

NOTE

Preparation of Barium Titanate-Polypyrrole Compositions and Their Electrical Properties

Various highly conducting polymers have been developed, arousing a great deal of experimental and theoretical interest. However, the dielectric properties of these products have not been investigated extensively. Some studies on doped polyacetylene have been reported.¹⁻³ Legros et al.⁴ showed, recently, that the relative permittivity of oxidized polypyrrole is comparatively high (ca. 100 at 1 MHz). Great interest is attached to the preparation of the composite dielectric materials derived from the conducting polymer.

In this paper, we carried out the polymerization of pyrrole on the surface of barium titanate for the purpose of the application to semiconductive dielectric materials.

Barium titanate with an average size of 1 μm (HBT-3) was purchased from the Fuji Titanium Co., and dried at 60°C for 6 h in vacuum before use. Pyrrole monomer and methyl alcohol were supplied by Nakarai Chemicals and purified by distillation. Ferric chloride from Nakarai Chemicals was used as received.

Pyrrole does not polymerize only with barium titanate. This is why ferric chloride, which is capable of initiating the polymerization of pyrrole, was deposited on the surface of barium titanate according to a process similar to the method reported by Nakamae et al.⁵ The mixing of barium titanate with ferric chloride was carried out by suspending in methyl alcohol and milling with a mortar for 12 h. Subsequently, methyl alcohol was removed under vacuum. The polymerization of pyrrole in the presence of barium titanate was performed in the following manner.

A given weight of pyrrole was mixed with a given weight of barium titanate containing a given amount of ferric chloride, and the mixture was allowed to react at 0°C for 5 h. An excess amount of methyl alcohol was added, then, to remove pyrrole monomer and ferric chloride. Moreover, the reaction mixture was Soxhlet-extracted with methyl alcohol for 24 h and dried in vacuum. The weight percentages of polypyrrole contained in the barium titanate were calculated from the nitrogen contents determined by elementary analysis. The polymerization conditions of pyrrole in the presence of barium titanate are shown in Table I. The amount of polypyrrole contained by the compositions increased with increasing ferric chloride content, although the conversion of the

TABLE I
Polymerizations of Pyrrole in the Presence of Barium Titanate Containing Ferric Chloride

Sample designation	Preparation conditions ^a			Polypyrrole calculated from nitrogen analysis (wt %) ^b
	Barium titanate used (g)	Pyrrole used (mL)	Ferric chloride (wt %) in barium titanate	
A ₁	5.0	3.0	1.0	trace
A ₂	5.0	3.0	3.0	0.3
A ₃	5.0	3.0	5.0	0.4
A ₄	5.0	3.0	10.0	0.7
A ₅	5.0	3.0	15.0	1.1
A ₆	5.0	3.0	20.0	1.4

^a Polymerizations of pyrrole were carried out at 0°C for 5 h in air.

^b Weight % of polypyrrole deposited on the surface of barium titanate.

