Polymer Vol. 39 No. 10, pp. 1857–1862, 1998
© 1998 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/98/$19.00+0.00

PII: S0032-3861(97)00308-X

Conductive polymer composites prepared by polypyrrole-coated poly(vinyl chloride) powder: relationship between conductivity and surface morphology

Meng Ouyang and Chi Ming Chan*
Department of Chemical Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong, People's Republic of China
(Received 15 July 1996; revised 24 March 1997)

A novel process for the preparation of the polypyrrolelpoly(vinyl chloride) (PPy/PVC) conductive composites is reported. The procedure involves chemically polymerizing pyrrole in the presence of a PVC powder dispersed in an aqueous solution of $FeCl_3$. The PPy-encapsulated PVC particles were compressed-molded into conductive composite materials. The PPy contents in the pre-localized PPy/PVC composites were determined by elemental analyses. The effect of PPy content and processing conditions on the electrical conductivity were studied and the thermal decay of the electrical conductivity and environmental stability were also investigated. A very low percolation threshold value (0.3 wt%) has been obtained with these composite materials. The electrical conductivity of the PPy/PVC composite samples with only 1.6 wt% of PPy can be at least 10 orders of magnitude greater than that of the pure PVC sample. The surface morphology of the pre-localized PPy/PVC composites was characterized by means of a dynamic contact angle (DCA) analyser, a scanning electron microscope (SEM) and an optical microscope. The results of the dynamic angle analyses agree qualitatively with the results predicted for a heterogeneous surface. In addition, the sharp transition in the plot of the receding angle as a function of the PPy content which occurs at about 2 wt% of PPy may be related to the sharp increase in the conductivity at approximately the same PPy content. © 1998 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

Polypyrrole (PPy) is regarded as one of the most promising intrinsically conductive polymers for practical applications due to its relatively high electrical conductivity, environmental stability and low toxicity[1–4]. The typical PPy, which is insoluble and infusible, exhibits poor processability and lacks essential mechanical properties, as with conventional polymers. Efforts to overcome these drawbacks have led to numerous research reports of the improved methods for both electrochemical and chemical synthesis of PPy[5,6]. Among them, a significant strategy to approach both high electrical conductivity and desirable mechanical properties is through the use of preparing the composites based on PPy and conventional polymers by different processes, such as inducing oxidative polymerization of a liquid or gaseous pyrrole on conventional polymer films or fibres[7–10], and mechanically blending of a PPy powder as a conductive filler with a conventional polymer in the melt or solution[11–13]. Nevertheless, the former route is not applicable to producing polymer articles with high electrical conductivity. The latter route, the mechanical blending, does not appear desirable because the conductivity of the blends decreases substantially owing to the thermal aging during processing at elevated temperatures. Furthermore, a rather high percentage (usually above 40 wt%) of PPy in the blends is required to produce composites with high conductivity. In order to take advantage of the desired mechanical properties, processability and cost of conventional polymers, it is necessary to keep the PPy concentration in the composites at a minimum.

PPy/polymer composites have been prepared by chemical polymerization of pyrrole on various polymer particles such as polypropylene[14–16], polyethylene[15], poly(methyl methacrylate)[15,17], polystyrene[18], polyurethane[19] and alkyd[19]. Poly(vinyl chloride) (PVC) is one of the important commercial polymers and available in powder form. Recently we have developed a novel process for the preparation of PPy/PVC conductive composites by chemically polymerizing pyrrole in the presence of a PVC powder dispersed in an aqueous solution of $FeCl_3$[20]. The PVC particles encapsulated with a thin layer of PPy can be transformed into useful conductive products by compression molding (see *Figure 1*). The conductive PPy was localized at the interfacial regions of the PVC particles. We refer to these composite as the pre-localized PPy/PVC composites.

