Polypyrrole conductive composites prepared by coprecipitation

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In order to improve the mechanical properties of polypyrrole, a three step procedure is employed to obtain polypyrrole/polymer composites. First, a concentrated emulsion which has the appearance of a gel is prepared by using a solution of polyurethane in chloroform as the dispersed phase and a solution of sodium dodecylsulphate in water as the continuous phase. In the second step, a finely divided polypyrrole powder (with a conductivity of about $1.6\,\mathrm{S\,cm^{-1}}$) is synthesized by the chemical oxidation method. Finally, the composite is obtained by blending the concentrated emulsion with an aqueous suspension of polypyrrole powder. The use of a concentrated emulsion instead of a polymer solution of polyurethane in chloroform results in a composite with a conductivity which is by a factor of about two higher. In addition, it is easier to prepare the composite via the concentrated emulsion pathway. The effect of the amount of polypyrrole on the conductivity of the composite was investigated to find an optimum composition of polypyrrole/polyurethane at about 68% polypyrrole (by weight). To further improve the mechanical strength of the polypyrrole/polyurethane composite, acrylamide was infiltrated into the composite and polymerized. The final composite polymer had a conductivity of the order of $0.2\,\mathrm{S\,cm^{-1}}$ and good mechanical strength. The composite polymer thus obtained has also a more stable conductivity than the pure polypyrrole, because the insulators (polyurethane and polyacrylamide) provide both physical support as well as protection against the environment for the polypyrrole.

(Keywords: polypyrrole; polymer composites; mechanical properties)

INTRODUCTION

Polypyrrole has attracted attention mainly because of its higher chemical and thermal stabilities compared to those of polyacetylene, and reasonably high conductivities ($>100\,\mathrm{S\,cm^{-1}}$). This heterocyclic polymer can be prepared either chemically[1] or electrochemically[2]. The polypyrroles prepared via the two routes have different physical appearances. The chemical oxidation method usually leads to fine polypyrrole powders, while the electrochemical synthesis provides free standing polypyrrole films. The resulting conductivity is generally higher in the latter method. However, the use of the electrochemical method is restricted by the size, shape and nature of the electrode involved, by the brittleness of the obtained films and by the difficulty in preparing thick films. The bulky and loose polypyrrole powder becomes, thus, the alternative choice for preparing large size conductive polymers. Unfortunately, the polypyrrole powder prepared by the chemical oxidation route has no mechanical strength. A number of procedures have been proposed to prepare composite polypyrrole polymers which can improve the mechanical properties of polypyrrole. Polypyrrole was blended with poly(vinyl chloride)[3], ionomer gel[4], and polyurethane[5] by using the electrochemical oxidation route. Colloidal polypyrrole was also prepared and blended with methylcellulose[6]. In addition, chemically prepared polypyrrole was infiltrated on thin paper sheets[7] or on thick porous materials[8] to form composite conductive polymers.

In this paper, a new method is proposed to prepare polypyrrole/polyurethane composites. Three steps are involved in this method. First, the conductive polypyrrole ($\simeq 1.6\,\mathrm{S\,cm^{-1}}$) is obtained by the chemical oxidation process[1] as a fine powder suspended in the aqueous reaction medium. In the second step, polyurethane is dissolved in chloroform and the solution obtained is used as the dispersed phase of a concentrated emulsion which contains a solution of sodium dodecylsulphate in water as the continuous phase. Finally, the concentrated emulsion is mixed with the suspension of polypyrrole in water. A precipitate containing a blend of polyurethane and polypyrrole forms, and a water layer above a chloroform layer separates. The chloroform which still imbibes the precipitate is eliminated by evaporation at room temperature in vacuum.

The polypyrrole/polymer composite is a porous material. Although the handling of this composite is possible, a secondary reinforcement is needed to improve its mechanical strength. The reinforcement was accomplished by infiltrating acrylamide into the composite and polymerizing. The final polymer had a conductivity of the order of $0.2\,\mathrm{S\,cm^{-1}}$ and good mechanical properties.

