# Processable conductive polypyrrole/poly(alkyl methacrylate) composites prepared by an emulsion pathway

**Eli Ruckenstein*** **and Shiyong Yang**
*Department of Chemical Engineering, State University of New York at Buffalo, Box 60, Buffalo, NY 14260-4200, USA*
*(Received 26 January 1993; revised 26 March 1993)*

Electrically conductive polymer composites of polypyrrole and poly(alkyl methacrylate) have been prepared using a two-step procedure. First, an emulsion is generated by dispersing a chloroform solution of poly(alkyl methacrylate) and pyrrole in a small amount of an aqueous surfactant solution. The surfactant is adsorbed upon the interface between the two phases and ensures, via double-layer repulsion, the stability of the emulsion. Second, the pyrrole present in the emulsion is polymerized and doped by introducing with stirring an aqueous solution of an oxidant in the emulsion. The polypyrrole deposits on the host polymer, and the composite formed is precipitated using a suitable non-solvent. Smooth, lustrous films or other shaped objects with good mechanical properties have been prepared by hot-pressing the obtained materials. The relation between conductivity and the polypyrrole content of the composite exhibits a percolation behaviour. The electrical conductivity can reach values as high as 6–7 S cm$^{-1}$. The mechanical properties of the material depend on the nature of the host polymer employed and on the content of polypyrrole in the composite. The effect of the length of the alkyl chain on the mechanical properties is investigated. The polypyrrole–poly(ethyl methacrylate) composites appear to be the most suitable because they have enough flexibility and also sufficient strength. Compared to cold-pressing, hot-pressing improves the mechanical characteristics, but decreases somewhat the conductivity. Two single-step procedures have also been employed, but they are less efficient than the two-step procedure and lead to very low conductivities.

**(Keywords: conductivity; composites; emulsion)**

## INTRODUCTION

Electrically conductive polymers have been the subject of considerable research effort due to their interesting and useful electronic, optical and redox properties[1–3]. These materials exhibit high conductivities and some of them have environmental stability. However, their practical use has been hampered by the fact that many of these conjugated polymers are insoluble and infusible. For this reason, the conventional methods for polymer processing, such as melt-processing and solution-casting, could not usually be applied to these materials. Numerous studies have been conducted and many methods developed for the improvement of their processability. For pyrrole-based conductive polymers these include synthesizing soluble N- or ring-substituted derivatives, i.e. introducing flexible side substituents to the main rigid chain[4] or grafting conducting polymer chains to a non-conducting polymer[5]. Polypyrrole (PPy) films have been prepared by electrochemical polymerization on the surface of an electrode[6–8], or by the interfacial oxidative polymerization method[9].

Of all the methods, the preparation of composites of conductive and non-conductive polymers, which was stimulated by the successful use of carbon- or silver-filled polymers in a variety of electronic devices, is considered to be a most suitable procedure. Several methods have been reported which combine strong insulating materials with conducting polymers. Initially, such conductive composites have been prepared by incorporating a chemically or electrochemically synthesized conductive polymer in an insulating polymer substrate. The process was carried out either by exposing an insulating sheet imbibed with an oxidant to the monomer or its vapour, or by electrochemical oxidation of a monomer-swollen matrix coated as a film on an electrode[10–12]. However, because of the low penetration of the monomer into the insulating substrate, only very thin conductive polymer films could be obtained. PPy–poly(methyl methacrylate) (PMMA) composite films have also been prepared via chemical polymerization by spreading a water-insoluble solvent solution of pyrrole and PMMA on the surface of an aqueous solution containing the oxidizing agent[13,14]. Another method for the preparation of composites consists in chemically polymerizing the monomer of the conductive polymer inside an insulating porous polymer matrix[15,16]. The uniform distribution, with a sufficiently high loading to reach the percolation threshold, of the conductive

---

* To whom correspondence should be addressed

0032-3861/93/224655-06

polymer into the insulating polymer constitutes the essential factor in the preparation of highly conducting polymer composites.