EXPERIMENTAL SECTION

Pyrrole (Riedel–de Haen, 98%) was purified by distillation under reduced pressure. PVC (SG4, Guangzhou Chemicals), which was produced by suspension polymerization, was used as received in powder form without further purification. The apparent density of the PVC powder is $0.42\ g\ ml^{-1}$ and the particle size varies from 0.063 to 0.25 mm (the average particle size is approximately 0.10 mm). $FeCl_3$ used as an oxidant was dissolved in distilled water (0.2 M aqueous $FeCl_3$ solution. A PVC powder (approximately 50 g) was added into the stirred

---

* To whom correspondence should be addressed

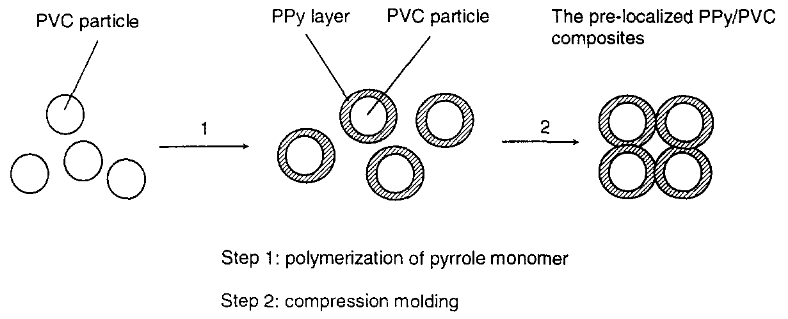

Figure 1 Schematic diagram showing the formation of the pre-localized PPy/PVC composites.

solution (approximately 200 ml) at 20°C, and then the pyrrole was gradually added to the reaction system which was continually stirred during the reaction process. It was observed that the colour of the PVC powder changed gradually from light yellow to dark brown within a few minutes. The reaction time was about 1 h. The resulting powder was filtered, washed with distilled water and then dried under vacuum at 40°C.

This PPy-encapsulated PVC powder was compression-molded at different temperatures and different pressures to obtain bulk samples, or pressed between two pieces of steel plate in a hot press set at an elevated temperature to obtain film samples.

The nitrogen and chlorine concentrations in the PPy-encapsulated PVC powder were determined using an elemental analyser (CHN-Rapid, Heraeus, Germany). The electrical conductivity of the PPy/PVC composites (cylindrical sample dimensions: diameter 12 mm, thickness 5 mm) was measured using a Hewlett Packard 34401A multimeter at room temperature. The sample contact surfaces were coated with silver ink to minimize the contact resistance. The thermal aging of the samples was performed in an oven at 90°C. The surface morphology of the PPy/PVC composites was studied by means of a dynamic contact angle analyser (DCA-322, Cahn Instruments, Inc., USA). Deionized water was used as a probe liquid. The platform speed was 149 mm s^{-1}. The contact angle values were obtained from the first cycle. The typical dimensions of the bulk and film samples for the DCA measurements were $20 \times 5 \times 1$ and $20 \times 10 \times 0.1$ mm, respectively. The surface morphology of the PPy/PVC composites was also observed with a JEOL JSM-6300F scanning electron microscope. The PPy coatings of the PVC powders were studied using an optical microscope (Olympus BH2-UMA).

RESULTS AND DISCUSSION

PPy contents in the composites

Based on the ratios of the nitrogen in PPy to the chlorine in PVC, the PPy contents in the pre-localized PPy/PVC composites were calculated. The results and the original ratios of pyrrole to the PVC powder in the reaction system are presented in *Table 1*. The calculated values of the PPy content are much lower than the original ratios of pyrrole to the PVC powder. There are at least three factors that cause this difference: (1) the incomplete conversion of the pyrrole monomer into PPy in the oxidative polymerization; (2) the loss of PPy due to its deposition on the reactor wall; and (3) an overestimate of the chlorine concentration due to the residual $FeCl_3$ absorbed on PVC particles.

Figure 2 shows the observation of the PPy-encapsulated PVC powders with different PPy contents by means of an optical microscope in the reflection mode. It can be seen that the typical dimension of the PVC particles is about 100 μm and their colour is silvery white [see *Figure* 2(a)]. It is evident that deposition of PPy on the PVC particles blackens the PVC particles [see *Figure* 2(b)–(f)]. The intensity of the colour of these PPy-encapsulated PVC powders increases with the PPy content, indicating an increase in the PPy layer thickness.

