RAPID COMMUNICATION

Development of Ni particle dispersed poly(methylmethacrylate) composites exhibiting conductor/insulator transition by the positive temperature coefficient effect of electrical resistivity

INTRODUCTION

A number of conductive polymer composites composed of crystalline polymer filled with carbon black,[1–5] carbon nanotubes[6] and metal particles[7–11] as conductive fillers exhibit the positive temperature coefficient (PTC) effect of electrical resistivity. The PTC effect implies that resistivity increases with rising temperature. The PTC intensity (peak resistivity ρ_H/resisitivity at room temperature ρ_L) of some composites is greater than 10^7, and composites demonstrate conductor/insulator transition with changing temperature. Therefore, some composites are usable for self-recovering fuses for electronic circuits.

The PTC effect of composites composed of crystalline polymer is explained by the following model. The resistivity of almost pure polymer without conductive filler exceeds $10^{12}\,\Omega$cm, and these polymers behave similar to insulators. When conductive filler content reaches a specific value, the resistivity of composites demonstrates a sudden decrease from insulating range to conducting range because the conductive filler is joined together similar to a network, forming a conductive path. Some composites with many metal particles exhibit a low ρ_L of $10^{-2}\,\Omega$cm.[8–10] These characteristics are known as the percolation phenomenon.[12–16] However, the resistivity of composites exceeds $10^9\,\Omega$cm[8–10] at near the melting point of the matrix polymer even with a large amount of conductive filler. This resistivity change is caused by a disconnection of conductive paths following the drastic volume expansion of matrix polymer due to melting.[2] Therefore, a

number of composites composed of crystalline polymer exhibit the PTC effect.

The PTC effect of composites was explained by the above models, and so it was assumed that composites composed of amorphous polymer, which do not exhibit the melting phenomenon, do not exhibit the PTC effect. In fact, it was reported that poly(methylmethacrylate) (PMMA)/carbon black composites do not demonstrate the PTC effect, because, unlike crystalline polymers, amorphous polymers do not exhibit drastic volume expansion.[2] Moreover, it was reported that the PTC intensity of polystyrene/carbon black composites is only in double digits.[5]

In this study, we investigated the influence of Ni content on the PTC effect of Ni particle dispersed PMMA composites. Composites with Ni contents of 20 and 25 vol.% exhibited the PTC effect. Moreover, the PTC intensity of a composite with a Ni content of 25 vol.% reached 10^8, a value equivalent to that of composites composed of crystalline polymer.

EXPERIMENTAL PROCEDURE

PMMA (HBS000, Mitsubishi Rayon, Tokyo, Japan), linear low-density polyethylene (LLDPE: Evolue 3010, Prime Polymer, Tokyo, Japan) and poly(vinylidene fluoride) (PVDF: KYNAR K720, Arkema, Colombes, France) were used as a matrix polymer of the composites. Ni particles manufactured by Inco (Toronto, Canada) were used as the conductive filler. Its average particle size was 2.5 μm, and its resistivity was 7×10^{-5} Ωcm. Polymer pellets and Ni particles were melt-blended at 200 °C and 60 r.p.m. for 15 min, using a two-roller mixer (4M150, Toyo Seiki, Tokyo, Japan). The composite was inserted between two steel boards (150 mm × 150 mm × 2.2 mm) and

molded to a 1-mm thick sheet (sample) using the hot-press method (G-12, TECHNO SUPPLY, Tokyo, Japan). Hot-press was performed at 10 MPa and 200 °C for 7 min. The sample between two steel boards was then cooled in air.

The PTC effect was evaluated by measuring resistance using the two-terminal method, whereas the sample was heated in an oven (DRX 320DA, Advantec, Tokyo, Japan) at a rate of 1 °C min^{-1}. A digital multimeter (PC520M, Sanwa, Tokyo, Japan) was used to measure resistance. In the two-terminal method, resistivity ρ was calculated using the equation $\rho = RS/d$ from resistance R, sample area S and sample thickness d. The sample area was 1 cm^2, and the sample thickness was 0.8 mm. Ni foil was heat-sealed at 5 MPa and 200 °C for 5 min to form electrodes on both sides of the sample. After Ni foil lamination, the sample was cooled in air.

