C than the T_g of PAAm.[26] Empirically the T_g of a two-component one-phase system is expected to be between the glass transition

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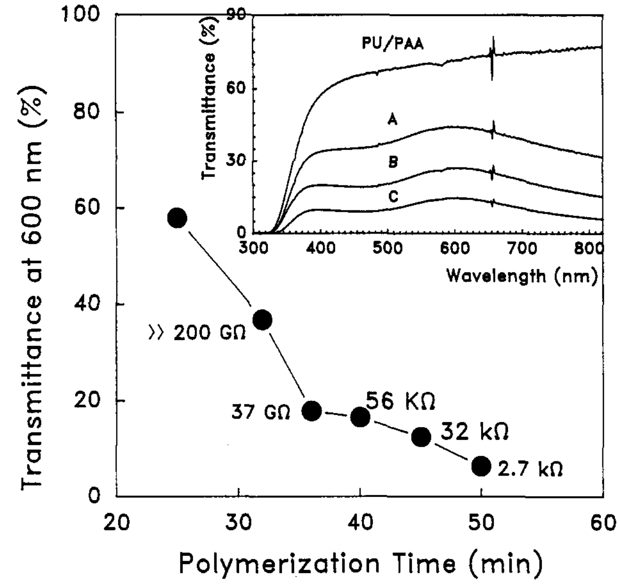

Figure 7. Transmittance–conductivity relation of PU/PAAm/PPy prepared in aqueous solution. Inserted: transmittance spectra of PU/PAAm and conducting composite after 28, 34, and 45 min of reaction (A, B, C, respectively).

temperature of the two components.[27] We have no explanation for this unusual observation and analysis of these phenomena is beyond the scope of this article.

When PPy was inserted into the grafted film, the features of the DSC curves were almost identical to those of PU/PAAm. The location of the T_g remained at the same position, but the heat capacity of this transition decreased. The temperature of the decomposition processes and the relative ratio of the two decomposition peaks were found to depend on the content of PPy in the membrane. On increasing PPy content the decomposition processes occurred at lower temperature (curves c and e) and the peak at 400 °C, which is assigned to the PU moiety, decreased (curves d and e). TGA of PPy powder showed a slow degradation at temperatures above 300 °C. Therefore it is assumed that some exothermic processes take place between PU and PPy and/or their decomposition products that cause a decrease in the overall endothermicity of the system.

Conductivity–Transparency Relation. Transparency to visible light and conductivity are in general contradicting properties, particularly when PPy is concerned. Therefore high transparency was reported for only very thin films.[28] Because PPy is homogeneously distributed in the PU/PAAm, and since C-EC method provides a convenient way to control the rate of PPy incorporation into the host matrix, it is useful to control the transparency by accurate adjustment of the amount of PPy incorporated in the matrix.

In the first set of experiments samples were removed from the aqueous reaction mixture after short time intervals. The spectra and conductivity of these experiments are presented in Figure 7. As seen in the figure after 30 min of reaction the film had 40% transmittance had their resistance was beyond the limit of the measuring instrument (200 GΩ). After 50 min of reaction the resistivity reached the value of 2.7 kΩ and the transmittance was only 7%. The transmittance spectra of PU/PAAm and several conducting composites are shown in the insert of Figure 7. Evidently during the PPy polymerization process there is a point where a sharp decrease of the resistance takes place without a significant change in the film transmittance. This observation is assigned to a percolation mechanism taking place after loading a critical concentration of PPy into the insulating film.

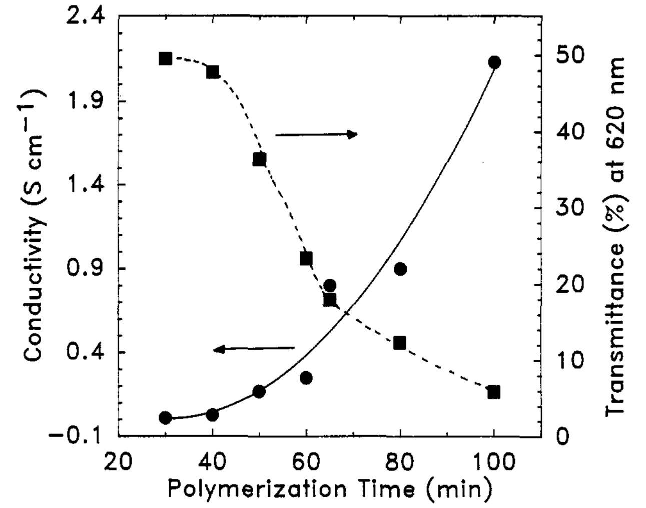

Figure 8. Dependence of transmittance and conductivity of PU/PAAm/PPy on the polymerization time. The reaction was carried out in 1:3 methanol/water solution.