Electrical conductivity

The electrical conductivity of the pre-localized PPy/PVC composite samples, prepared by compression molding under different conditions as a function of the PPy content. is illustrated in *Figure 3*. For the samples compression-molded at 20°C and 1000 MPa, the electrical conductivity increases significantly when only 0.3 wt% of PPy is incorporated. The percolation threshold value for the pre-localized PPy/PVC composites is much lower than those for the conventional composites with a random distribution of the PPy fillers. The electrical conductivity increases sharply as the PPy content increases until the PPy content is above 1.6 wt%, then the conductivity increases very slowly with an increase in the PPy content. It should be noted that the electrical conductivity of the composite samples with only 1.6 wt% of PPy is approximately 10 orders of magnitude greater than that of the pure PVC sample, whereas the incorporation of 40 wt% or more of the PPy powder is required to achieve the same conductivity for the composites with a random distribution of the PPy filler[12,13]. These results confirm that chemical polymerization of pyrrole in the presence of a PVC powder, dispersed in an aqueous solution of $FeCl_3$, leads to the deposition of PPy on the surface of the PVC particles as the PPy precipitates. The

Table 1 PPy contents in the pre-localized PPy/PVC composites

Sample number	Nitrogen	Chlorine (wt%)	PPy content (wt%)	Pyrrole (wt%)
1	0.048	55.48	0.3	0.5
2	0.150	57.34	0.8	1.0
3	0.32	56.82	1.6	2.0
4	0.68	55.06	3.3	5.0
5	1.06	53.95	5.2	10.0

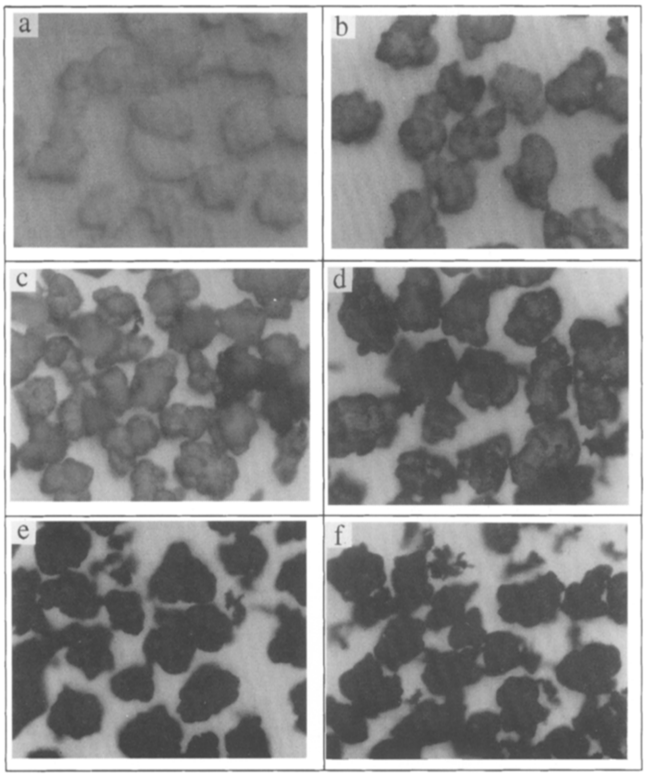

Figure 2 Optical micrographs (magnification × 100, reflection mode) of the PPy-encapsulated PVC powders with different PPy contents: (a) pure PVC powder; (b) 0.3 wt% PPy; (c) 0.8 wt% PPy; (d) 1.6 wt% PPy; (e) 3.3 wt% PPy; (f) 5.2 wt% PPy.

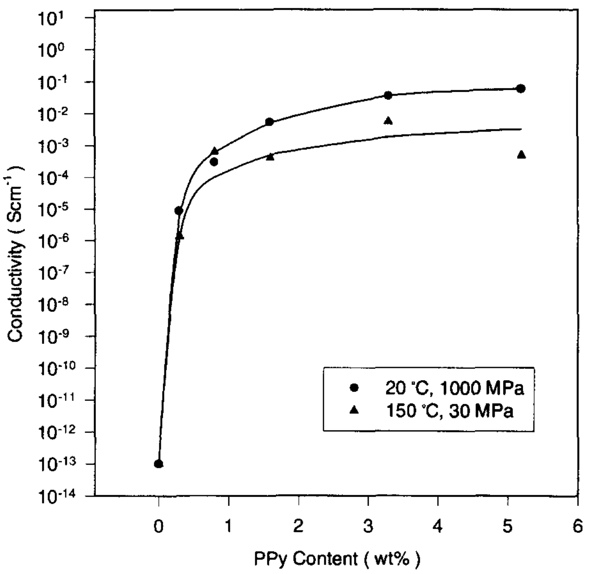

Figure 3 Electrical conductivity of the pre-localized PPy/PVC composite samples, prepared by compression molding under different conditions, as a function of PPy content.