*FT*i.r. experiments were conducted to investigate the possible chemical interactions between polypyrrole and polyurethane. Scanning electron microscopy was also carried out to provide information on the structure of the composite polymer.

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EXPERIMENTAL

Chemicals and equipment

Pyrrole was purchased from Kodak and used as received. Ferric chloride ($FeCl_3$, anhydrous), chloroform, potassium persulphate ($K_2S_2O_8$) and sodium dodecylsulphate (SDS) were products of Aldrich. Acrylamide was obtained from Polyscience Co. Potassium persulphate and acrylamide were recrystallized from distilled water and methanol, respectively. Polyurethane (Tecoflex, TR 7525) was supplied by Thermedics Inc. Scanning electron microscopy was carried out with an Amray 1000A Microscope, and *FT*i.r. experiments were performed on a Mattson Alpha Centauri *FT*i.r. instrument.

Preparation of the polypyrrole/polyurethane composite

A solution of polyurethane in chloroform was employed to prepare a concentrated emulsion in which the solution constitutes the dispersed phase and water containing sodium dodecylsulphate (0.1 g/g water) the continuous phase. In a concentrated emulsion, the volume fraction of the dispersed phase is very large. The continuous phase has a low volume fraction and is in the form of a network of thin liquid films which separate polyhedral droplets of the dispersed phase. The concentrated emulsion is a kind of liquid–liquid foam and has the appearance of a gel. In our experiment the volume ratio of the dispersed to the continuous phase was 10:1. The continuous phase was placed in a round bottom flask equipped with a mechanical stirrer and an addition funnel. The concentrated emulsion was prepared by dropwise addition of the dispersed phase (solution of polyurethane in chloroform) to the stirred continuous phase (surfactant in water).

The polypyrrole was prepared by the chemical oxidation method[1] using water as the reaction medium. Various amounts of ferric chloride (9.7, 7.3, 4.85, 3.5, 2.4, and 1.2 g) were added to a fixed amount of water (53 g) in a flask containing a magnetic stirrer. Pyrrole was then added to the stirred aqueous $FeCl_3$ solution. The molar ratio of $FeCl_3$/pyrrole was chosen 2:1 and was kept fixed during our experiments, because it led with high yield to a high conductivity polypyrrole. The reaction lasted 1 h at room temperature.

After pyrrole polymerization, the concentrated emulsion of polyurethane was mixed with the suspension of polypyrrole in water. The black polypyrrole powder blended with the polyurethane and the mixture precipitated. The separated liquid layer containing a thick layer of water above and a thin layer of chloroform below was removed, and the precipitate was filtered. The precipitate was pressed to obtain a compact material. The black solid thus obtained was washed with a sufficient amount of 10% HCl in water followed by distilled water. Further, the remaining chloroform and water were removed by evaporation under vacuum at room temperature.

Secondary reinforcement of polypyrrole/polyurethane composite

The polypyrrole/polyurethane composite is a porous material. A secondary reinforcement was therefore employed to improve its mechanical strength. A water soluble polymer, polyacrylamide, was chosen for the secondary reinforcement, because both polyurethane and polypyrrole are insoluble in water. Methanol-recrystallized acrylamide monomer and a suitable initiator (potassium persulphate) (0.02 g/g monomer) was dissolved in water (1 g monomer/g water). The polypyrrole/polyurethane composite was imbibed with the solution until saturation. The polymerization of polyacrylamide was carried out at 45°C for 24 h. It should be noted that the washing procedure to remove the excess amount of oxidant (ferric chloride) in the previous step should be thorough in order to obtain high molecular weight polyacrylamide.

Conductivity measurement

For measuring the conductivity of polypyrrole, the powder was first moulded into a disc (about 0.45 cm thick) at an applied pressure of about 24 MPa. The standard four-point method was employed to measure the conductivity of polypyrrole and its composites at room temperature. The average value of four different measurements is given in the paper.