Recently, a two-step pathway, involving an emulsion in the first step, has been developed in our laboratory for the preparation of composites of polyaniline and an insulating polymer. A solution of the host polymer and monomer in an organic solvent constitutes the dispersed phase, while an aqueous surfactant solution constitutes the continuous phase of the emulsion. In the second step, an oxidant solution is introduced in the emulsion. The materials thus prepared could be processed by cold- or hot-pressing, and possess excellent mechanical properties and good electrical conductivities[17,18]. In this paper, the same pathway is employed to prepare a series of processable conductive composites that combine PPy and poly(alkyl methacrylate). The effect of the length of the alkyl side chain on the mechanical properties of the composites is investigated.

The present method represents an improvement of a previous method[19] developed in this laboratory. In ref. 19 a PPy–polyurethane composite was obtained by mixing (1) a concentrated emulsion containing polyurethane in chloroform as the dispersed phase and sodium dodecyl sulfate in water as the continuous phase, with (2) a suspension of PPy in water prepared by the chemical oxidation method. In the same year, a patent was published[20] suggesting a single-step emulsion pathway. An emulsion of PMMA, pyrrole, $CH_2Cl_2$, poly(vinyl alcohol), emulsifier and water was subjected to oxidative polymerization with $FeCl_3{\cdot}6H_2O$. The method is similar to method III of the present paper, which, as demonstrated later, leads to much lower conductivities than the two-step method employed by us. The conductivity obtained in the patent was indeed low ($\sim 10^{-3}\,S\,cm^{-1}$). Finally, another patent[21] should be noted, in which a monomer was oxidatively polymerized in a reaction medium containing latex particles of a suitable polymer. The conductivity obtained was low.

## EXPERIMENTAL

### *Chemicals*

Pyrrole (98%, Aldrich) was purified by distillation in vacuum and stored in a refrigerator before use. PMMA (very high molecular weight, Aldrich), poly(ethyl methacrylate) (PEMA, high molecular weight, Aldrich) and poly(butyl methacrylate) (PBMA, very high molecular weight, Aldrich), ferric chloride (98%, Aldrich), $FeCl_3{\cdot}6H_2O$ (97%, Aldrich), $Fe(ClO_4)_3{\cdot}6H_2O$ (Aldrich), $CuCl_2$ (anhydrous, Aldrich), $Cu(ClO_4)_2{\cdot}6H_2O$ (Aldrich), sodium dodecyl sulfate (SDS, 99.5%, Polysciences), sodium dodecylbenzene sulfate (Aldrich), sodium octadecyl sulfate (97%, Aldrich), chloroform (99%, Aldrich), methanol (99% Aldrich), benzene (99%, Aldrich), 1,2-dichloroethane (99%, Aldrich) and octane (99%, Aldrich) were used as received. Water was deionized and double distilled.

### *Preparation of the electrically conductive composites*

The composites were prepared starting from an emulsion in which a solution of surfactant in water constitutes the continuous phase and a solution of the host polymer (PMMA, PEMA or PBMA) and the monomer pyrrole in an organic solvent the dispersed phase. The surfactant molecules are adsorbed upon the interface between the two phases; because of their charge these generate electrical double layers which ensure, via electrostatic repulsion, the stability of the emulsion. The pyrrole dispersed in the emulsion was polymerized and doped by introducing an aqueous solution of oxidant in the emulsion with vigorous stirring. In a typical experiment, 10 ml chloroform solution containing 0.8 g PEMA and 0.1 g pyrrole were added to a 100 ml flask containing a solution of 0.2 g SDS in 2 ml water with vigorous stirring. In the emulsion thus generated, 10 ml of an aqueous solution containing 0.5 g ferric chloride was introduced dropwise with stirring to polymerize the pyrrole and to dope the formed polypyrrole. The polymerization reaction lasted 3 h with stirring. For the precipitation of the composite formed, 25 ml methanol was added to the emulsion with stirring. The entire process took place at room temperature. The solid material was filtered, washed with methanol several times, and finally dried at 40°C in vacuum for 24 h. Some 0.86 g of polypyrrole/poly(ethyl methacrylate) (PPy/PEMA) composite was thus obtained. The yield of the composite was 96% and was estimated using the expression:

$$\text{yield of composite } (\%) = \frac{100 \times \text{composite (g)}}{\text{pyrrole (g)} + \text{host polymer (g)}}$$

and neglecting, because of the difficulty in evaluating it, the doping of the PPy. The elemental analysis of this composite (wt%) is: C = 64.24, H = 8.28, N = 1.89, Fe = 0.11, Cl = 1.6. The values calculated from the amounts of reactants used are: C = 64.26, H = 8.36, N = 2.39 and O = 24.89. The PPy/PMMA and the PPy/PBMA composites were synthesized in the same way.