deposited PPy forms a thin conductive sheath encapsulating the PVC particles. When this PPy-encapsulated PVC powder is compression-molded into bulk samples without excessive destruction of the PPy sheaths, a conductive PPy network is expected to be localized at the interface of the PVC particles. It is interesting to observe that the shape of the plot of the conductivity as a function of the PPy content is very similar to the loading curve of a conductive polymer composite, consisting of a random distribution of a conductive filler in a polymer matrix[21]. However, in this new system, the percolation threshold is very small because the conductive phase is segregated at the interfacial regions of the PVC particles. Conceptually, this system is very similar to that reported by Gubberls *et al.*[22,23] Although the dependency of the electrical conductivity on the thickness of the PPy sheath has not been established, 1.6 wt% of the PPy appears to be the concentration at which the percolation region ends.

Samples obtained by compression molding of the PPy-encapsulated PVC powder at 150°C and 30 MPa show a decrease in electrical conductivity by 1–2 orders of magnitude when compared to samples obtained at 20°C and 1000 MPa. Two factors may be responsible for this result. One is the thermal decay of electrical conductivity during compression molding at elevated temperatures because of degradation of the PPy. Another is the partial destruction of the PPy sheaths due to the flow of molten PVC during the molding process.

Thermal stability

In order to observe the stability of the pre-localized PPy/PVC composites under the ambient conditions, the conductivity of the samples compression-molded at 20°C and 1000 MPa was measured as a function of storage time. The results are shown in *Figure 4*. Although the electrical conductivity decreases gradually with time, it is reasonable to state that at the ambient conditions the pre-localized PPy/PVC composites are as stable as the pure PPy synthesized chemically[24].

Figure 5 shows the thermal decay of electrical conductivity of the prelocalized PPy/PVC composites, prepared by compression molding at 20°C and 1000 MPa, after thermal aging in an oven at 90°C. A dramatic decrease in electrical conductivity (0.5–1 order of magnitude) occurs at the early stage of thermal aging of the samples. This

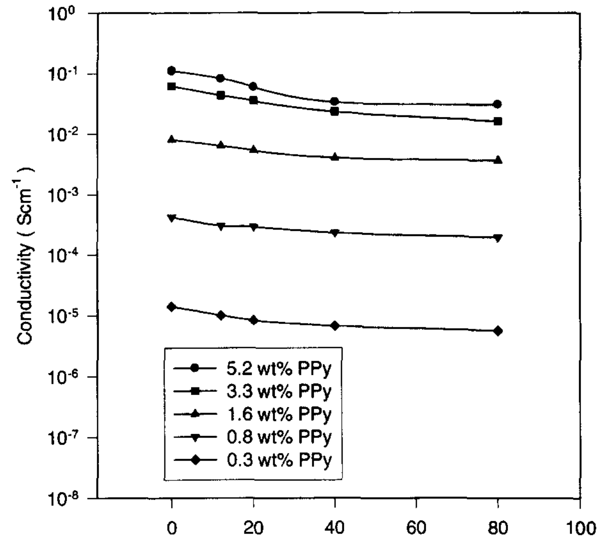

Figure 4 The conductivity of the PPy/PVC composites, prepared by compression molding at 20°C and 1000 MPa, as a function of time under ambient conditions.

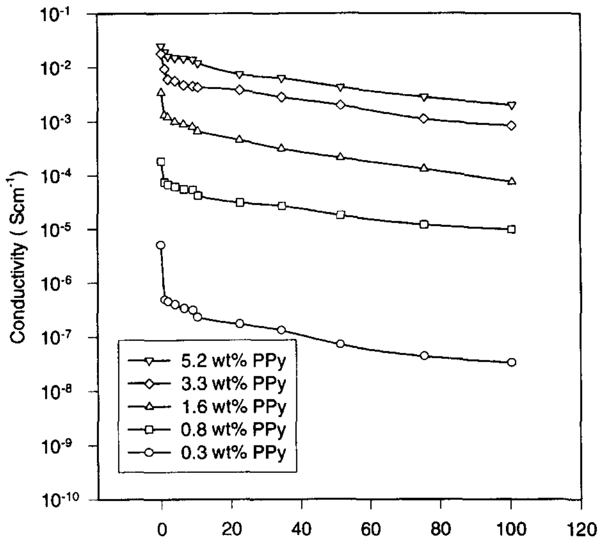

Figure 5 The conductivity of the pre-localized PPy/PVC composites, prepared by compression molding at 20°C and 1000 MPa, as a function of time at 90°C.

