The Electrical Properties of Magnetite-Loaded Polyethylene Composites

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Synopsis

Magnetite–polyethylene composites containing various concentrations of magnetite have been prepared and their electrical properties have been investigated. The electrical resistivities of the specimens were studied as function of filler concentration and temperature. The current density-electric field characteristic and the current variation with time were measured. The thermionic and field emission models provide good explanations for the electrical conduction in the specimens, and space-charge-limited conduction is discussed based on the results.

INTRODUCTION

Electrically conductive plastics have been used as materials for electromagnetic shielding,[1] antistatic electricity,[2] preparation of conducting discs for information storage,[3] thermoelectric switching,[4] and self-temperature-control heating.[5] It is known that the electrical properties of polymer composites are influenced by factors such as filler concentration, polymer and filler morphology, orientation of conducting species, temperature, applied pressure, and applied voltage.

Graphite-based polymer composites have been investigated by many researchers,[1-4] and carbon black has been used as a reinforcing ingredient in polymer composites for a long time. Furthermore, carbon black is used in appreciable quantities to increase the electrical conductivity of natural rubber[6] and synthetic polymers.[7,8] Randomly distributed nickel powder also makes an appreciable contribution to the electrical conductivity for concentrations below 20 vol % in PVC composites.[9]

Although polymers may have measurable electrical properties, generally no intrinsic magnetic properties exist in polymers. However, they can be used as matrices for magnetic fillers, such as of the metallic ferrite type. In this work, we have fabricated magnetite–polyethylene composites with a variety of magnetite concentrations. This paper reports their electrical properties, such as electrical resistivity, current density-voltage characteristics, and current variation with time. From the results the electrical conduction mechanism in the composite is discussed.

EXPERIMENTAL

Materials. Magnetite (Fe_3O_4) powder was obtained by the following steps. γ-Fe_2O_3 powder was prepared by the reaction of $FeCl_2$ and $(CH_2)_6N_4$ solution, using the method described in a previous paper.[10] The γ-Fe_2O_3 was

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reduced to Fe_3O_4 at 523 K under $\sim 10^{-3}$ torr for 6 h and then slowly cooled to room temperature. The crystalline phase of the magnetite was identified by X-ray diffractometry. The concentration of impurities, detected by inductively coupled plasma emission spectroscopy (ICP), was less than 100 ppm of total impurities such as Mn, Ni, Co, Ti, Zn, and Cu. A scanning electron micrograph showed the magnetite particles to be needle-shaped, and the average density obtained with a pycnometer was 5.16 g/cm^3. The magnetite powder consisted of very fine particles ($< 0.07 \mu m$) and with surface area of 110 m^2/g measured by the BET method.

The high density polyethylene (HDPE) used in the present study was obtained from Yuwha Petro. Chem. Lab. in the form of pure grains, additive free. The HDPE has a density of 0.96 g/cm^3 and a melt flow index of 5 g/10 min. The degree of crystallinity was found to be about 90% by X-ray diffractometry. The melting point and T_g measured by DSC were 140 and $-110°C$, respectively. The IR spectrum showed that the terminal groups consisted of hydroperoxide (R_3COOH) and the unsaturated vinyl group ($RCH{=}CH_2$).

Fabrication. Magnetite–polyethylene composites were prepared by mixing and compression molding. The magnetite–HDPE mixtures were milled in a ballmill for 72 h and compression-molded at 200–250°C under an applied pressure of 19.6 MPa. The specimens were disc-shaped, 10 mm in diameter and 1–2 mm thick. The average density of the pellets was 95–98% of the theoretical density, indicating that the specimens contained some voids.