The same procedure described above is subsequently referred to as method I. Two variants of method I were also employed. In the first (method II), an aqueous solution containing the oxidant was added with stirring to the organic solvent containing pyrrole and the host polymer. In the second (method III), the composite was prepared by mixing the organic solution containing pyrrole and the host polymer with an aqueous solution of surfactant and oxidant. While method I is a two-step procedure, the other two methods are single-step procedures.

### *Instruments*

The powder was shaped into a disc (2.5 cm diameter × 0.2 cm) at room temperature, by pressing for a few minutes with a pressure of 120 MPa (cold-pressing). In addition, films were prepared by hot-pressing at 150°C for 2 h under an applied pressure of 20 MPa the discs prepared by cold-pressing. The electrical conductivity of the discs and films was measured by the standard four-point technique. The mechanical properties of the films were determined with an Instron Universal Testing Instrument (model 1000). The morphologies of the composites were investigated by scanning electron microscopy (SEM, Hitachi S-800). The elemental analysis was carried out by Quantitative Technologies, Inc. (Whitehouse, NJ, USA).

## RESULTS AND DISCUSSION

The conductive polymer composites were prepared using methods I–III, described above. In method I, an emulsion

**Table 1** Comparison of the polypyrrole/poly(alkyl methacrylate) composites prepared by the three procedures

| Method | Composite (PPy wt%) | Yield (%) | Conductivity ($S\,cm^{-1}$) | |
|---|---|---|---|---|
| | | | Cold-pressing | Hot-pressing |
| I | PMMA/PPy (20%) | 87 | 0.8 | 0.5 |
| | PEMA/PPy (20%) | 93 | 0.6 | 0.4 |
| | PBMA/PPy (20%) | 73 | 0.5 | 0.5 |
| II | PEMA/PPy (20%) | 85 | <0.01 | 0.04 |
| III | PMMA/PPy (20%) | 92 | <0.001 | 0.02 |

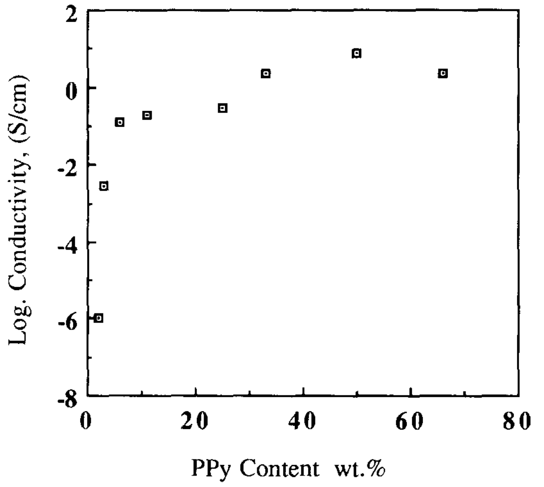

**Figure 1** Dependence of the conductivity of the composite on the polypyrrole content. The composites were prepared under the following conditions: $[FeCl_3]/[pyrrole] = 1:1$ (mol/mol); volume fraction of the dispersed phase ($\phi$) of the emulsion prepared in the first step = 0.83; surfactant concentration in the continuous phase of the emulsion prepared in the first step = $0.1\,g\,ml^{-1}$ chloroform; PEMA concentration in the dispersed phase of the emulsion prepared in the first step = $0.08\,g\,ml^{-1}$; polymerization time = 3 h; polymerization temperature = 25°C. A solution of 0.14 M of oxidant in water is employed

