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# Positive temperature coefficient of resistance effects in $BaPbO_3$/polyethylene composites

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The positive temperature coefficient of resistance (PTCR) properties of $BaPbO_3$/polyethylene composites have been investigated as a function of the volume ratio of $BaPbO_3$ to polyethylene. The PTCR effect increased up to nine orders of magnitude greater than that of semiconducting $BaTiO_3$ ceramics. However, the PTCR effect decreased with increasing $BaPbO_3$ content. The PTCR effect was dependent on the tunnelling current in the $BaPbO_3$ intergrain gap. When the PTCR effect was measured repeatedly, the resistivity at room temperature increased, the PTCR effect decreased, and the transition temperature shifted to a lower value. These results could be explained by the thermal properties of polyethylene and the large structural change of composites in the repeated measurements.

## 1. Introduction

In the case of usual positive temperature coefficient (PTC) ceramics [1, 2], practical uses have been restricted because of their relatively high room-temperature electrical resistivity, the high costs of materials and fabrication, and the difficulty of controlling the transition temperature.

Many studies were performed to find a means of overcoming these problems, and finally a PTC composite of conducting filler/insulating polymer was investigated [3]. Newnham *et al.* [4, 5] subsequently reported a composite which shows negative temperature coefficient of resistance (NTCR) and PTCR effects together. In the PTC composites, the choice of materials is variable and the room-temperature electrical resistivity depends on filler content only, thus the difficult control of doping effect and transition temperature can be easily overcome. These composites also show low room-temperature electrical resistivity above a critical concentration of filler, and exhibit a sizeable PTCR effect in the vicinity of the polymer melting point. That is, when the conducting filler is dispersed in a nonconducting matrix, the electrical resistivity of the composite transforms from nonconductor to conductor or semiconductor above a critical concentration of filler [6–9]. Moreover, when one of the above two materials changes in electrical resistivity or structure at an arbitrary temperature, the system can show either the NTCR or the PTCR effect. The decisive factors for these effects are the composition and the fabrication conditions. Perovskite $BaPbO_3$ is an electrical conducting ceramic with a room-temperature electrical resistivity of $8.0 \times 10^{-4}\,\Omega\,m$ [10, 11]. When it is mixed with an insulating polymer, the composite is expected to show low room-temperature electrical resistivity above a critical concentration of $BaPbO_3$. Polyethylene is an insulating crystalline polymer which expands abruptly around the melting point. Owing to the microstructural change in $BaPbO_3$/polyethylene composite at that point, the PTCR effect is expected.

The purpose of this study was to investigate the PTCR characteristics in $BaPbO_3$/polyethylene composites as a function of volume ratio of $BaPbO_3$ to polyethylene.

## 2. Experimental procedure

The $BaPbO_3$ powders were prepared with $BaCO_3$ and $Pb_3O_4$ powders (>99% purity) as raw materials, which were mixed in the mole fraction of 3:1 and calcined at 880 °C for 2 h under an oxygen atmosphere. The polymer used was a high-density polyethylene ($d = 0.948\ g\,cm^{-3}$) sieved to be 44–74 μm.

$BaPbO_3$/polyethylene composites were prepared by mixing the above two precursors, as shown in Table I, and then hot pressed at 150–155 °C, for 20 min under $1.77\ ton\,cm^{-2}$. The dependence of the PTCR effect on thermal expansion of polyethylene was studied using a dilatometer and differential thermal analysis (DTA). SEM was used to investigate the relationship between PTCR characteristics and $BaPbO_3$ distributions in the composites. The d.c. resistivities of the composites

TABLE I composition of specimens

| Specimen no. | $BaPbO_3$/polyethylene vol (%) |
|---|---|
| BP-1 | 6 |
| BP-2 | 10 |
| BP-3 | 12 |
| BP-4 | 15 |
| BP-5 | 17 |
| BP-6 | 20 |
| BP-7 | 25 |

were measured as a function of temperature by a voltage drop method [12].