Measurements. Resistivity was measured by a four-probe technique at temperatures from 80 to 300 K under a low applied field to ensure ohmic behavior. The sample was placed in a temperature-controlled chamber and the required temperature was obtained using liquid nitrogen. The current and voltage were measured by a Keithley 616 Digital Electrometer and a 642 Digital Multimeter, respectively. The J-V characteristics were obtained with dc power supply and electrometer. Both faces of the disc-shaped sample were coated with silver paste and then dried in a vacuum desiccator for 72 h. In most cases the adhesion was satisfactory, and the current density was homogeneous across the sample. To measure current variation with time, the specimen was annealed at 120°C for 3 h under vacuum followed by slow cooling to room tmeperature, and then the current variation was recorded as a function of time at 4×10^4 V/m.

RESULTS AND DISCUSSION

Figure 1 is a plot of resistivity as a function of magnetite concentration. It has been known that insulator-based conductor systems undergo an insulator–conductor transition at a critical concentration of the conductive filler.[11, 12] At this critical threshold concentration, continuous conducting networks are first formed. The magnetite–polyethylene composite can be regarded as a semiconductor–insulator system consisting of semiconducting magnetite and insulating polyethylene. The electrical conduction in magnetite–polyethylene composites might originate from magnetite networks whose elements either make contact between themselves or are separated by very small gaps. Therefore, charge carriers may migrate from one aggregate to a neighboring one by hopping or tunneling. Since the tunneling or hopping probability of an
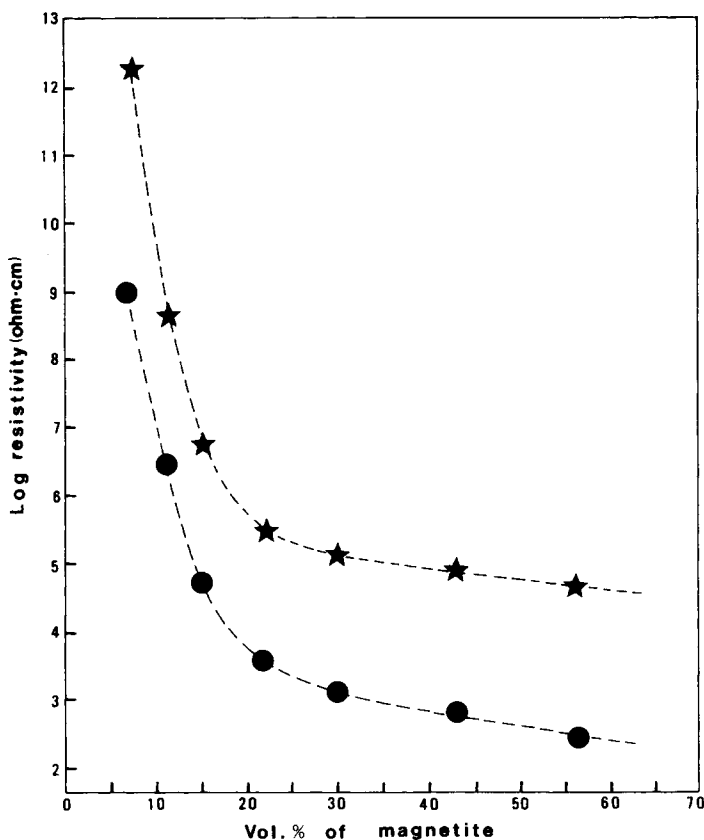
Fig. 1. Resistivity as a function of magnetite vol % in magnetite–polyethylene composites: (★) 173 K; (●) 273 K.

electron is an inverse exponential function of the width of the gap, as the concentration of magnetite is reduced, the gap between magnetite aggregates widens and the resistivity increases, as shown in Figure 1. The critical concentration of magnetite representing an insulator–semiconductor transition occurs in the concentration range between 8 and 11 vol %.