The aggregate structure of Ni particles was observed by scanning electron microscope (SEM: TM-1000, Hitachi High-Technologies, Tokyo, Japan). Composites were fractured at room temperature, and the sectional area was observed. The GNOMIX PVT apparatus (Gnomix, CO, USA) was used to measure the specific volume of pure PMMA from room temperature to 200 °C, and at pressures between 10 and 200 MPa in steps of 10 MPa. Data were extrapolated to zero pressure.

RESULTS AND DISCUSSION

Figure 1 plots the PTC curves of PMMA/Ni composites with Ni contents of 20, 25, 30, 35 and 40 vol.%. The ρ_L decreased with increasing Ni content, which is consistent with percolation.[8,10,12–16] The resistivity of composites with Ni contents of 20 and 25 vol.% increased drastically with rising temperature, and these composites exhibited the PTC effect. These composites exhibited constant values of $10^9\,\Omega$cm of ρ_H because

they reached the upper measurement limit of the digital multimeter. Therefore, it is assumed that the PTC intensity of a composite with the Ni content of 20 vol.% exceeds 10^4, and that of a composite with the Ni content of 25 vol.% exceeds 10^8. These high PTC intensities of composites composed of amorphous polymer have not yet been reported and are a unique finding among the numerous studies. However, in composites with Ni contents of 30, 35 and 40 vol.%, resistivity was maximum at 90 °C. In these composites, ρ_H and slopes of PTC curves decreased with increasing Ni content. Moreover, ρ_H and slopes of PTC curves in these composites were much smaller than those of composites with Ni contents of 20 and 25 vol.%. Therefore, we conclude that composites with Ni contents of 30, 35 and 40 vol.% do not exhibit the PTC effect.

The mechanism of the PTC effect for PMMA/Ni composites that do not exhibit

Figure 1 PTC curves of PMMA/Ni composites with various Ni contents.

Figure 2 Pressure–volume–temperature curve of PMMA at the pressure of 0 MPa.

melting is discussed in detail below. One theory regarding the PTC effect in composites is the thermal-fluctuation-induced tunneling theory by Sheng et al.[2,8,17] Currently, it is assumed that the electrical conduction mechanism of composites is tunneling conduction between fillers. According to this theory, resistivity depends exponentially on the gap length between fillers.[2,8] That is, electron transfer from a filler to the nearest neighboring filler decreases because the tunneling gap width (potential barrier width) increases with increasing gap length between fillers. Therefore, resistivity increases drastically with a slight increase of gap length between fillers. To clarify the factor affecting the gap length between fillers in PMMA/Ni composites, we evaluated the pressure–volume–temperature behavior of PMMA. Figure 2 plots the pressure–volume–temperature curve of PMMA at 0 MPa. No significant change in specific volume due to melting (for example, crystalline polymer) was observed in PMMA, but the specific volume of PMMA increased slightly with rising temperature. If a gap between Ni particles is generated by increased specific volume in PMMA, it is reasonable to assume that PMMA/Ni composites exhibit the PTC effect, following the fluctuation-induced tunneling model.

We seek to determine why only PMMA/Ni composites with Ni contents of 20 and 25 vol.% exhibit the PTC effect. First, we analyze the cluster structures forming fillers (that is, conductive paths) for PMMA/Ni composites with various Ni contents. Figure 3 presents SEM images of PMMA/Ni composites with Ni contents of 25 and 40 vol.%. Ni particles were dispersed uniformly in the PMMA matrix, and the cluster composed of Ni particles in composites with a Ni content of 25 vol.% was smaller than that of those with 40 vol.%. In our previous studies on the influence of Ni content on electrical properties of LLDPE/Ni composites,[10] high-density polyethylene/Ni composites[9] and PVDF/Ni composites,[8] we found that the number of conductive paths decreases with decreasing Ni content. Moreover, Wu et al.[2] analyzed the lattice model and demonstrated that the gap length between carbon black particles in high-density polyethylene/carbon black composites increases with decreasing carbon black content.