## 3. Results and discussion

It was confirmed through the particle size distribution analysis that the average particle size of calcined $BaPbO_3$ powder was 4.1 μm. The polyethylene used was confirmed to be crystalline polymer and to have pure $[CH_2–CH_2]_n$ structure by using X-ray diffraction (XRD) and infrared methods. Its crystalline melting point was about 133 °C determined by DTA.

Fig. 1 shows the thermal expansion behaviour of polyethylene prepared by the same method as the composite specimen. It shows a nearly linear expansion up to the melting point and an anomalous thermal expansion above it. These phenomena are typical characteristics of crystalline polymer [13] and correspond to the microBrownian motion by local segment rotation in the low-expansion region and whole macrobrownian motion with a relatively large decrease of viscosity in the high-expansion region, respectively. Therefore, it is expected that the composite will suddenly change in structure near the crystalline melting point due to the thermal properties of the polymer, and that a very large PTCR effect will occur.

Fig. 2 shows the dependence of room-temperature electrical resistivities on $BaPbO_3$ (vol %) to polyethylene content in $BaPbO_3$/polyethylene composites. The specimens with low $BaPbO_3$ concentration have large resistivities. With increasing $BaPbO_3$ content, on the other hand, the resistivity decreases and gradually approaches that of the $BaPbO_3$. These results show that the resistivity of the composite largely depends on the $BaPbO_3$ concentration. Resistivities of the specimens appear to change as an exponential function of the $BaPbO_3$ volume percentage. This is consistent with Ohe and Naito's report [3], in which resistivity is an exponential function of the filler intergrain gap when tunnelling currents flow.

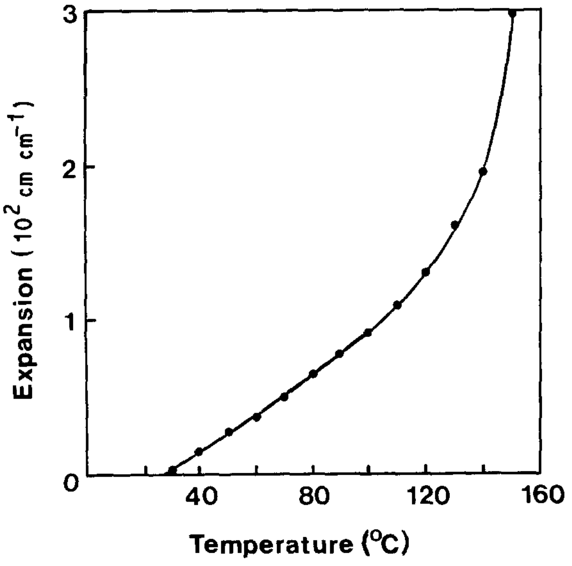


*Figure 1* Thermal expansion of polyethylene.