In Figure 1, the curve at 173 K in the plot of log resistivity vs. vol % of magnetite is more steep than that at 273 K. This can be explained by the thermal expansion effect; the relative volume of the magnetite is somewhat larger at 173 K than at 273 K, since the thermal expansion of HDPE ($\sim 10^{-4}$ cm/cm K) is greater than that of magnetite ($\sim 10^{-6}$ cm/cm K). The critical value in the present composites is larger than those (5–10 wt %) in crosslinked polyethylene-based carbon black composites[13] and is comparatively smaller than 20 vol % in nickel-loaded polyethylene composite.[14] Since no continuous current pathway is expected in the composite loaded with less than 8 vol % magnetite, the electrical conduction may be dominated by the electron tunneling across the small barriers separating the magnetite particles.

Because magnetite (Fe_3O_4) exists in two valence states (Fe^{2+} and Fe^{3+}), hopping of electrons in iron oxides is depicted as follows.

$$Fe^{2+} \quad O \quad Fe^{3+} \longrightarrow Fe^{3+} \quad O \quad Fe^{2+}$$
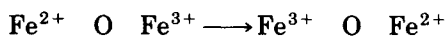
Thus, an electron migrates from the Fe^{2+} in one magnetite aggregate to the Fe^{3+} in a neighbor aggregate and the Fe^{2+} becomes Fe^{3+}. In composite materials, the conducting particle size distribution and distance between conducting particles are important in determining the conduction model. The magnetite used in the present work was not distributed homogeneously in the polyethylene, and it was difficult to determine the size distribution due to the low contrast between magnetite and polyethylene in the electron micrographs obtained of the magnetite composites. These were serious problems in comparing our data to the theory of crystalline semiconductors. The charging energy model proposed by Abeles et al.[15] has been used to explain electrical conduction in composite materials. However, in the case of the present specimens, the charging energy required to remove an electron from a neutral aggregate is negligible because of the large size of the conducting magnetite aggregate. Hence, we considered thermionic emission of carriers over the potential barrier. Thermionic emission conduction is represented by[16]

$$\rho = \rho_0 T^{1/2} \exp(\phi/kT) \tag{1}$$

where ρ is the resistivity and ϕ the activation energy. Figure 2 is a plot of the electrical resistivity as a function of temperature for 8, 11, and 15 vol % magnetite-loaded samples based on eq. (1). As shown in Figure 2, the temperature dependence of the resistivity changes at around 160 K, and this implies an alternation in the electrical conduction mechanism or composite structure at that temperature. The inflection point (160 K) corresponds to the glass temperature (T_g) of polyethylene. Thus, it is believed that the phase change of polyethylene from the rigid glassy state to the rubbery fluid state influences the electrical conduction in magnetite–polyethylene composites. From the results in Figure 2, at temperatures above 160 K it seems likely that thermal activation is the main mechanism responsible for charge carrier transport, for thermal energy can play an important role in the conduction. The estimated apparent activation energies are listed in Table I, and the values are lower than the reported values, which are generally in excess of 1 eV, for thermal emission of electrons from metal particles.[17] It is reported that in polycrystalline materials the conductivity varies with temperature at a relatively slower rate than that determined by the thermionic emission of charge carriers over the potential barriers, and the value of the activation energy[18] is smaller, though the reason is not clear yet. In the case of the present specimens, the thermal expansion effect seems to be responsible for the low apparent activation energy. The thermionic emission current can increase with increasing temperature, but the electrical conduction can be decreased by the thermal expansion of the polyethylene in the composite with increasing temperature. Thus, as the temperature is raised, the electrical conduction increases due to a combination of the thermally assisted current and the thermal expansion effect. This can result in a lower activation energy than that predicted by the thermionic emission model.