of an organic solvent (containing the host polymer and pyrrole) in an aqueous solution of surfactant was first formed. In the present work, the emulsion was a concentrated emulsion with a volume fraction of the dispersed phase ($\phi$) equal to 0.83; it had the appearance of a gel. The continuous phase is in the form of a network of liquid films that separate the cells of the dispersed phase. The stability of the emulsion is ensured by the surfactant adsorbed upon the interface between the two phases as an oriented, charged interfacial film. The size of the cells of the dispersed phase is in the range of micrometres[22]. Consequently, the dispersed phase, which contains the pyrrole, possesses a very large surface area of contact with the continuous phase. The aqueous solution of the oxidant, which is introduced in the second step in the emulsion, can therefore be more uniformly distributed among the micrometre-sized cells. The absence of such a structure in the other two one-step procedures does not allow a sufficiently good contact between pyrrole and oxidant. As a result, lower conductivities for methods II and III than for method I are expected.

*Table 1* lists the composites prepared by the three procedures and allows a comparison to be made between them. It shows that the conductivities of the composites prepared by method I are much higher than those of the composites prepared by methods II and III. The amounts of components employed are indicated in the Experimental section for method I; for method II, the 2 ml of water containing 0.2 g of surfactant is missing; for method III, the 2 ml of water is missing.

Because the host polymers employed can be moulded by melt-processing (the glass transition temperatures of PEMA and PBMA being 66 and 27°C, respectively), the composites containing these polymers can be shaped by hot-pressing at suitable temperatures and pressures. Lustrous films, either flexible or robust, have been thus obtained. The samples prepared by hot-pressing have, however, a somewhat lower conductivity than those prepared by cold-pressing, perhaps because of the degradation of some PPy chains caused by the high temperature, which decreases the conjugation length.

All the experimental data discussed below are based on method I. The experimental data regarding the dependence of the electrical conductivity at room temperature on the weight fraction of PPy are presented in *Figure 1* for the PPy/PEMA composite. They show a percolation behaviour, with reasonably high conductivities even for composites with relatively low content of conductive polymer. For example, the sample containing 10 wt% PPy has a conductivity of $0.3\,S\,cm^{-1}$. The percolation threshold occurs in the range 4–10 wt%. Similar results have been obtained in this laboratory for composites prepared from polyaniline and poly(alkyl methacrylate) or polystyrene[17,18]. The small percolation threshold indicates that the conductive polymer molecules are well dispersed in the composite. Electron tunnelling may also play a role.

*Figure 2* shows the effect of the mole ratio of oxidant (ferric chloride) to pyrrole on the conductivity. There is an optimum mole ratio of oxidant to pyrrole in the range of 1–2. The conductivity of the composite increases rapidly with increasing amounts of oxidant below the optimum value, and decreases with a further increase in the oxidant mole ratio. As expected, the yield of the composite increases with increasing oxidant concentration. The decrease of the conductivity beyond

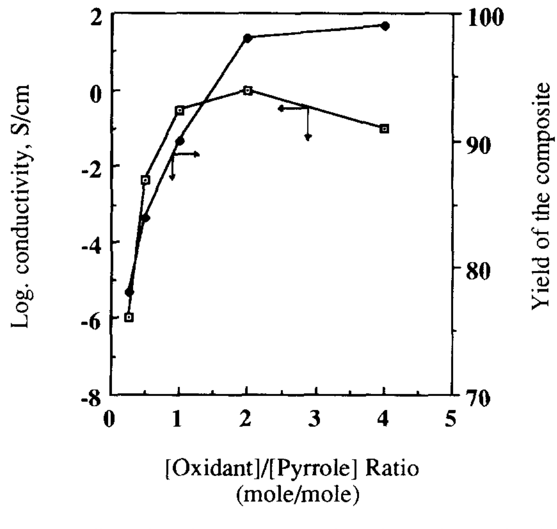

**Figure 2** Effect of oxidant/pyrrole mole ratio on the conductivity and yield of the composite. PEMA/pyrrole = 4:1 (w/w); the other conditions are as in *Figure 1*

**Table 2** Effect of the oxidant employed on the conductivity of the composite[a]

| No. | Oxidant | Yield (%) | Conductivity ($S\,cm^{-1}$) Hot-pressing | Conductivity ($S\,cm^{-1}$) Cold-pressing |
|---|---|---|---|---|
| 1 | $FeCl_3$ | 87 | 0.4 | 0.6 |
| 2 | $FeCl_3{\cdot}6H_2O$ | 85 | 0.2 | 0.4 |
| 3 | $Fe(ClO_4)_3{\cdot}6H_2O$ | 90 | 0.03 | 0.03 |
| 4 | $CuCl_2$ | 80 | $<10^{-3}$ | 0.03 |
| 5 | $Cu(ClO_4)_2{\cdot}6H_2O$ | 75 | $<10^{-4}$ | |