Second, we determine the disconnection of conductive paths (that is, onset of the PTC effect) for PMMA/Ni composites with various Ni contents. Ni content dependence on the PTC effect in the PMMA/Ni composites can be explained in terms of the following
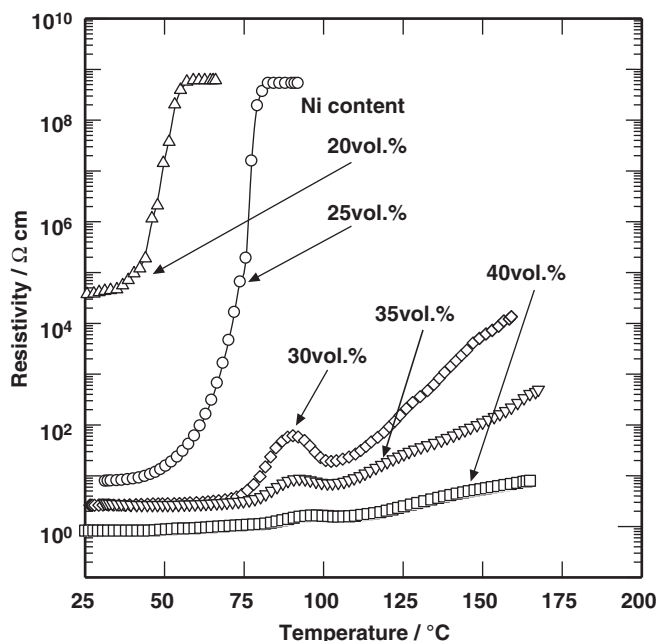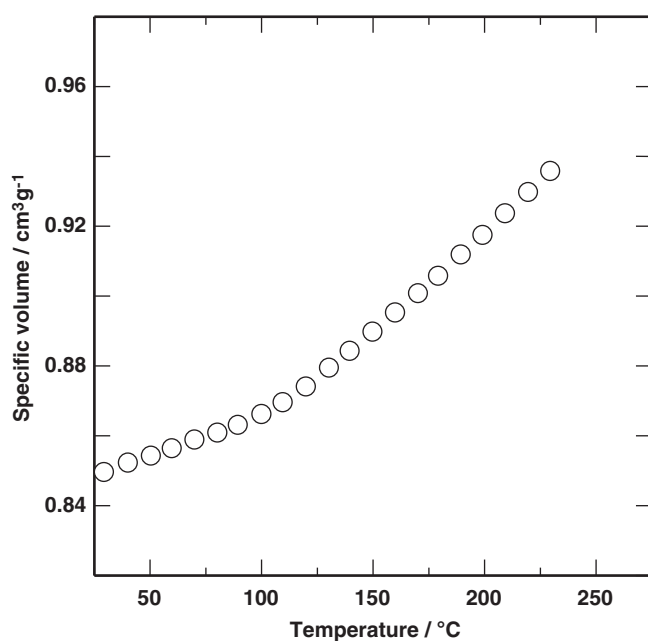
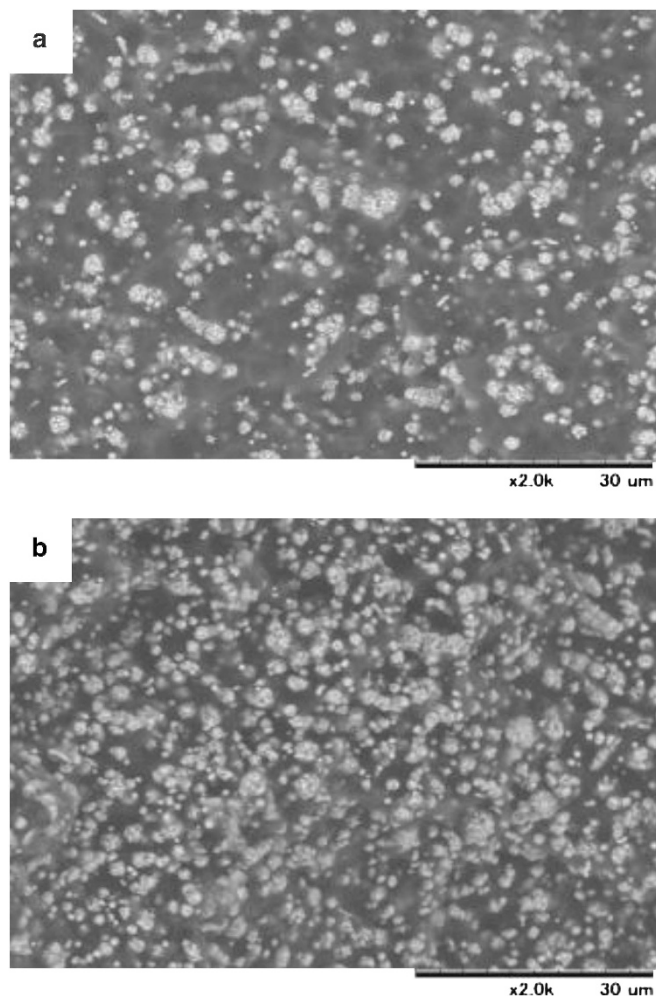**Figure 3** SEM images (×2000) of PMMA/Ni composites. (**a**) Ni content = 25 vol.% (highest PTC intensity). (**b**) Ni content = 40 vol.% (no PTC effect).
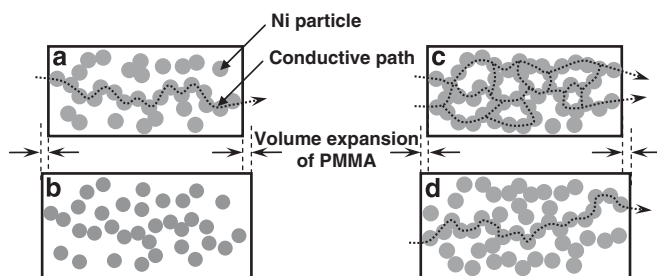