On the other hand, in the temperature range from 80 to 160 K, the resistivity shows a weak dependence on temperature, and this means the charge carriers are not fully activated in this range. The resistivity in this region is similar to that of other amorphous semiconductors, and the phenome-
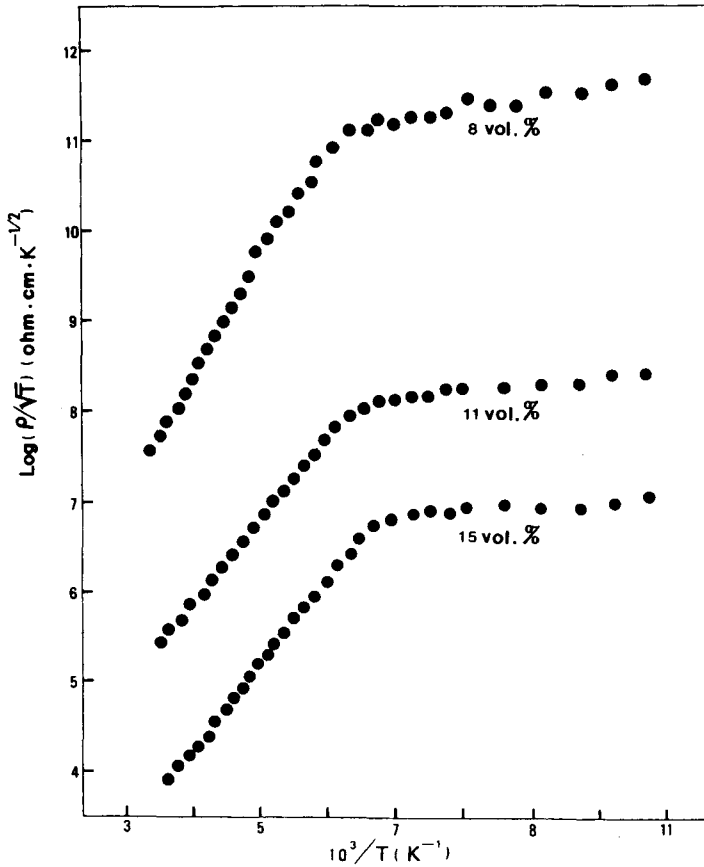
Fig. 2. Electrical resistivity as a function of temperature under low field for several magnetite-loaded polyethylenes.

non has been explained in different ways.[16,19] It is believed that the weak temperature dependence of the resistivity is due to the thermally assisted tunneling of the charge carriers through the potential barrier. Although it has been known that the tunneling current does not depend on temperature, the thermal fluctuation-induced tunneling model suggested by Sheng et al.[20] gives a good explanation for the results in the range of 80–160 K. According to this model, modulation of the tunneling barriers by thermal fluctuation plays a role in determining the dependence of the resistivity on temperature. In this region, the field emission may be dominant in the emitted current.

TABLE I
Apparent Activation Energies Obtained from the Slopes in Figure 2

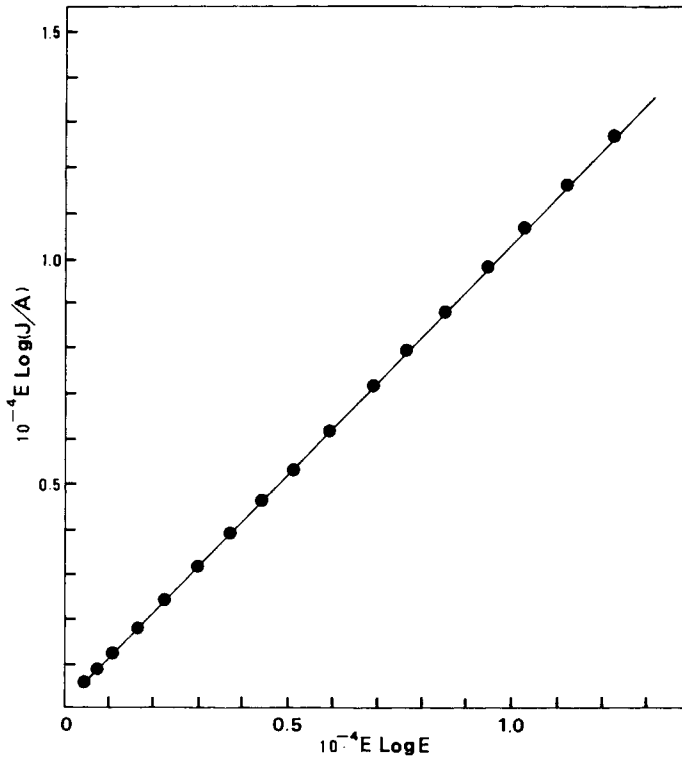| Loaded magnetite (vol %)	Apparent activation energy (eV)	
	160–300 K	80–160 K
8	0.26	0.028
11	0.20	0.021
15	0.18	0.017