[a] The composites were prepared under the following conditions: PEMA/pyrrole (w/w) = 4:1; [oxidant]/[pyrrole] (mol/mol) = 1:1; volume fraction of the dispersed phase of the emulsion prepared in the first step ($\phi$) = 0.83; SDS concentration in the continuous phase of the emulsion prepared in the first step = $0.1\,g\,ml^{-1}$; PEMA concentration in the dispersed phase of the emulsion prepared in the first step = $0.08\,g\,ml^{-1}$; polymerization time = 3 h; polymerization temperature = 25°C. A solution of 0.14 M of oxidant in water is employed

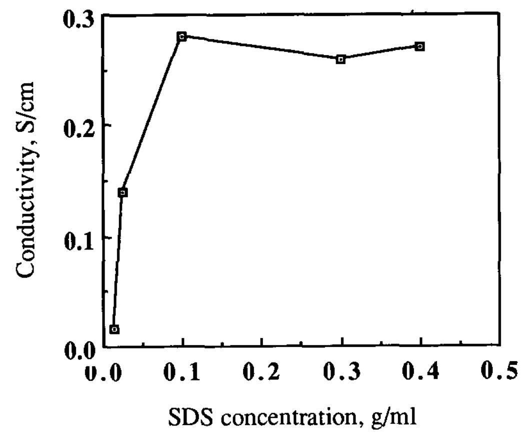

**Figure 3** Dependence of the conductivity of the composite on the surfactant concentration in the continuous phase of the emulsion obtained in the first step. The conditions are as in *Figure 2*

the maximum is probably due to the decrease in the average degree of polymerization. This implies shorter conjugation lengths. Other oxidants were also employed and the results are summarized in *Table 2*, which shows that ferric chloride and its hydrate lead to composites with high conductivities. While the polymerization of pyrrole can also be initiated by copper chloride or copper perchloride, long times (about 20–24 h) were needed to complete the polymerization process, and the conductivities achieved were low.

The dependence of the composite conductivity on the concentration of surfactant in the continuous phase of the emulsion prepared in the first step is presented in *Figure 3*. A minimum amount of SDS ($0.1\,g\,ml^{-1}$) is needed to obtain a composite with high conductivity. Three common surfactants are compared in *Table 3*. As already noted, the role of the surfactant is to ensure, through its adsorption on the interface of the phases, the stability of the emulsion both during its preparation and during the polymerization. The composite prepared with sodium dodecylbenzene sulfate has a relatively low conductivity; the films obtained by hot-pressing were no longer lustrous and some oil was present on their surface.

The effect of the solvent used for the dispersed phase on the conductivity of the composite is examined in *Table 4*. Chloroform, 1,2-dichloroethane and benzene are good solvents, but the composite based on ethyl acetate exhibits a low conductivity. This is because no emulsion is generated by dispersing the ethyl acetate solution of PEMA and pyrrole into the SDS aqueous solution. The relatively low hydrophobicity of ethyl acetate is responsible for this behaviour, since an emulsion is stable only when one of the phases is sufficiently hydrophobic and the other sufficiently hydrophilic. Although octane is a hydrophobic solvent, it could not be used because poly(alkyl methacrylate) is insoluble in this solvent. Consequently, a suitable solvent for the dispersed phase should possess enough hydrophobicity but should also be a solvent for the host polymer and pyrrole.