situation can be explained by partial interruption of the conductive network due to the differences in the thermal expansion between the PVC particles and PPy sheaths at elevated temperatures[12]. It is also possible that this decrease is caused by the degradation of the surface region of the PPy layer, for it is known that intrinsically conductive polymers are not stable at elevated temperatures in the presence of oxygen. The largest initial decay appears to be associated with the sample with the smallest amount of PPy—the thinnest PPy coating. This result is consistent with the fact that the surface region of the PPy coating will represent a larger volume fraction at small coating thicknesses. Further oxidation requires the diffusion of oxygen into the PPy layer; hence, after the initial sharp decay, the electrical conductivity then decreases much more gradually.

DCA study

Since a liquid makes contact with the outermost molecular layer of a surface, contact angles are sensitive to chemical and structural changes which occur at the surface. Assuming that the surface of the PVC particles is modified by the deposited PPy, contact angle measurements are therefore useful for analysing the surface changes of the pre-localized PPy/PVC composites. The dynamic contact angles are known to be sensitive to surface roughness and surface heterogeneity[25]. The polymer surface may comprise several components. For example, a plasma-treatment on semicrystalline polymer surfaces may produce both high- and low-energy surface regions[26,27]. *Figure 6* shows an example of a surface consisting of both high- and low-energy-surface regions. As the liquid drop periphery advances over such a surface, the liquid front tends to stop at the region boundaries where a barrier exists. Johnson and Dettre[28] performed a theoretical analysis of a two-region surface consisting of concentric circles of alternative low- and high-energy surface regions with the intrinsic contact angles for the low- and high-energy surface regions equal to 120 and 0°, respectively. *Figure 7* presents a family of curves showing the changes of the advancing and receding angles with fraction coverage of the high-energy surface area. For the advancing angle, 5 and 90% coverages give about the same contact angles. For the receding angle, it decreases very rapidly with the increase of the high-energy surface area and reaches a steady-state value when

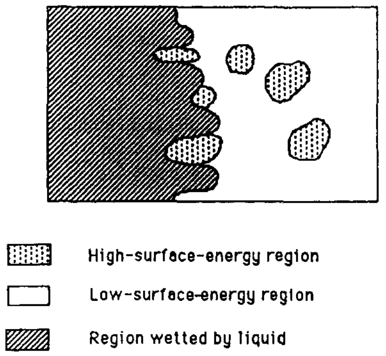

Figure 6 A liquid spreading on a heterogeneous surface[22].

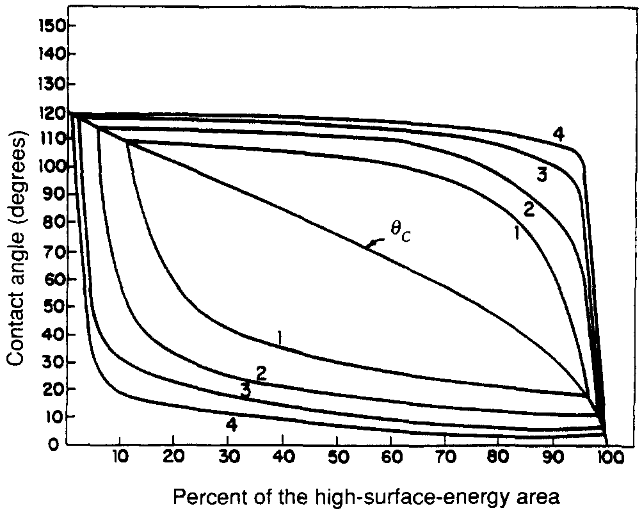

Figure 7 Contact angle hysteresis on a model hetergeneous surface: curves 1–4 were generated with different energy barrier values[25].

