Electrically Conducting Composites of Colloidal Polypyrrole and Methylcellulose

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The oxidation of pyrrole by iron(III) chloride in aqueous solutions of methylcellulose yields colloidal solutions of conducting polypyrrole which can be used to prepare thin films with maximum conductivity of 0.2 S/cm.

Efforts to improve the mechanical properties of electrically conducting polypyrrole have resulted in numerous reports of electrochemically[1] and chemically[2] prepared composites having polypyrrole as a conducting component. These composites can have quite high conductivities (10—50 S/cm) and have improved mechanical properties compared with polypyrrole itself.

We report here the synthesis of a composite incorporating colloidal polypyrrole which when spread on surfaces yields thin films having maximum conductivities of 0.2 S/cm. Normally insoluble polypyrrole is prepared as a colloidal solution by oxidizing pyrrole in an aqueous solution of methylcellulose. The product polycationic polypyrrole is presumably held in solution by electrostatic repulsion between the counter-ions distributed in a diffuse layer surrounding each particle. Conductivities of films made from the composite solutions can be controlled by varying the concentrations of pyrrole, chemical oxidant, and methylcellulose used in the synthesis.

A series of syntheses were done in which 1.0, 3.0, 5.0, and 7.0 g $FeCl_3 \cdot 6H_2O$ were dissolved in 200 cm^3 H_2O containing 0.8 g methylcellulose (M.W. 95,000, degree of methyl substitution about 2). A two-fold excess of pyrrole monomer was added to each solution and the reaction mixtures were stirred for 6 hours. The black polymer product was washed by raising the temperature to 70 °C so that the methylcellulose gelled,[3] thus making it possible to decant the $FeCl_2$ solution (Cl/Fe = 2.03). Further washing with hot water was followed by drying at 70 °C in an oven, washing with ethanol and drying. Analyses of the products indicated that essentially no Fe was present in the composites and that Cl^- was the anion neutralizing the charge of the polymer chain in agreement with results reported for pure polypyrrole prepared with $FeCl_3$.[4] Table 1 lists compositions for the composites (**1**)—(**4**) calcu-

Table 1. Properties of composites.

	Fe^{III}	$C_4H_3N/C_8H_{14}O_5$	Cl^-/C_4H_3N	n[d]	Abs.[e]	σ[f]
(**1**)	1.85×10^{-2}[a]	0.4	0.30	2.2	0.16	1.0×10^{-9}
(**2**)	5.55×10^{-2}[a]	1.1	0.24	2.3	0.46	2.5×10^{-8}
(**3**)	9.25×10^{-2}[a]	1.9	0.28	2.3	0.78	5.5×10^{-5}
(**4**)	1.30×10^{-1}[a]	2.7	0.20	2.3	1.0	2.2×10^{-3}
(**5**)	9.25×10^{-2}[b]	9	0.20	2.2	0.68	2.0×10^{-1}
(**6**)	9.25×10^{-2}[c]	14	0.22	2.3	0.62	1.0×10^{0}[g]

[a] Initial Fe^{III} concentration, mol dm^{-3}. Initial $(C_8H_{14}O_5)_n$ concentration was 2.1×10^{-2} mol dm^{-3}. Initial pyrrole concentration = 2 Fe^{III}. [b] Initial $(C_8H_{14}O_5)_n$ concentration was 4.2×10^{-3} mol dm^{-3}. [c] Initial $(C_8H_{14}O_5)_n$ concentration was 2.1×10^{-3} mol dm^{-3}. [d] Electrons transferred in the reaction. Calculated from moles Fe^{III} reacted/moles pyrrole polymerized. [e] Absorbance of reaction mixture after constant value was reached at 800 nm normalized to the absorbance for product (**4**). [f] Conductivities (S/cm) of 0.010 mm thick films by the four point method. [g] Conductivity of a pressed pellet.