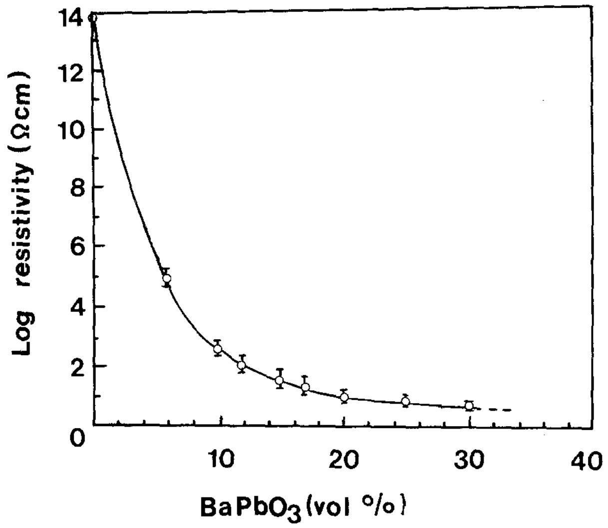
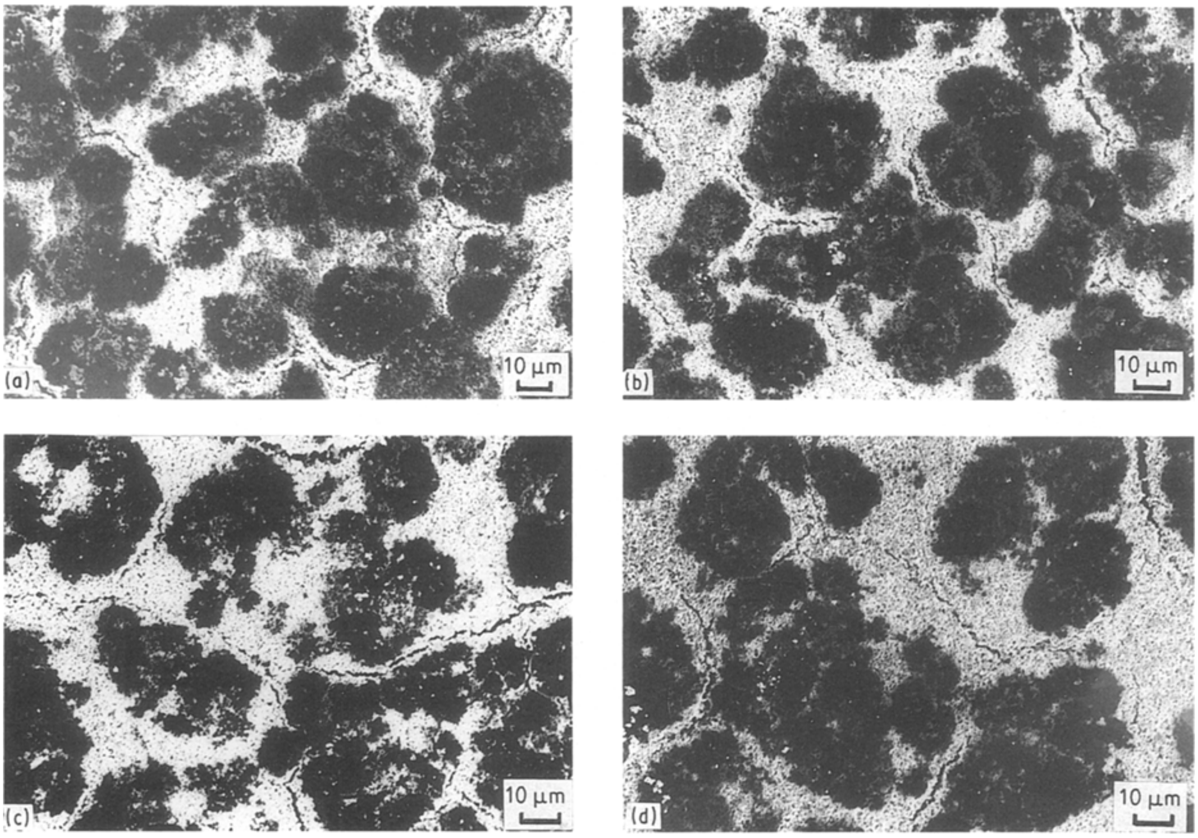


*Figure 2* Room-temperature electrical resistivity versus $BaPbO_3$ content curves of $BaPbO_3$/polyethylene composites.

The concept of tunnelling current is regarded as an important mechanism for the current flow of polymeric composite systems which consist of polymer matrix and filler [14–16]. It also applies well to the change in the room-temperature electrical resistivity of this system. That is, supposing that the $BaPbO_3$ powders of this system are dispersed homogeneously, the intergrain gap of the $BaPbO_3$ powders shortens and the $BaPbO_3$ conducting network is easily formed as the $BaPbO_3$ content increases. Thus the tunnelling current easily flows and the electrical resistivity of the composite decreases as an exponential function. This phenomenon is also found in reports of Aharoni [7], Mallaris and Turner [8], and Bueche [9], among other.