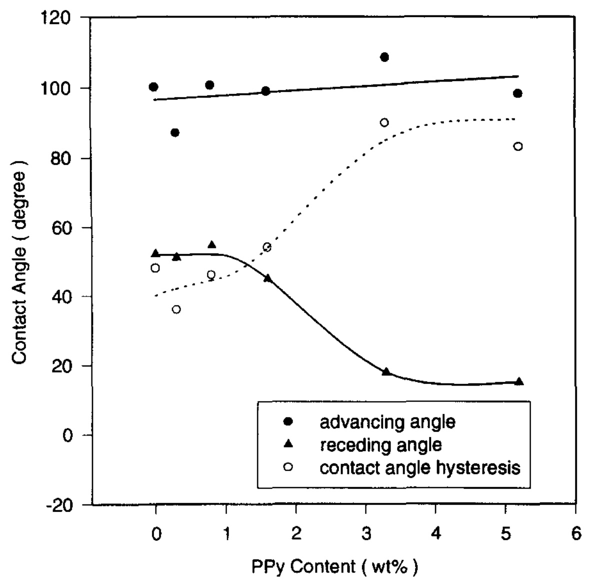

Figure 8 Dynamic water contact angle on the samples of the pre-localized PPY/PVC composites, prepared by compression molding at 150°C and 30 MPa, as a function of PPy content.

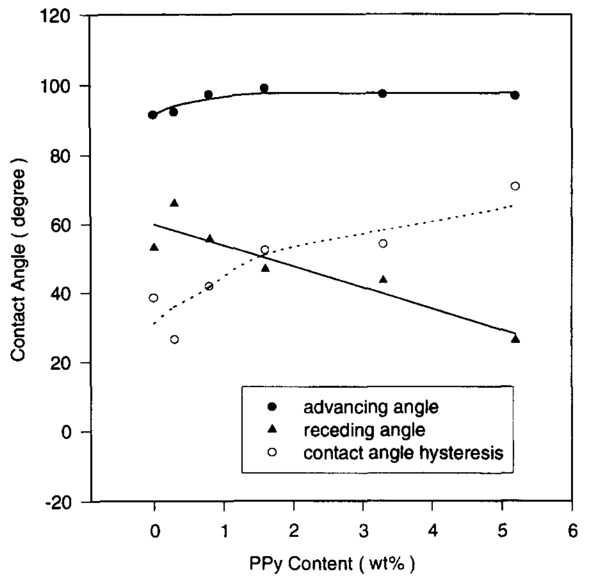

Figure 9 Dynamic water contact angle on the film samples of the pre-localized PPy/PVC composites, prepared using a hot-press at 150°C, as a function of the PPy content.

the high-energy surface region reaches a certain coverage, depending on the activation energy barrier. Johnson and Dettre also proposed that an advancing angle is a good measure of the wettability of the low-energy surface part of the surface, and a receding angle is more characteristic of the high-energy surface part[28].

Figure 8 shows the dynamic contact angles of water on the PPy/PVC composite bulk samples, prepared by compression molding at 150°C and 30 MPa, as a function of the PPy content. The difference in the advancing and receding angles for the pure PVC sample is a reflection of the surface roughness of the sample. The deposition of PPy on the surface of the PVC particles leads to an increase in the surface energy of the samples—a decrease in the receding angle. The receding angle increases slowly with the PPy content and then drops sharply at the PPy content of about 2 wt%. Finally, its value stays approximately constant even with further increases in the PPy content. This behaviour is similar to the plot of the receding angle as a function of the percentage of the high surface-energy area, as shown in *Figure 7*. It is interesting that this transition which occurs at about 2 wt% of PPy may be related to the sharp increase in the conductivity at approximately the same PPy content.

The advancing angle, which is a measure of the wettability of the low surface-energy part of the heterogeneous surface, does not change significantly with the PPy content in the composites. If we assume that the advancing angle is a measure of the wettability of the PVC regions of the surface, then it is reasonable that its value does not change with the PPy content until the surface is more or less totally covered with PPy (cf. *Figure 7*). Both the receding and advancing angles qualitatively agree with the theoretical analyses of Johnson and Dettre.

Figure 9 shows the dynamic contact angles of water on the film samples of the pre-localized PPy/PVC composites, prepared by pressing the materials between two pieces of steel plate in a hot-press at 150°C and 90–120 MPa, as a function of the PPy content. The receding angle decreases linearly with the PPy content. This behaviour is different from that of the bulk samples prepared by compression molding. It is believed that the excessive shear deformation of the PVC particles during the preparation of the film samples at 150°C and a high pressure results in the destruction of the PPy sheaths. Consequently, it is logical to assume that the surfaces of these composite materials are rougher than those of the bulk samples prepared at a lower pressure. As pointed out in the earlier discussion the dynamic contact angle is strongly affected by the surface heterogeneity and surface roughness of the sample; hence, it is possible that changes in the shape of the plot of the receding angle as a function of the PPy content are due to the additional surface roughness of these samples. This difference is also reflected in the conductivity of the composite films being very similar to that of pure PVC.