Fig. 3. $E \log J/A$ vs. $E \log E$ under lower field at 100 K for 11 vol % magnetite-loaded polyethylene, from $J = AE \exp(B/E)$. ($A = 1.78 \times 10^{-17}$, $B = 249$)

The current–voltage characteristic can give more useful information on the dominant conduction mechanisms. In most conduction mechanisms, the current is exponentially dependent on the electric field as follows[17]:

$$J = AE^m \exp(B/E^n) \tag{2}$$

where A, B, m and n are constants, J is the current density, and E is the electric field. We measured the current density as a function of applied electric field at 100 K for 11 vol % magnetite-loaded polyethylene. The data obtained for lower fields fit eq. (2) well with $m = 1$ and $n = 1$, as shown in Figure 3. Abeles et al.[15] reported that in granular metal composites both m and n have the value of 1 for fields lower than the ionization voltage for tunneling between metal particles. This report is in agreement with the equation for internal field emission current given by Chynoweth: $J = AE \exp(B/E)$.[21] Field emission describes a number of conduction mechanisms by which charge carriers have a finite probability of crossing the potential barrier and tunneling current is a special case of internal field emission. The results in Figure 3 indicate that field emission tunneling occurs between magnetite aggregates separated by a narrow insulating gap. Figure 4 is a plot of the current density as a function of electric field at higher fields where highly nonohmic behavior is observed. At moderate fields, the current density is proportional to the square of the electric field. Generally, space-charge-limited conduction (SCLC)
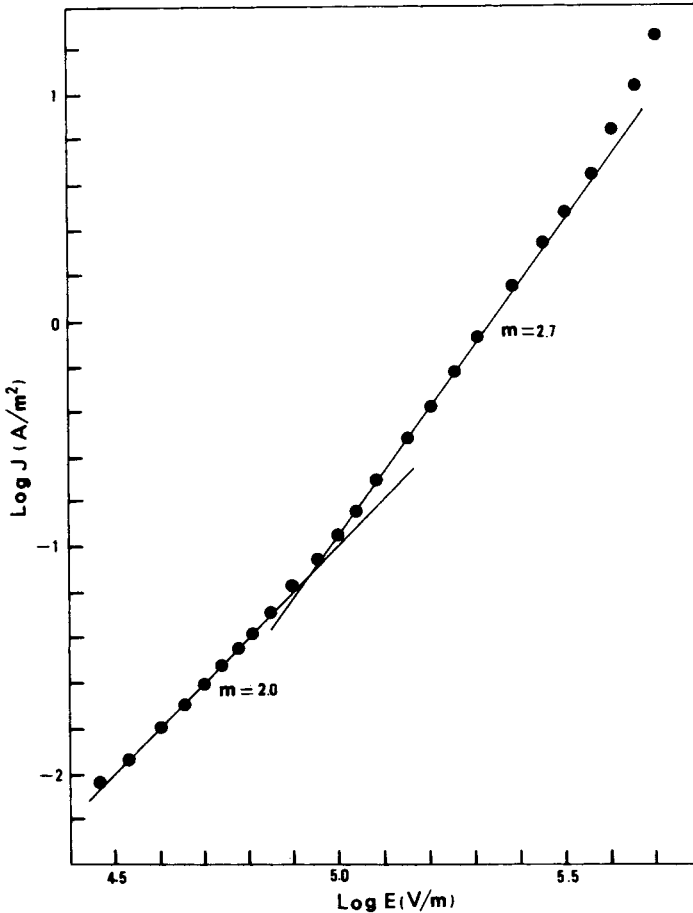
Fig. 4. Current density vs. applied electric field at higher fields at 100 K for 11 vol % magnetite-loaded polyethylene, from $J \propto E^m$.