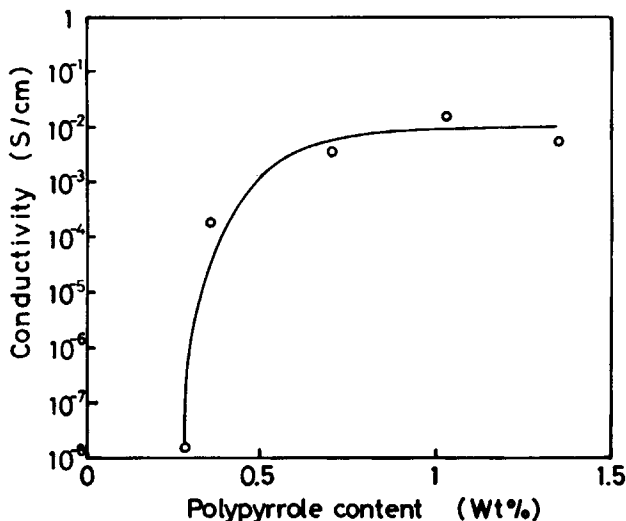


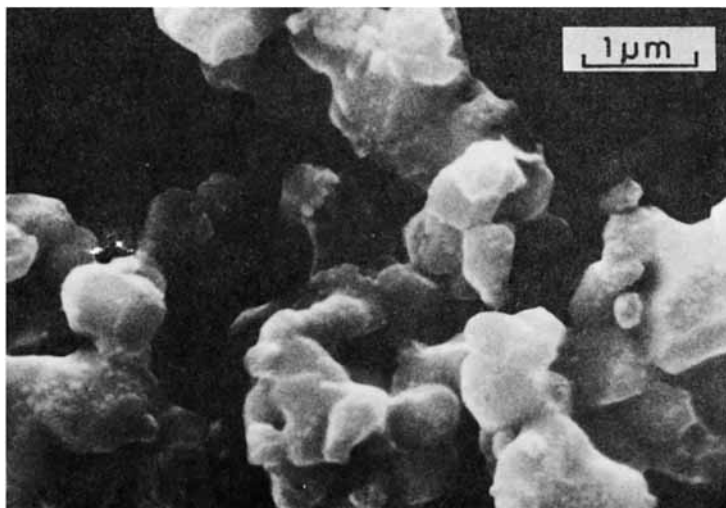
Fig. 1. Relationship between conductivity and polypyrrole content.

monomer to polymer was low. The color of the composition became darker as the wt % of polypyrrole increased, which suggests that polypyrrole covered the surface of the particles. This was confirmed by observation of the barium titanate samples with a scanning electron microscope (Nihon Densi JEOL-TSM-T100), as shown in Figures 2 (a)–(c).

To measure the electrical properties of barium titanate–polypyrrole composite particles, disclike samples were manufactured by means of a press (Hand Press Model SSP-10 purchased from the Shimadzu Corp.). After grinding dried substance in a mortar, ca. 1 g of powder was weighed, placed in the mold and pressed at 10 ton/cm² for 1 h under vacuum. Gold was deposited on both sides of the disc as electrodes.

The conductivities of the particles against the wt % of polypyrrole are shown in Figure 1. The conductivity of the composition increased with increasing polypyrrole content. It is probable that conductive paths are rapidly formed through the polypyrrole. The conductivities leveled off at a value of ca. 0.01 S/cm for a content higher than 1.1 wt %. This value is lower than that of polypyrrole (2×10^2 S/cm) prepared by chemical polymerization when ferric chloride is used as an initiator.⁶ However, if one judges from the polypyrrole content of the composition, the conductivity is not so low. Qualitative XMA analyses of the compositions were carried out. While a small amount of ferric chloride was detected for A₄–A₆, little ferric chloride was found in the case of A₁–A₃. It follows that oxidation by oxygen from the air as well as by ferric chloride seems to be responsible for the conductivity of the compositions.

The permittivity of the compositions was measured at a frequency of 100 Hz–10 MHz using an impedance analyzer (Yokogawa Hewlett Packard, HP4192A). The frequency dependence of the permittivity (ϵ'_r) is shown in Figure 3. For samples with a high conductivity (A₄–A₆), a large resonance was observed and the relative permittivity (ϵ'_r) gave negative values between a low frequency region, as reported in the case of polypyrrole.⁴ Accordingly, no reliable values were found in that case. A disclike sample prepared from barium titanate powder exhibited a relative permittivity (ϵ'_r) of 30, which was constant in the range 100 Hz–1 MHz (as shown in Fig. 3). The values of the relative permittivity (ϵ'_r) displayed by the compositions were higher than that of barium titanate powder, and increased with increasing polypyrrole content. It is apparent that the high permittivity of the compositions should be ascribed to polypyrrole. It was found that the relative permittivity (ϵ'_r) of A₃ was about 10^3 – 10^4 in the range 100 Hz–1 MHz. This value was higher than the relative permittivity of polypyrrole reported by Legros et al. (ca. 100 at 1 MHz). The reason why the permittivity of the composite material was higher than that of polypyrrole is not clear.