Fig. 3 shows the scanning electron micrographs of $BaPbO_3$/polyethylene composites prepared with different volume percentages of $BaPbO_3$: the bright areas are $BaPbO_3$ and the dark areas polyethylene. Small $BaPbO_3$ grains are homogeneously dispersed around the polyethylene. The degree of penetration of $BaPbO_3$ powders into polyethylene is very small; this assists the homogeneous segregation of $BaPbO_3$ to form the conductive infinite chain. The $BaPbO_3$ conducting network shows up clearly beginning from 6 vol % $BaPbO_3$ and increases markedly as the $BaPbO_3$ content increases. In the 15 vol % specimen near the saturation region, the dispersion degree of polyethylene is similar to that of $BaPbO_3$. For the 25 vol % specimen with low room-temperature electrical resistivity, polyethylene is isolated. These results are in good agreement with room-temperature electrical resistivity changing characteristics which depend on the $BaPbO_3$ intergrain gap in Fig. 2. Also, it can be found that homogeneous distribution of $BaPbO_3$ as well as the critical concentration of it is very important for reproducible room-temperature electrical resistivity.

Fig. 4 shows the electrical resistivities of the $BaPbO_3$/polyethylene composites prepared with different volume percentages of $BaPbO_3$, as a function of



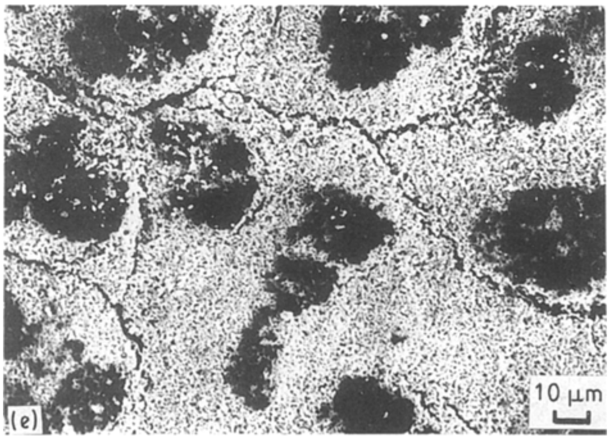


*Figure 3* Scanning electron micrographs of $BaPbO_3$/polyethylene composites prepared with different $BaPbO_3$ contents: (a) 6 vol %, (b) 10 vol %, (c) 15 vol %, (d) 20 vol %, (e) 25 vol %.

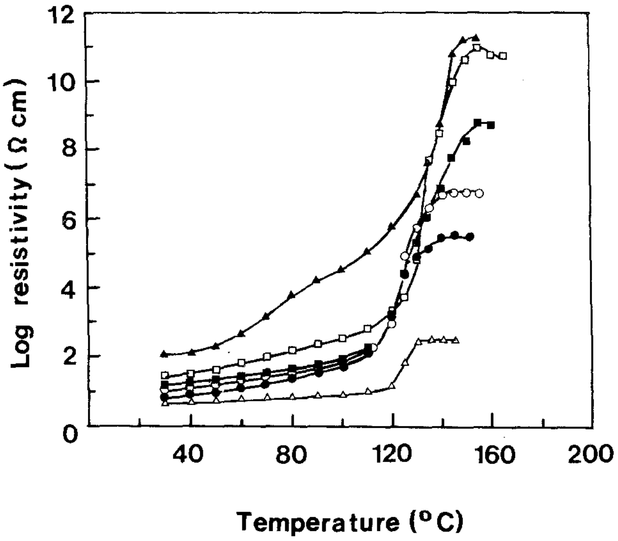


*Figure 4* Electrical resistivity versus temperature curves of $BaPbO_3$/polyethylene composites prepared with different $BaPbO_3$ contents: (▲) 10 vol %, (□) 12 vol %, (■) 15 vol %, (○) 17 vol %, (●) 20 vol %, (△) 25 vol %.

temperature. By increasing the $BaPbO_3$ content, the room-temperature electrical resistivity decreases, and the specimens containing $> 12$ vol % show a sharp PTCR effect.