SEM study

It is well known that any high resolution study of insulating polymer samples by means of SEM is often limited by significant charging effects. One common solution involves the deposition of a metal or carbon coating (about 200 Å thick) as a discharge layer. To test the effectiveness of the PPy layer as a discharge layer, the pre-localized PPy/PVC composite samples are directly examined using SEM without depositing a metal or carbon coating. The surface morphology of the PPy-encapsulated PVC powders with different PPy contents, prepared by compression molding at 20°C and 1000 MPa, is shown in a series of SEM micrographs [see *Figure 10*(a)–(f)]. For the pure PVC sample, the picture is too blurry to reveal anything clearly. This demonstrates that the charging effect is so pronounced that observation of detail morphological structures is almost impossible. It is interesting that the picture for the PPy/PVC composite sample even with only 0.3 wt% of PPy is an striking contrast to that for the pure PVC sample. The high quality SEM pictures of the pre-localized PPy/PVC composites can be obtained with an increase in the PPy content. The aggregate of the ball-like, submicron diameter grains, one of typical morphologies of PVC powders, can be observed distinctly. This indicates that the electrically conductive PPy deposited on the surface of the PVC particles acts as a discharge layer similar to the

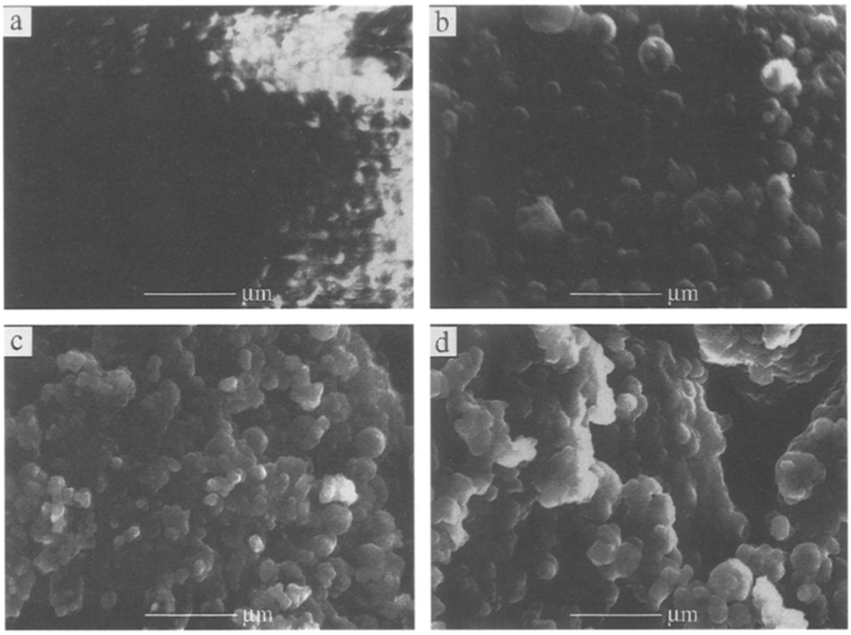

Figure 10 SEM micrographs of the pre-localized PPy/PVC composite samples with different PPy contents, prepared by compression molding at 20°C and 1000 MPa: (a) pure PVC; (b) 0.3 wt% PPy; (c) 0.8 wt% PPy; (d) 1.6 wt% PPY.

deposited metal or carbon coating. From this fact, it is reasonable to deduce that the PVC particles are satisfactorily encapsulated by the PPy during the oxidative polymerization of pyrrole.

CONCLUSIONS

A novel process for the preparation of pre-localized PPy/PVC composites has been developed. The procedure involves chemically polymerizing pyrrole in the presence of a PVC powder dispersed in an aqueous solution of $FeCl_3$. This process leads to the deposition of PPy on the surface of solid PVC particles as the PPy precipitates. The PPy-encapsulated PVC particles can subsequently be compression-molded into conductive composite materials. A conductive PPy network is found to be localized in the interfacial regions of the PVC particles. This process can produce conductive polymer composite materials with a very low percolation threshold value (approximately 0.3 wt%). The electrical conductivity of the PPy/PVC composites with only 1.6 wt% of PPy can be at least 10 orders of magnitude greater than that of the pure PVC sample. In addition, the electrical properties are reasonably stable at ambient conditions. The dynamic contact angles prove to a very useful parameter for the study of the surface morphology of the composite materials. It is interesting that the sharp transition in the plot of receding angle as a function of PPy content which occurs at about 2 wt% of PPy may be related to the sharp increase in conductivity at approximately the same PPy content.