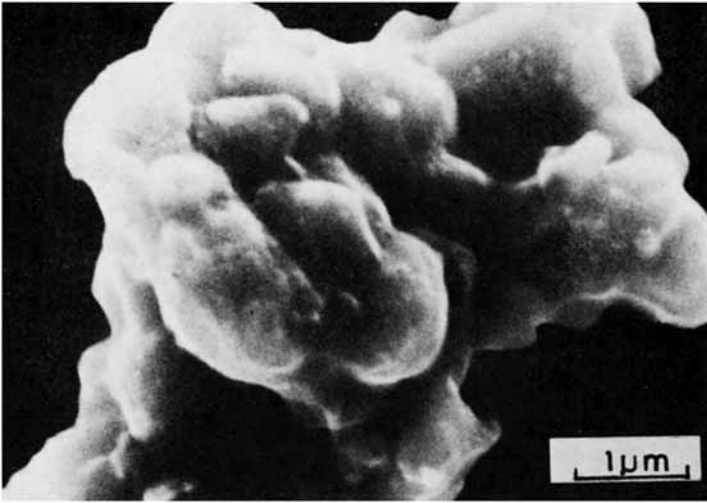


(a)



(b)

Fig. 2. Micrographs of barium titanate surfaces: (a) without polymerization treatment; (b) treated with pyrrole, polypyrrole content, 0.3%; (c) treated with pyrrole, polypyrrole content 1.38%.



(c)

Fig. 2. (Continued from the previous page.)

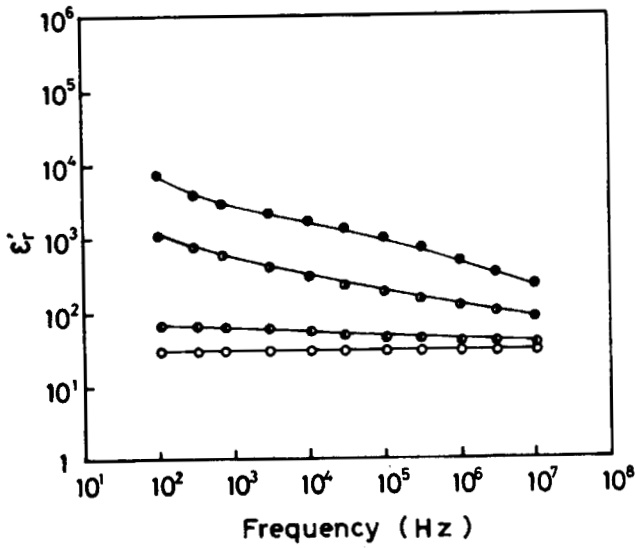


Fig. 3. Frequency dependence of relative permittivity ϵ' : (○) barium titanate; (●) A₁; (○) A₂; (●) A₃.

References

1. G. Mihaly, G. Vancso, S. Pekker, and A. Janossy, *Synth. Met.*, **1**, 357 (1979/1980).
2. A. J. Epstein and H. W. Gibson, *Phys. Rev. Lett.*, **45**, 21, 1730 (1980).
3. A. Feldblum, Y. W. Park, A. J. Heeger, and A. G. Macdiarmid, *J. Polym. Sci., Polym. Phys. Ed.*, **19**, 173 (1981).
4. F. Legros and A. Fourrier-Lamer, *Mater. Res. Bull.*, **19**, 1109 (1984).
5. K. Nakamae, K. Sumiya, M. Imai, and T. Matsumoto, *Nihon Settyaku Kyokaiishi*, **16** (1), 4 (1980).
6. V. Bocchi and G. P. Gardini, *J. Chem. Soc., Chem. Commun.*, 148 (1986).

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