RESULTS AND DISCUSSION

Use of the concentrated emulsion of polyurethane

As already mentioned, the (gel-like) concentrated emulsion of chloroform solution of polyurethane in water contains polyhedral droplets of the solution separated by thin films of the continuous phase (water). The polyhedral droplets are of the order of a few 10^3Å (ref. 9). The polypyrrole powder contains particles of about 1 μm. Because the polyurethane/chloroform droplets and the polypyrrole powder are both dispersed phases of comparable sizes, the polypyrrole particles can have connections with each other to form channels for electron transport. The polyurethane/chloroform particles can have also contacts among themselves and with the polypyrrole. After the solvent (chloroform) evaporates, the polyurethane will remain inside the composite as a substrate for the material. Instead of the concentrated emulsion, one can also use the solution of polyurethane in chloroform. In this case, the polypyrrole powder constitutes the dispersed phase in the continuous phase of the polyurethane solution. The molecules of polyurethane can adsorb on the polypyrrole particles preventing, to some extent, the connections among the particles. SEM and conductivity measurements were conducted to compare the procedures based on the polyurethane concentrated emulsion and polyurethane solution.

Figures 1a and *b* show that when the polyurethane concentrated emulsion pathway is employed the composite polymer has two types of morphologies: one, cloud like (marked C), is due to the polypyrrole powder, and the other, ribbon like (marked R), is due to the polyurethane. For the polyurethane solution pathway, *Figures 1c* and *d* show that the morphology of the composite polymer is quite different from that of *Figures 1a* and *b.* They contain flake-like structures of polyurethane with small cloud particles of polypyrrole attached to the flakes. *Figure 1e* is a micrograph of polypyrrole powder prepared by the chemical oxidation method.

In addition to differences in morphology, the composite polymers prepared by the above two procedures exhibit somewhat different conductivities.