in a pure insulator gives $m = 2$ and $n = 0$.[19] This leads us to expect that SCLC may be dominant in the electrical conduction in the specimen. In the case of SCLC, trap centers present in the specimen can capture the charge carriers, resulting in the experimental results with values of m in excess of 2.[17] When the applied electric field and the injected charge from electrodes are sufficiently large so that all trap states become filled, a rapid rise of current over a limited voltage range is predicted. We measured the charging current as a function of time under a high electric field in order to investigate whether the SCLC is a trap-limited conduction or not. As observed in Figure 5, a current peak is found, and the results show similarities to the transient SCLC peak reported by Mizutani et al.[22] This implies the electrical conduction is not due to trap-limited conduction. Polyethylene may contain many ionic species due to absorbed oxygen and water or the residue of catalyst used during the preparation, but the observed transient peak implies that the ionic species in the specimen are associated with charge carriers injected from the electrodes into the specimen. An ambiguous drift mobility can be estimated from the equation $\mu = L^2/t_p V$, where μ is the mobility of the charge carrier,
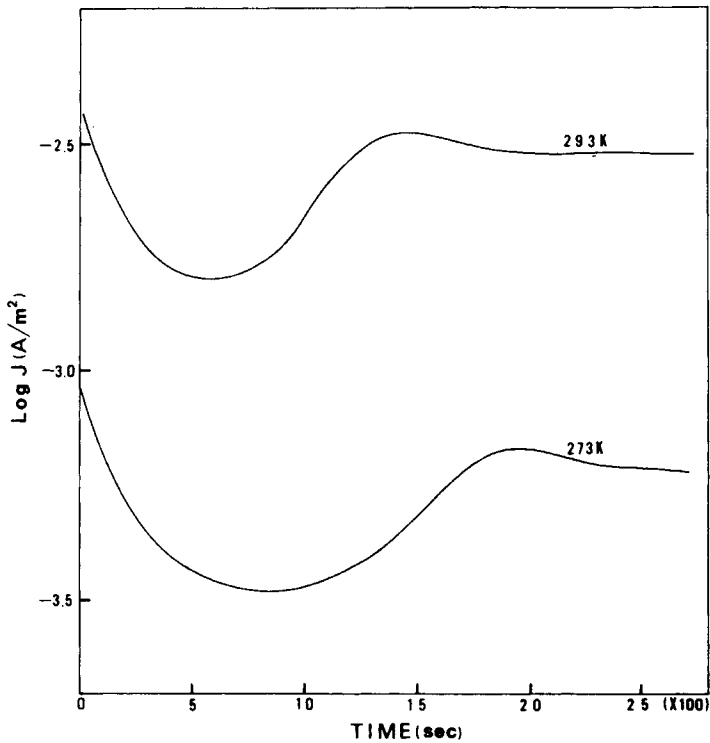
Fig. 5. Current density vs. time curves at 273 and 293 K for 11 vol % magnetite-loaded polyethylene (dc electric field: 4×10^4 V/m).

L is the thickness of the sample, t_p is the peak time, and V is the applied electric field. The estimated mobilities have values of about 3×10^{-11} m^2/V s, and the values are near the value for pure low density polyethylene.[23] From the results in Figures 4 and 5, it is concluded that the electrical conduction in the magnetite-loaded polyethylene is trap-filled limited, and the charge injection process from electrodes to sample is important for the electrical conduction.

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