*Figure 4* presents the effect of the polymerization time on the conductivity of the composite. Two hours were needed to complete the polymerization of pyrrole, but

**Table 3** Effect of the nature of the surfactant on the conductivity of the composite[a]

| No. | Surfactant | Yield (%) | Conductivity ($S\,cm^{-1}$) Hot-pressing | Conductivity ($S\,cm^{-1}$) Cold-pressing |
|---|---|---|---|---|
| 1 | Sodium dodecyl sulfate | 87 | 0.4 | 0.6 |
| 2 | Sodium dodecylbenzene sulfate | 89 | 0.01 | 0.03 |
| 3 | Sodium octadecyl sulfate | 93 | 0.2 | 0.8 |

[a] The conditions are as in *Table 2*

**Table 4** Effect of the solvent used in the dispersed phase on the conductivity of the composite[a]

| No. | Solvent | Yield (%) | Conductivity ($S\,cm^{-1}$) Hot-pressing | Conductivity ($S\,cm^{-1}$) Cold-pressing |
|---|---|---|---|---|
| 1 | Chloroform | 87 | 0.4 | 0.6 |
| 2 | Benzene | 80 | 0.6 | 1.1 |
| 3 | 1,2-Dichloroethane | 85 | 0.4 | |
| 4 | Ethyl acetate | 81 | 0.005 | 0.01 |
| 5 | Octane | –[b] | –[b] | |