The resistivity increases gradually between the room temperature and the transition temperature in the specimens with low contents of $BaPbO_3$, and this effect decreases with increasing $BaPbO_3$ concentration. In Fig. 1, thermal expansion occurred gradually between room temperature and the crystalline melting point, and when the composite specimens were heated, it was observed that the viscosity of the composite decreased a little in that interval. From these phenomena, it can be seen that on heating, the $BaPbO_3$ distribution becomes somewhat inhomogeneous with changes in the $BaPbO_3$ intergrain gap. Therefore, for stability of resistivity below the crystalline melting point, a high enough $BaPbO_3$ concentration is needed to form the conducting network to give low room-temperature electrical resistivity, but not to be disrupted, due to volume expansion or mobility increase in the specimen.

The PTCR transition temperature of composites is almost consistent with the crystalline melting point of polyethylene in Fig. 1. Thus, this proves that there is a close connection between the thermal expansion of composites at the melting temperature and the PTCR effect. However, the length of the polyethylene specimen at 150 °C was only 1.03 times that at room temperature, as shown in Fig. 1. The large PTCR effect was due to the volume expansion of polyethylene and the inhomogeneous distribution of $BaPbO_3$ particles with increasing temperature [3]. In addition, the macrobrownian motion of the polyethylene promotes the above phenomenon. That is, a sudden increase in average $BaPbO_3$ intergrain gap after the polyethylene melting point, therefore disrupts the tunnelling current, which results in a large PTCR effect.

As the $BaPbO_3$ concentration is increased, the PTCR effect gradually decreased: it is very small at 25 vol %. One interpretation is that when there is more $BaPbO_3$ content than is needed for the formation of conducting chains, the excess content gradually covers the total region of the specimen. Therefore, the role of the polyethylene decreases relatively, so that the PTCR effect decreases while the room-temperature electrical resistivity is lowered. This can be predicted from the microstructural photographs in Fig. 3. The PTCR effects were about 2–9 orders of magnitude for the respective specimens and much greater than the usual PTC ceramics. The range of PTCR transition temperature is only about 20 °C, which is much narrower when compared with the PTC ceramics. Therefore, a very effective switching role can be expected.

A small NTCR effect is shown above the PTCR transition temperature. When the PTCR phenomena were measured, the resistivity was irregular for a moment and then decreased soon after the PTCR effect was nearly complete. Therefore, the NTCR effect is due to the recovery of the homogeneous distribution of the $BaPbO_3$ particles to some extent, because neither a greater thermal expansion nor a greater decrease of viscosity occurs after the PTCR effect. These results also support the mechanism of the PTCR phenomena discussed previously.

Fig. 5 shows a change in the PTCR effect in 12 vol % $BaPbO_3$/polyethylene specimen with repeated measurements. As measurements were repeated, the room-temperature electrical resistivity increased, the PTCR effect decreased gradually, and the PTCR transition temperature decreased. When oxygen substitutes for the carbon atom in the molecular structure of polyethylene, $[CH_2–CH_2]_n$, intermolecular distances decrease [13]. This results in a decrease of crystallinity and crystalline melting point. Meyer *et al.* [17] reported that the oxygen absorption of polyethylene increased very rapidly from 120 °C. In addition, Narkis *et al.* [18] reported that the PTCR transition temperatures in PTCR hysteresis agreed with the endothermic or exothermic temperature of the differential scanning calorimeter (DSC) curve. From these reports, it can be said that the decrease in the transition temperature is the result of the decrease in polyethylene crystallinity. This is due to the oxygen absorption near the PTCR transition temperature. The increase in room-temperature electrical resistivity and decrease of the PTCR effect are thought to be caused by the incomplete recovery of the large structural change in the composite when cooling it to room temperature, which occurred in the PTCR phenomena. Thus, further studies of the reproducible PTCR phenomena are required.