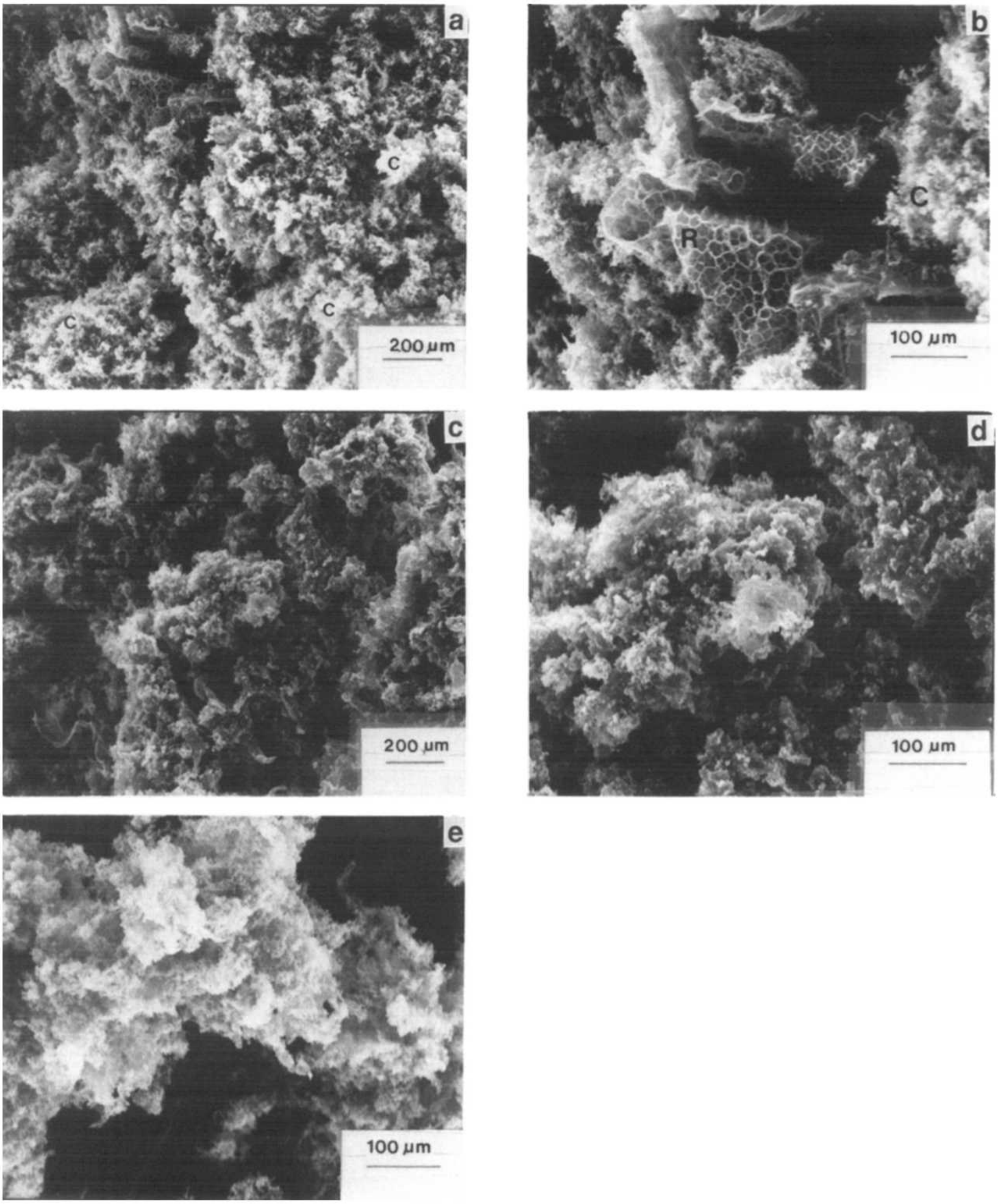

Figure 1 Scanning electron micrographs of polypyrrole/polyurethane composites prepared by the concentrated emulsion and so pathways. (a) Composite prepared by the concentrated emulsion pathway. (b) The same composite as in (a) at a different magnification. (c) Composite prepared by the solution pathway. (d) The same composite as in (c) at a different magnification. (e) Polypyrrole powder prepared by the chemical oxidation method

The results are presented in *Figure 2*. The composite polypyrrole based on the polyurethane concentrated emulsion has a higher conductivity than that prepared with the polyurethane solution. It should be noted that, as expected, the difference in the conductivities becomes insignificant when either polypyrrole or polyurethane is in excess.

In the case of polyurethane solution in chloroform, the evaporation of the solvent affects the distribution of polyurethane in the composite. A greater amount of polyurethane accumulates on the surface which thus becomes stickier.

Effect of the amount of polypyrrole on conductivity

The effect of the amount of polypyrrole on the conductivity of the composite polymer is examined in *Figure 2*. An optimum composition of 68% of polypyrrole by weight when the polyurethane concen-

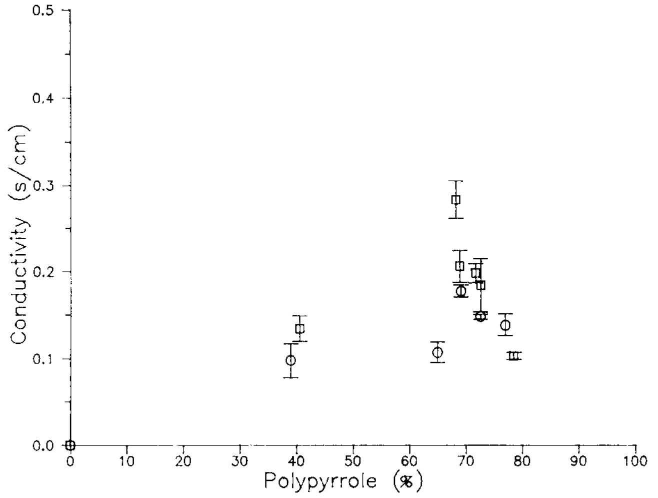

Figure 2 Conductivity of polypyrrole/polyurethane composite against the amount of polypyrrole in the composite (by weight). □, Composites prepared by the concentrated emulsion pathway; ○, composites prepared by the solution pathway