ACKNOWLEDGEMENTS

This work was supported by Hong Kong Government Research Fund under grant number RI93/94.EG11.

REFERENCES

1. Kuhn, H.H., *Intrinsically Conducting Polymers: An Emerging Technology*. Kluwer, Dordrecht, 1993, p. 25.
2. Gottesfeld, S., Uribe, F.A. and Armes, S.P.J., *Electrochemistry Society*, 1992, **139**, L14.
3. Whang, Y.E., Han, J.H., Nalwa, H.S., Watanabe, T. and Miyata, S., *Synthetic Metals*, 1992, **41-43**, 3043.
4. Naarmann, H., *Polymer Science: Polymer Symposium*, 1993, **75**, 53.
5. Wang, H.L. and Fernandez, J.E., *Macromolecules*, 1993, **26**, 3336.
6. Bocchi, V. and Gardini, G.P.J., *Journal of the Chemistry Society, Chemical Communications*, 1986, **148**.
7. Ojio, T. and Miyata, S., *Polymer Journal*, 1986, **18**, 95.
8. Li, C. and Song, Z., *Synthetic Metals*, 1991, **40**, 23.
9. Bjorklund, R.B. and Liedberg, B., *Journal of the Chemistry Society, Chemical Communications*, 1986, **1293**.
10. Loh, L.H., Moody, R.A. and Huang, J.C., *Journal of Membrane Science*, 1990, **50**, 31.
11. Olmedo, L., Hourquebie, P. and Jousse, F., *Advanced Materials*, 1993, **5**, 373.
12. Chen, X.B., Devaux, J., Issi, J.P. and Billaud, D., *Polymer Engineering Science*, 1995, **35**, 637.
13. Han, J.H., Motobe, T., Whang, Y.E., Miyata, S., *Frontiers of Polymer Research*. Plenum, New York, 1991, p. 335.
14. Omastová, M., Pionteck, J. and Kosina, S., *European Polymer Journal*, 1996, **32**, 681.
15. Omastová, M., Kosina, S., Pionteck, J., Janke, A. and Pavlinec, J., *Synthetic Metals*, 1996, **81**, 49.
16. Omastová, M., Pionteck, J., Kosina, S. and Haeussier, L., *Material Science Forum*, 1995, **191**, 47.
17. Abel, M.-L., Camalet, J.L., Chehimi, M.M., Watts, J.F. and Zhdan, P.A., *Synthetic Metals*, 1996, **81**, 23.
18. Lascelles, S.F. and Armes, S.P., *Advanced Materials*, 1995, **7**, 864.
19. Wiersma, A.E., Steeg, L.M.A.vd and Jongeling, T.J.M., *Synthetic Metals*, 1995, **71**, 2269.
20. Ouyang, M. and Chan, C.-M., *Polymer Engineering Science*, 1996, **36**, 2676.
21. Chan, C.-M., *Polymer Engineering Science*, 1996, **36**, 495.
22. Gubberls, F., Jérôme, R., Teyssiê, Ph., Vanlathem, E., Deltour, R., Calderone, A., Parentê, V. and Brêdas, J.L., *Macromolecules*, 1994, **27**, 1972.
23. Gubberls, F., Blacker, S., Vanlathem, E., Jérôme, R., Deltour, R., Brouers, F. and Teyssiê, Ph., *Macromolecules*, 1995, **28**, 1559.
24. Thieblemont, J.C., Planche, M.F., Petrescu, C., Bouvier, J.M. and Bidan, G., *Synthetic Metals*, 1993, **59**, 81.
25. Chan, C.-M., *Polymer Surface Modification and Characterization*. Hanser, 1994.
26. Morra, M., Occhiello, E. and Garbassi, F., *Surface Interface Analysis*, 1990, **16**, 412.
27. Garbassi, F., Morra, M., Occhiello, E., Barino, L. and Scordamaglia, R., *Surface Interface Analysis*, 1989, **14**, 585.
28. Johnson, R.E. and Dettre, R.H., *Journal of Physical and Chemistry*, 1964, **68**, 1744.