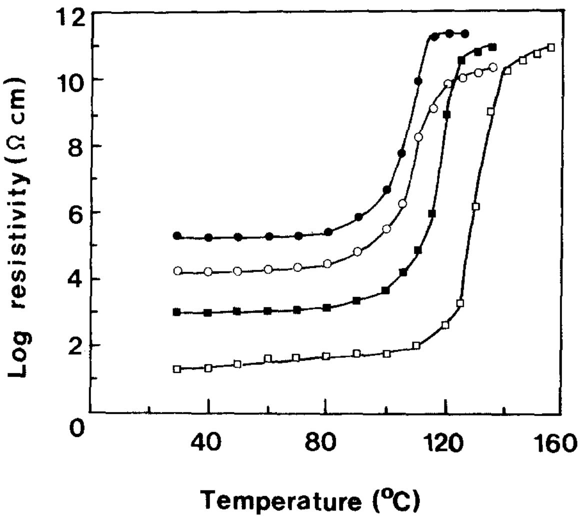


*Figure 5* Change of the PTCR effect in repeated PTCR measurements in a $BaPbO_3$/polyethylene composite containing 12 vol % $BaPbO_3$. Run: (□) 1, (■) 2, (○) 3, (●) 4.

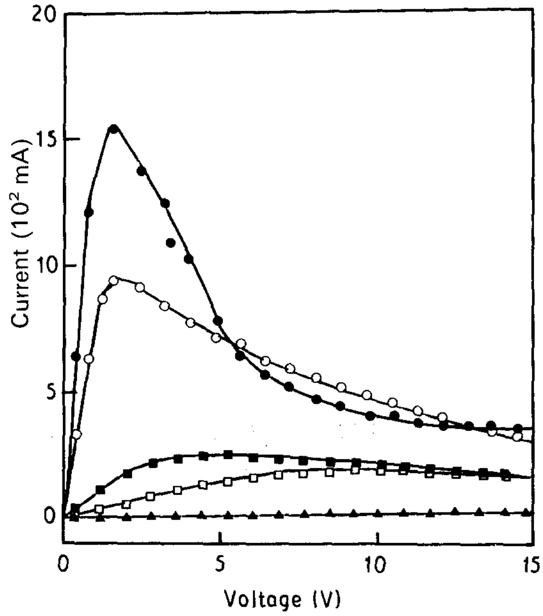


*Figure 6* Current versus voltage curves of $BaPbO_3$/polyethylene composites prepared with different $BaPbO_3$ contents: (▲) 10 vol %, (□) 12 vol %, (■) 15 vol %, (○) 17 vol %, (●) 20 vol %.

Fig. 6 shows the change in the current when using variations in the applied electric field in $BaPbO_3$/polyethylene composites prepared with different volume percentages of $BaPbO_3$. While the specimen with low $BaPbO_3$ content shows a little change with current, the current is largely increased as the $BaPbO_3$ content increases. Therefore, room-temperature electrical resistivity decreases. The phenomenon that the current increases linearly with some critical voltage in all samples shows that ohmic contact forms up to that voltage [19]. Currents decrease above the critical voltage due to self heating caused by the PTCR effect of the specimens. These results are in good agreement with the PTCR phenomena in Fig. 4.

## 4. Conclusions

1. In the conducting $BaPbO_3$/insulating polyethylene composites, the room-temperature electrical resistivity decreased as an exponential function of the $BaPbO_3$ content to polyethylene content.

2. The PTCR effect of the composite was maximum with nine orders of magnitude at the specimen with 12 vol % $BaPbO_3$.

3. By repeatedly measuring the PTCR effect at the specimen with 12 vol % $BaPbO_3$, the transition temperature shifted lower, the room-temperature electrical resistivity increased, and the magnitude of the PTCR effect decreased.

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