[a] The conditions are as in *Table 2*

[b] PEMA does not dissolve in octane

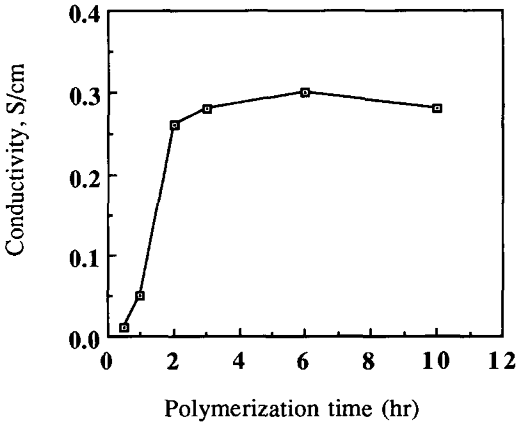

**Figure 4** Effect of the polymerization time on the conductivity of the composite. The conditions are as in *Figure 2*

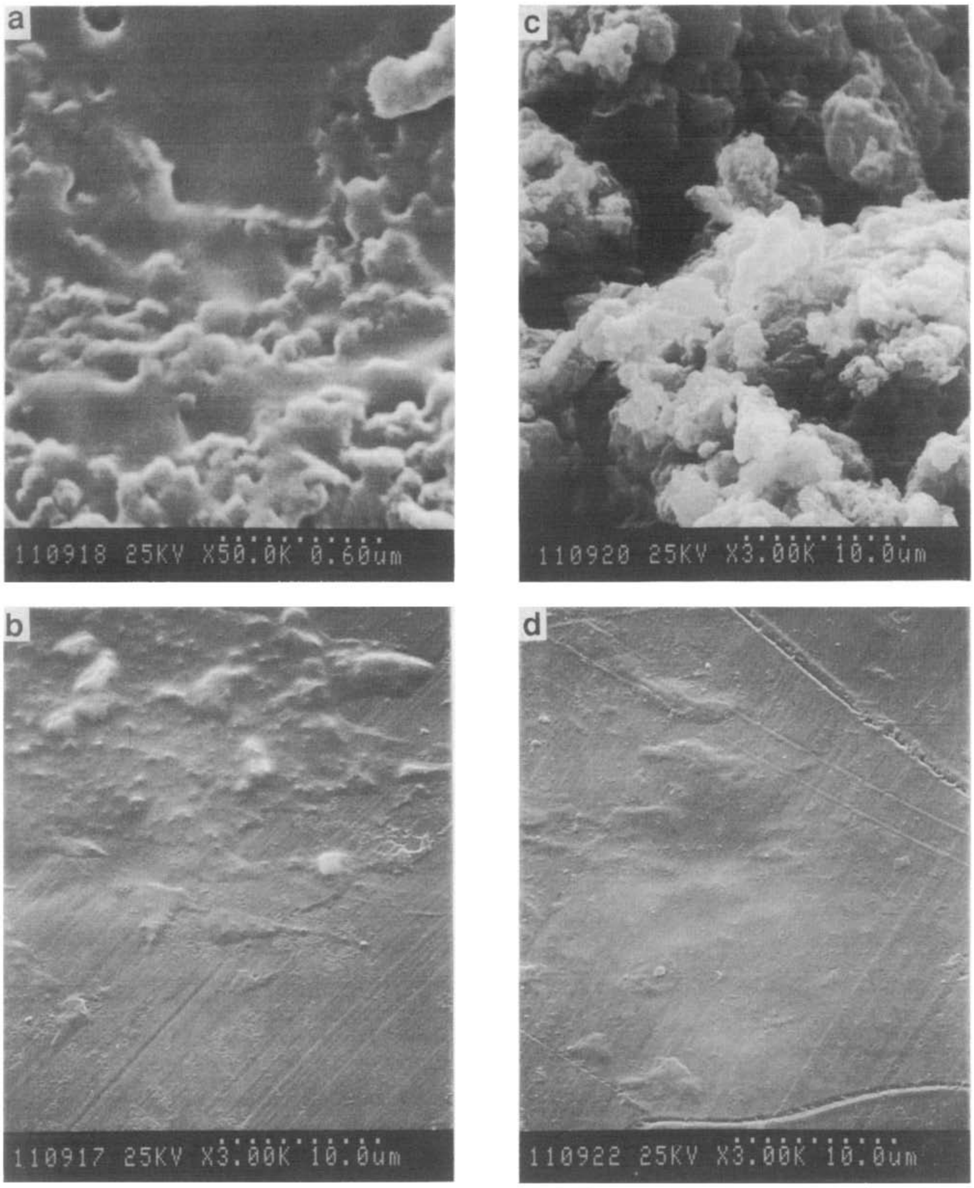

**Figure 5** Scanning electron micrographs of PPy/PEMA composites: (a) PPy/PEMA (11 wt% PPy) prepared by cold-pressing; (b) PPy/PEMA (11 wt% PPy) prepared by hot-pressing; (c) PPy/PEMA (20 wt% PPy) prepared by cold-pressing; (d) PPy/PEMA (20 wt% PPy) prepared by hot-pressing

**Table 5** Mechanical properties of polypyrrole/poly(alkyl methacrylate) composites[a]

| Composite (PPy wt%) | Elongation at the breakpoint (%) | Tensile strength at the breakpoint (MPa) | Conductivity ($S\ cm^{-1}$) | |
|---|---|---|---|---|
| | | | Cold-pressing | Hot-pressing |
| PMMA/PPy (20) | 15 | 25 | 0.8 | 0.5 |
| PEMA/PPy (20) | 45 | 13 | 0.6 | 0.4 |
| PBMA/PPy (20) | 150 | 8 | 0.5 | 0.5 |

[a] The conditions are as in *Table 2*

no differences in conductivity were detected for longer polymerization times.

Scanning electron micrographs for the PPy/PEMA composites containing 11 and 25 wt% PPy are presented in *Figure 5*. Morphologies based on aggregated particles are observed for the samples prepared by cold-pressing (*Figures 5a* and *c*). The particle sizes are estimated to be in the range 0.05–0.1 μm. Dramatic changes in morphologies occur in the films prepared by hot-pressing (*Figures 5b* and *d*). In these films, the primary particles are replaced by completely non-particulate, homogeneous phases. A distinct PPy phase could not be detected by SEM.

*Table 5* lists the mechanical properties of three typical composites: PPy/PMMA, PPy/PEMA and PPy/PBMA. The tensile strength at the breakpoint decreases and the corresponding elongation increases as the alkyl side chains in the host polymer become larger, due to the

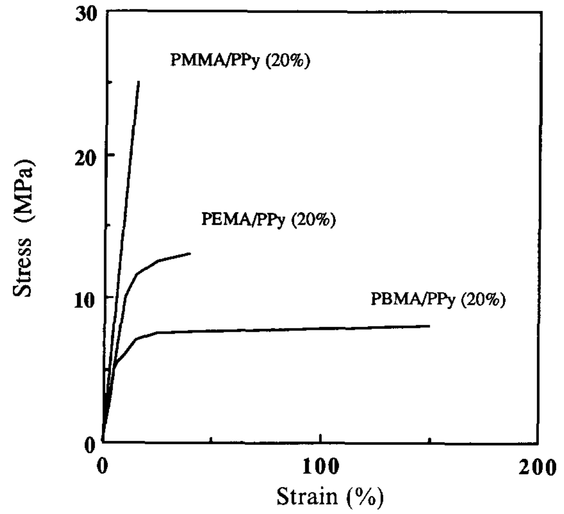

**Figure 6** Strain–stress curves for the composites prepared with different host polymers. Polymer concentration = 0.08 g/ml chloroform; the other conditions are as in *Figure 1*