trated emulsion pathway was used, and of about 70% when the polyurethane solution was employed occurs. The decrease in conductivity with increasing amount of insulator (polyurethane) is due to the increasing prevention of formation of polypyrrole channels for electron transport. For large amounts of polypyrrole, the conductivity also decreases with increasing amount of polypyrrole. This might be due to the loose nature of the polypyrrole powder. Small amounts of polyurethane are not able to hold the polypyrrole powder in a more compact form. The increasing amount of gaps among the polypyrrole particles results in a decrease in conductivity.

Secondary reinforcement with polyacrylamide

Although the polypyrrole/polyurethane composite can be handled, its mechanical properties are still poor. A secondary reinforcement is therefore necessary for practical applications. Polyacrylamide infiltration was therefore used to enhance the mechanical properties of the composite polymer. Because acrylamide is soluble in water and the composite is hydrophobic, the incorporation of an acrylamide aqueous solution in the matrix is not expected to affect in a major way the morphology of the polypyrrole/polyurethane composite. *Figure 3* presents the conductivities of polypyrrole/polyurethane and polypyrrole/polyurethane/polyacrylamide composites when the concentrated emulsion pathway was employed. The conductivity is somewhat decreased by the reinforcement.

The morphology of the reinforced composite was also examined by scanning electron microscopy. *Figure 4a* shows that the polyacrylamide is incorporated in the polypyrrole/polyurethane composite by filling the pores rather than breaking the matrix structure of the original composite.

The reinforcement of polypyrrole/polyurethane composite was also carried out when the polyurethane solution pathway was employed in the preparation of the polyurethane/polypyrrole composite. *Figure 4b* shows the morphology of this composite. As in *Figure 4a*, the polyacrylamide fills the pores. The results of the conductivity measurements are presented in *Figure 5*. There is no drastic decrease in conductivity after reinforcement.

FT*i.r. characterization of the composite polymer*

Since the polyurethane is distributed in the composite, some physical and/or chemical interactions should occur

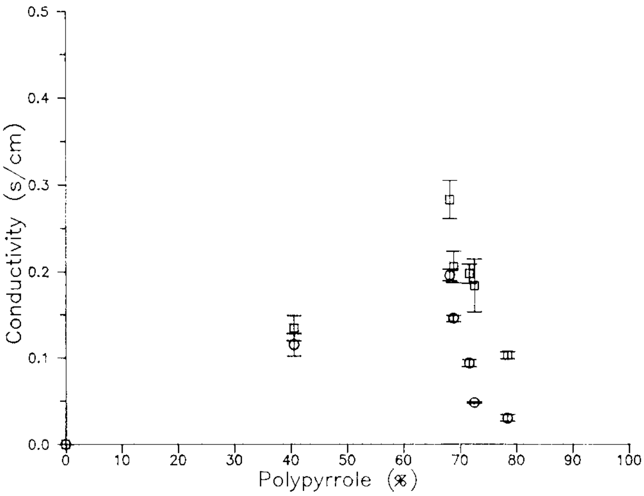

Figure 3 Conductivity of polypyrrole/polyurethane composites (□), and polypyrrole/polyurethane/polyacrylamide composites (○) against the amount of polypyrrole in the composites (by weight). The amounts of polypyrrole in these composites are expressed based on polypyrrole/polyurethane. The composites were prepared by the concentrated emulsion pathway