The reaction in aqueous media is fast and therefore it was difficult to control. When methanol–water mixtures were used it was possible to achieve the exact critical concentration for percolation. Under these conditions the polymerization rate of PPy is slowed down and fine control of the concentration of PPy in the film is feasible. It was found that a ratio of 1:3 methanol/water was suitable to control the polymerization of PPy within 100 min. As seen in Figure 8 after 50 min of reaction the conductivity of the films reached the value of 0.2 S cm^{-1} and the transmittance is close to 40%. The thickness of the film remained unchanged (17 ± 1 μm) during the reaction. This particular film is at least one order of magnitude thicker than the conducting films with similar transparency reported in the literature.[28]

Composition and Morphology of the Conducting Composites. The content of PAAm in the PU film, which was expressed by %G,[18] can be expressed by the mole of ratio of the urethane and acrylamide monomers in the film. For example, the composition of PU/PAAm (%G = 109), taking into account the relative molecular weight of the monomers, could be described by the formula $U{\cdot}AAm_{20}$ plus water of hydration. Good agreement was found between the proposed structure $PU{\cdot}PAA_{20}{\cdot}(H_2O)_{17}$ and the empirical structure. Anal. Found: C, 50.57%; H, 7.07%, N, 9.88%. Calcd: C, 50.62%; H, 7.07%; N, 10.15%.

The surface composition of three samples loaded with different amounts of PPy and having conductivity of 20, 66, and 96 S cm^{-1} (I, II, and III, respectively) were carried out. Surface analysis (by EDAX) showed the existence of sulfur, carbon, nitrogen, and oxygen in addition to small amount of Fe and Cl. The source of the sulfur is from *p*-toluenesulphonic acid used as the dopant and electrolyte in the E-CE process. Iron and chlorine are from the $FeCl_3$ or its product. Homogeneous distribution of Fe and S was found by EDAX in films I, II, and III.

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(27) Ture, E. A., Ed. *Thermal Characterization of Polymeric Materials*; Academic Press: New York, 1981; p 188.

(28) (a) Ratclife, N. M. *Synth. Met.* **1990**, *38*, 87. (b) Ojio, T.; Miyata, S.; *Polym. J.* **1986**, *18*, 95.

Table II. Composition of Conducting Composites[a]

film	conductivity, S cm^{-1}		element percentage found	element percentage calcd	proposed structure[b]
I	20.03	C	51.30	52.23	
		H	6.37	6.12	
		N	10.14	10.36	$PU{\cdot}PAA_{20}{\cdot}(Py_3/TOS)_{1.5-2}{\cdot}(H_2O)_{17}$
		S	1.46	1.34	
		Cl			
		Fe	<0.01[c]		
II	66.53	C	53.58	53.84	
		H	6.11	6.14	
					$PU{\cdot}PAA_{20}{\cdot}(Py_3/TOS)_{2.8-3.3}{\cdot}(H_2O)_{17}$
		N	10.59	10.53	
		S	4.47	4.33	
		Cl			
		Fe	0.04		

[a] Elemental analysis of PU/PAAm (grafting percentage 109%). [b] The calculations were based on the assumption that the pyrrole/tosylate ratio was 3:1 and that the content of water is constant. The range in the PPy/TOS content refers to calculations which yield structures within the experimental error of the analysis. [c] Below the determination limit of the experimental technique.

The elemental analysis of the bulk of films I and II is presented in Table II together with the calculated element percentage for the proposed structure of the composite. A ratio of 3:1 between the pyrrole unit and the tosylate was used for the calculation. This ratio is typical of PPy prepared in either aqueous and nonaqueous solutions.[11,29] The amount of water in the films was kept constant in all the calculated structures. As seen in the table, the chlorine percentage was below the detection limit of the elemental analysis (0.5%). The content of iron was very low but increased with the conductivity of the film. These two elements were ignored in the calculation due to their negligible contribution to the structure. Evidently the insertion of the conducting phase to PU/PAAm is accompanied by an increase in the contents of sulfur, carbon and nitrogen (Table II). An agreement was found between the conducting/insulation molar ratio and the weight gain of the films. For example, film I showed a 22.16% weight gain after polymerization of PPy which results in a molar ratio of 1.85. A similar ratio between the insulation phase (PU/PAAm) and the PPy/TsO was obtained from the structure based upon the elemental analysis.

The morphology of the conducting films was investigated using scanning electron microscopy. Typical surfaces of films I, II, and III are shown in Figure 9a–c. In all the films the PPy is uniformly dispersed in the host matrix forming a continuous domain. The two faces of a film are identical, unlike the situation in the PU/PPy films reported previously.[12] The surface of the less conducting film (20 S cm^{-1}) is smooth, whereas that of film III is homogeneously covered with deposited granular vesicles, the size of which is 0.1–0.5 μm. The surface of film II (σ = 66 S cm^{-1}) is partly covered with similar deposited particles. EDAX showed that the content of Fe and Cl is greater in these rough grainy regions in comparison to the flat areas. Hence, the grainy regions are made of PPy doped also with species derived from the oxidant.