increase in the free volume of the polymers. The stress–strain curves for these materials are presented in *Figure 6*. The PPy/PEMA composite appears to be the most suitable because it has enough flexibility and also has sufficient strength. The PPy/PMMA composite is somewhat brittle, while the PPy/PBMA composite does not have enough strength.

## CONCLUSION

Processable composites of polypyrrole/poly(alkyl methacrylate) have been prepared by chemically polymerizing the pyrrole present in an emulsion which also contains poly(alkyl methacrylate). A percolation behaviour with a low percolation threshold of approximately 4–10 wt% was observed in the relation between the conductivity and the polypyrrole content. Conductivities as large as 6–7 S $cm^{-1}$ have been obtained. The mechanical properties of the composite films prepared by hot-pressing depend on the nature of the host polymer employed, the tensile strength at the breakpoint decreasing and the corresponding elongation increasing as the alkyl side chains in the host polymer become larger.

## REFERENCES

1 Skotheim, T. A. (Ed.) 'Handbook of Conducting Polymers', Vol. 1, Marcel Dekker, New York, 1986
2 Burroughes, J. H., Bradly, D. D. C., Brown, A. R., Marks, R. N., Mackay, K., Friend, R. H., Burnes, P. L. and Holmes, A. B. *Nature* 1990, **347**, 539
3 Stevens, T. *Mater. Eng.* 1991, **108**, 21
4 Dao, L. H., Leclerc, M., Guay, J. and Chevalier, J. W. *Synth. Met.* 1989, **29**, E377
5 Li, S., Cao, Y. and Xue, Z. *Synth. Met.* 1987, **20**, 141
6 Diaz, A. F. and Kanazawa, K. K. *J. Chem. Soc. Chem. Commun.* 1979, 635
7 Kuwabata, S., Okamoto, K., Ikeda, O. and Yoneyama, H. *Synth. Met.* 1987, **18**, 101
8 Peres, R. C. D., Pernault, J. M. and DePaoli, M. A. *J. Polym. Sci. A. Polym. Chem.* 1991, **29**, 225
9 Nakata, M., Taga, M. and Kise, H. *Polym. J.* 1992, **24**, 437
10 Diaz, A. F., Paoli, M. and Waltman, R. J. *J. Polym. Sci. A. Polym. Chem.* 1985, **23**, 1687
11 Yoshikawa, T., Machida, S., Ikegami, T. N., Techagumpuch, A. and Miyata, S. *Polym. J.* 1990, **22**, 1
12 Li, C. J. and Song, Z. G. *Synth. Met.* 1991, **40**, 23
13 Moreta, M., Hashida, I. and Nishimura, M. *J. Appl. Polym. Sci.* 1988, **36**, 1639
14 Chan, H. S. O., Hor, T. S. A., Ho, P. K. H., Tan, K. L. and Tan, B. T. G. *J. Macromol. Sci.-Chem.* 1990, **A27**, 1081
15 Ruckenstein, E. and Park, J. S. *J. Appl. Polym. Sci.* 1991, **42**, 925
16 Ruckenstein, E. and Park, J. S. *Synth. Met.* 1991, **44**, 293
17 Ruckenstein, E. and Yang, S. Y. *Synth. Met.* 1993, **53**, 283
18 Yang, S. Y. and Ruckenstein, E. *Synth. Met.* 1993, **59**, 1
19 Ruckenstein, E. and Chen, J. H. *Polymer* 1991, **32**, 1230
20 Kato, K., Mineura, Y., Tuchida, Z. and Saito, T. Japanese Patent 03.234.733, 18 Oct. 1991
21 Jasne, S. J. European Patent 229992, 29 July 1987
22 Ruckenstein, E., Ebert, G. and Platz, G. *J. Colloid Interface Sci.* 1989, **133**, 432