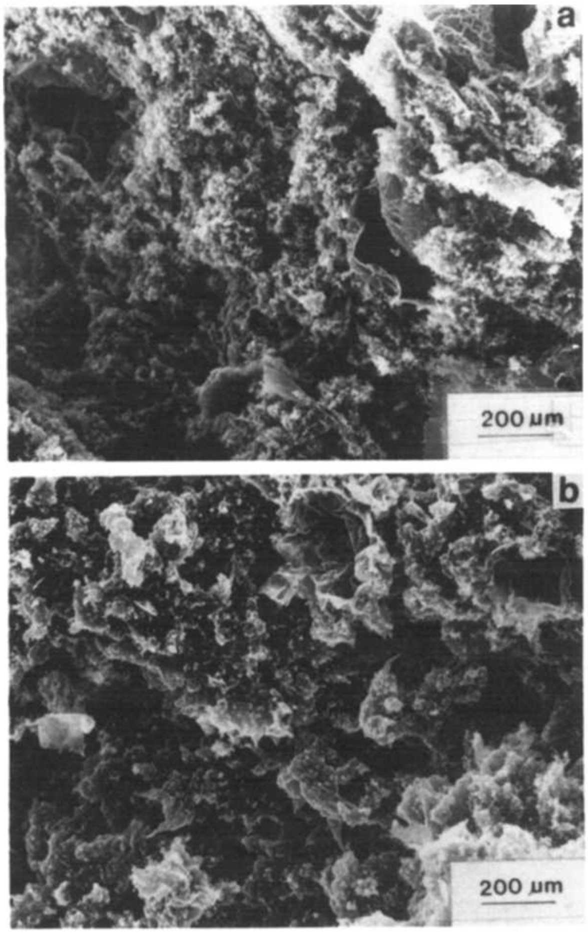

Figure 4 Scanning electron micrographs of (a) polypyrrole/polyurethane/polyacrylamide composite prepared by the concentrated emulsion pathway, and (b) polypyrrole/polyurethane/polyacrylamide composite prepared by the polyurethane solution pathway

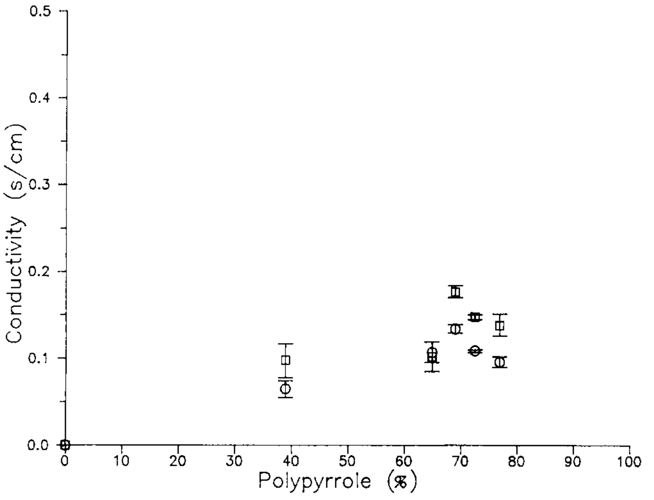

Figure 5 The conductivity of polypyrrole/polyurethane composites (□), and polypyrrole/polyurethane/polyacrylamide composites (○) against the amount of polypyrrole in the composites (by weight). The amounts of polypyrrole in these composites are expressed based on polypyrrole/polyurethane. The composites were prepared by the polyurethane solution pathway