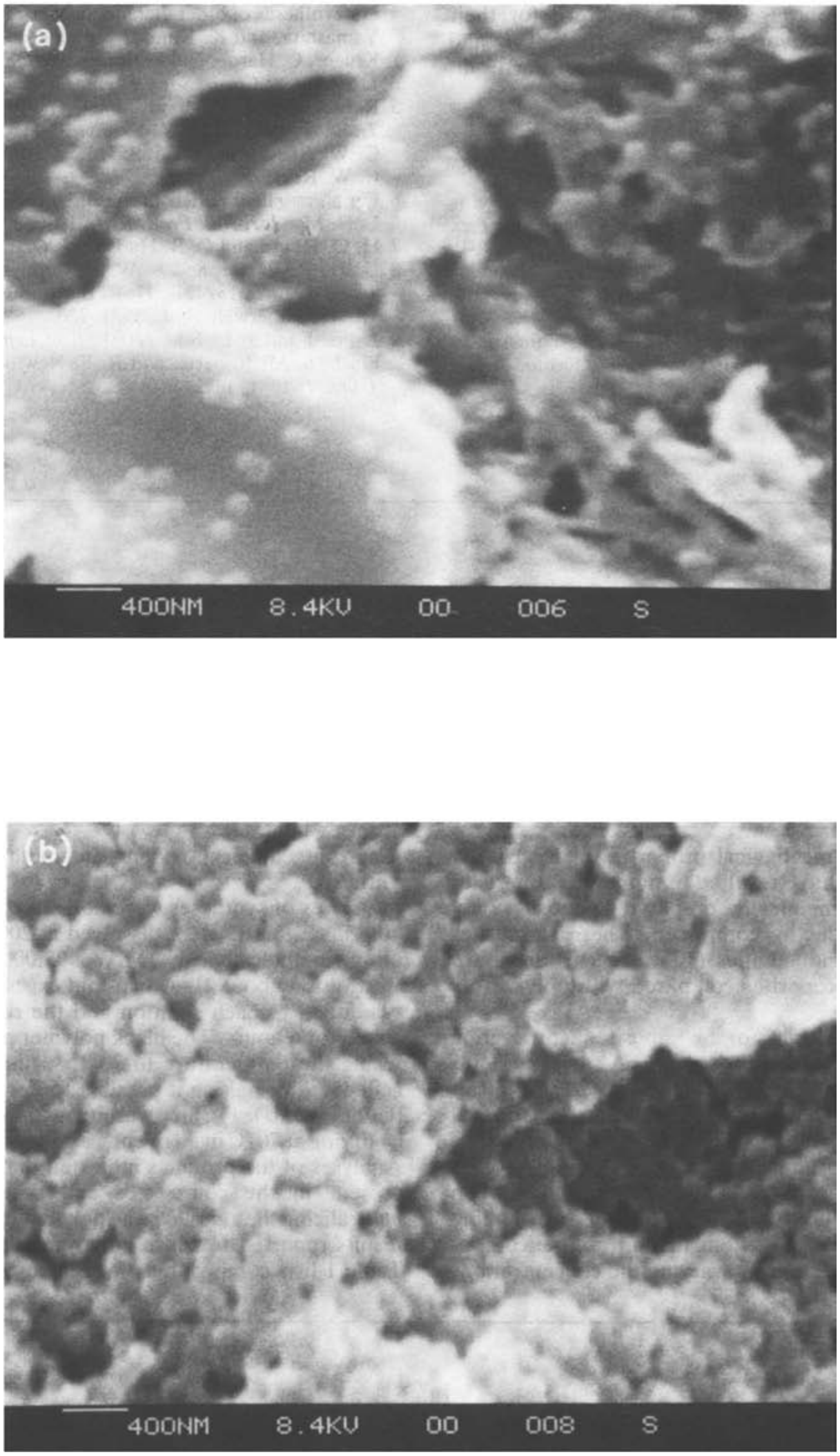

Figure 1. SEM micrographs of films made from (a) composite (**3**) and (b) composite (**5**) of Table 1.

lated in terms of the ratio of pyrrole rings : methylcellulose rings. Two additional syntheses were done using 5.0 g $FeCl_3 \cdot 6H_2O$ in solutions of 0.16 and 0.08 g methylcellulose in 200 cm^3 H_2O. Compositions for these products (**5**) and (**6**) are shown in Table 1.

Polypyrrole in the composite solutions had absorption maxima at 450 and 950 nm and the i.r. spectrum for product (**6**) (which was a powder and could be treated with the KBr technique) had the following band positions (cm^{-1}) and relative intensities: 1558 s, 1476 w, 1327 m, 1207 s, 1094 w, 1048 s, 969 w, 935 s, 798 w, 684 w. Thin films made from composites (which had first been washed as described and directly redissolved in cold H_2O) exhibited conductivities as shown in Table 1.

Analysis by SEM (scanning microscopy) indicated that in the solid-state the composites were composed of a globular polypyrrole phase embedded in flakes of methylcellulose [Figure 1(a)]. For higher polypyrrole concentrations, it was difficult to distinguish a separate methylcellulose phase [Figure 1(b)] and the micrographs were very similar to those reported for electrochemically prepared polypyrrole.[5] The size distribution of the polypyrrole in the films between 100 and 200 nm indicates that the composites form as colloidal solutions but the role of methylcellulose in the synthesis is not clear. Only product (**6**) of Table 1 has been observed to settle out of solution after several months standing.

Several other water-soluble polymers such as polyvinyl alcohol, polyacrylamide, and polyvinyl pyrrolidone can be used in producing soluble composites in combination with many of the oxidants named in reference 2. However, substituted celluloses with their inverse temperature solubility dependence afford a unique system for washing the composites free of salts which can interfere with mechanical and electrical properties of thin films made from solutions.

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