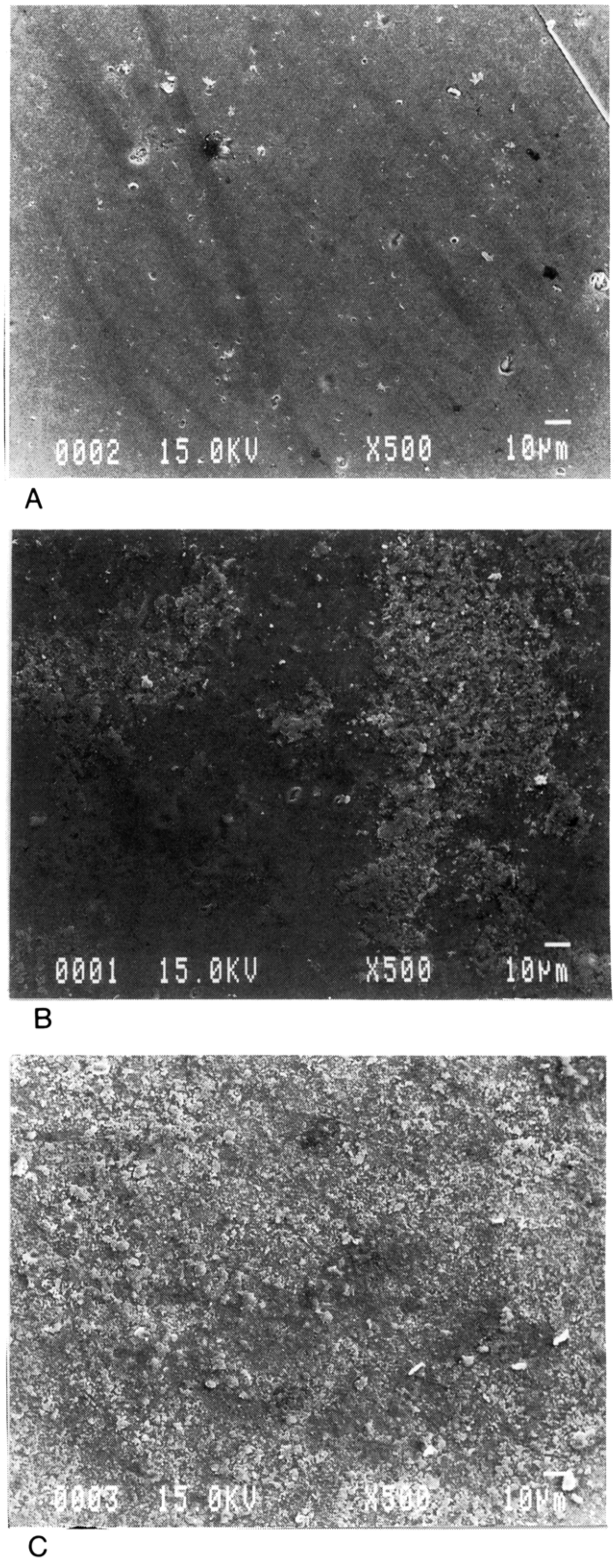

Figure 9. Scanning electron micrographs of PU/PAAm/PPy. Grafting percentage 109%. The conductivity of the film is (a) 20, (b) 66, and (c) 96 S cm^{-1}; films I, II, and III, respectively.

Summary

The new chemical–electrochemical catalytic method, developed for the preparation of conducting ionomers, was extended to prepare conducting composite from hydrophilic uncharged membranes. The hydrophilicity of the matrix is essential for the incorporation of the conducting phase throughout the film in aqueous environment. The interaction between the insulation matrix and the conducting polymer is important to obtain a high conductivity level. The maximum conductivity obtained for PU/PAAm/PPy (%G = 109%) was 103 S cm^{-1}, whereas EVAL/PAAm/PPy (%G = 200%) showed a conductivity of only 30 S cm^{-1}. The preparation of the PU/PAAm membrane and polymerization of pyrrole was carried out in nontoxic inexpensive aqueous medium. Flexible, strong,

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and stretchable PU/PAAm/PPy films were obtained. Elongation of 24% was measured for a film having conductivity of 73 S cm^{-1}. Because of the high conductivity of PU/PAAm/PPy, it was possible to obtain thick (17 μm) transparent films which exhibited reasonable conductivity. Correlation between the conductivity, the PPy content in the composite was observed. The presence of PPy did not alter the thermal stability of these composites, and they were stable up to 220 °C. The environmental stability of these films was very good: 97% of the initial conductivity remained after 100 days.

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