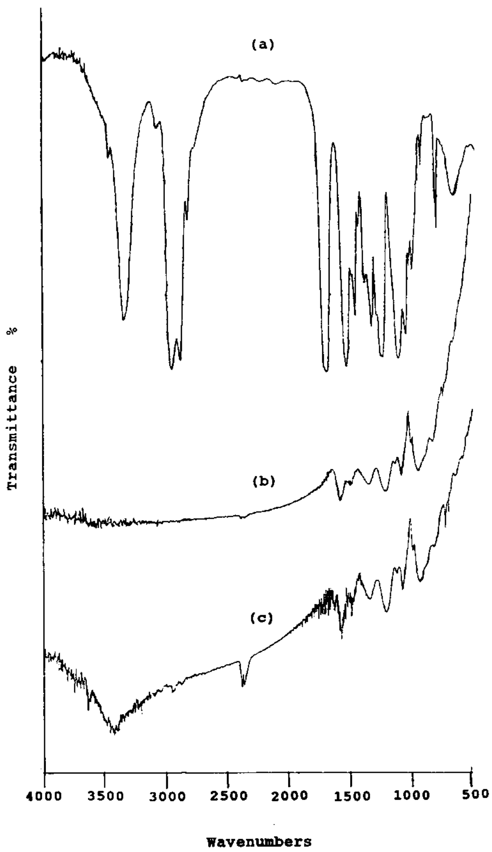

Figure 6 The *FT*i.r. spectra of curve a, polyurethane (Tecoflex, TR 7525); curve b, polypyrrole; and curve c, polypyrrole/polyurethane composite. The polypyrrole was prepared by the chemical oxidation method. The polypyrrole/polyurethane composite, in which polypyrrole was 68% by weight, was prepared by the concentrated emulsion pathway

between polypyrrole and polyurethane. *FT*i.r. experiments were performed to study these interactions. Curve a in *Figure 6* presents the i.r. spectrum of polyurethane and curve b that of polypyrrole. The region below 1800 cm^{-1} contains bands at 1543, 1303, 1168, 1040, and 904 cm^{-1} which are characteristic for the pyrrole moiety[10]. The i.r. spectrum of the polypyrrole/polyurethane composite is given in curve c in *Figure 6*. The i.r. spectrum of the composite in the region below 1800 cm^{-1} is identical to that of polypyrrole. One can therefore conclude that there is no strong chemical bonding between polypyrrole and polyurethane. Polypyrrole appears to be only mechanically blended with polyurethane. However, some hydrogen bonding may exist between the two. *Figure 7* shows the chemical structures of polypyrrole and polyurethane. The hard segments of polyurethane have electron-donor oxygen atoms in the $\overset{\text{O}}{\overset{\|}{\text{–C–}}}$ groups which are capable of forming hydrogen bonds with the electron-accepting hydrogen atoms in the $\overset{\text{H}}{\overset{|}{\text{–N–}}}$ groups of polypyrrole. These interactions, in addition to some physical interactions, may be responsible for the precipitation of the blend with the exclusion of some chloroform. In other words, the interactions between the hard segment of the polyurethane and polypyrrole may be stronger than those between the hard segment and chloroform.

Stability of the composite material

Although polypyrrole is more stable than other conductive polymers to the action of the environment, its conductivity still decreases during its exposure to the environment. *Figures 8* and 9 present the conductivity of polypyrrole and its composites against the exposure time. The polypyrrole prepared here has lost almost 60% of its conductivity after 30 days of exposure to the atmosphere. On the other hand, the polypyrrole/polyurethane composites remained more stable. For polyacrylamide enforced composites, the conductivity is also relatively stable. The composite polymers have higher stability in the environment than the pure polypyrrole, because the insulators (polyurethane and polyacrylamide) do not provide only mechanical strength but also prevent the exposure of polypyrrole to the atmosphere.

CONCLUSIONS

The blending of polypyrrole with polyurethane via the concentrated emulsion pathway provides a better composite polymer than the blending with polyurethane via the solution pathway. The conductivities of the composites prepared via the concentrated emulsion pathway ($\simeq$0.28 S cm^{-1}) are higher than those prepared

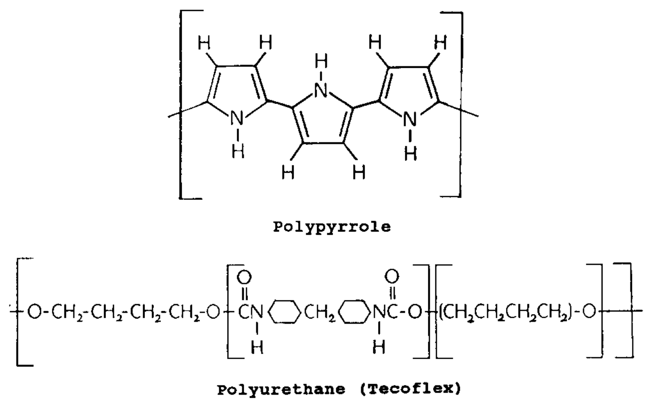

Figure 7 The chemical structures of polypyrrole and polyurethane (Tecoflex)

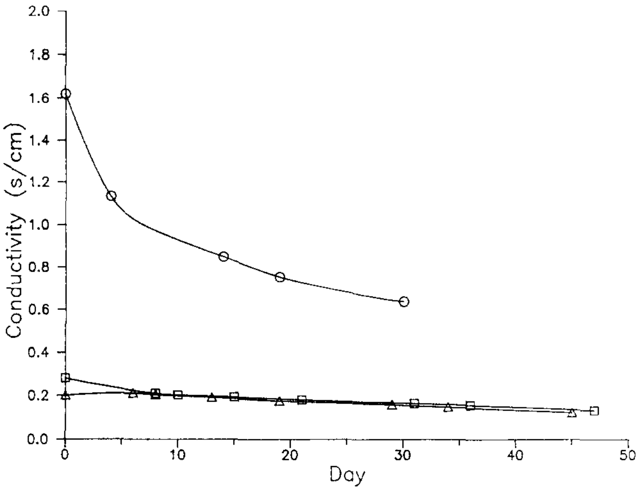

Figure 8 Conductivity of polypyrrole and polypyrrole/polyurethane composites against the storage time. ○, Polypyrrole; □, polypyrrole (68% by weight)/polyurethane composite; △, polypyrrole (71% by weight)/polyurethane composite. The polypyrrole was prepared by the chemical oxidation method, and then was pressed into a platelet. The composites were prepared by the concentrated emulsion pathway

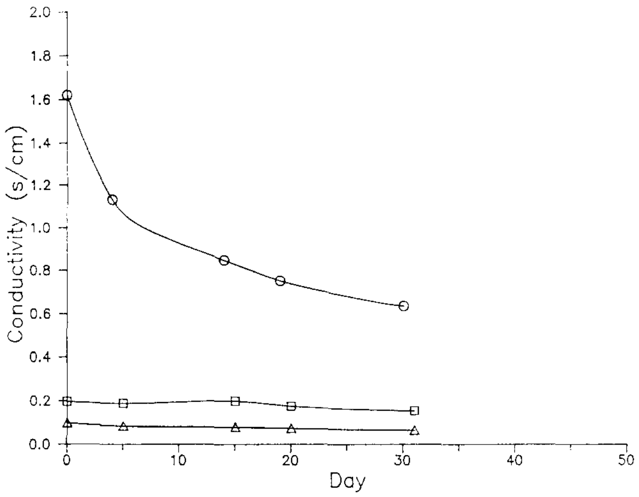

Figure 9 The conductivity of polypyrrole and polypyrrole/polyurethane/polyacrylamide composites against storage time. ○, Polypyrrole; □, polypyrrole (14.4% by weight)/polyurethane (6.8% by weight)/polyacrylamide (78.8% by weight); △, polypyrrole (13.6% by weight)/polyurethane (5.6% by weight)/polyacrylamide (80.8% by weight). The polypyrrole was prepared by the chemical oxidation method, and then was pressed into a platelet. The composites were prepared by the concentrated emulsion pathway and reinforced with polyacrylamide

via the solution pathway ($\simeq 0.17\,\mathrm{S\,cm^{-1}}$). In addition, it is easier to handle the composite prepared using the concentrated emulsion pathway than that using the solution pathway in moulding the composite polymer.

An optimum composition of polypyrrole/polyurethane composite occurs at about 68% (by weight) of polypyrrole.

The composite polypyrrole has not only higher mechanical strength but also better stability to the action of the environment.

The polypyrrole/polyurethane composite can be reinforced with polyacrylamide without drastically changing its conductivity.

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