Figure 4 Schematic illustrations of the change in Ni particle connections. (**a**) Composite with a few Ni particles at low temperature. (**b**) Composite with a few Ni particles at high temperature. (**c**) Composite with many Ni particles at low temperature. (**d**) Composite with many Ni particles at high temperature.

model. Figure 4a–d schematically illustrate the conductive path of the PMMA/Ni composite estimated from SEM observation and previous studies.[8–10] Fewer conductive paths exist when Ni content is low (Figure 4a). Therefore, it is assumed that a small gap between Ni particles is generated even with

slight volume expansion of PMMA, due to temperature rising (Figure 4b). According to the fluctuation-induced tunneling model, the resistivity of composites increases drastically with the generation of even a small gap between fillers. Thus, PMMA/Ni composites with Ni contents of 20 and 25 vol.% exhibit

the PTC effect. However, the number of conductive paths increases with increasing Ni content. Composites with high Ni content have large network-like conductive paths (Figure 4c). Therefore, a gap between Ni particles is difficult to generate with a slight volume expansion of PMMA. In addition, if the gap between Ni particles is generated in part of the network but contact is maintained in the other parts, the conductive path is maintained (Figure 4d). Thus, composites with Ni contents of 30, 35 and 40 vol.% exhibit low PTC curve slopes and no PTC effect.

Resistivity is maximum at 90 °C with Ni contents of 30, 35 and 40 vol.% (Figure 1). The molecular motion of PMMA becomes active near the glass transition point of 105 °C. We assume that the positions of the Ni particles change momentarily with the molecular motion of PMMA, and the conductive path disconnects temporarily. However, it is assumed that the Ni particles reassemble when PMMA becomes rubbery and the conductive path increases.[18] The result is a maximum in PTC curves. This phenomenon should occur even with composites with Ni contents of 20 and 25 vol.%. However, this phenomenon could not be observed because the PTC effect increases the resistivity of these composites.

Figure 5a and b present the PTC curves of PVDF/Ni and LLDPE/Ni composites. All PVDF/Ni and LLDPE/Ni composites exhibited the PTC effect. The onset temperature of the PTC effect in these composites rose with increasing Ni content. It is assumed that the number of conductive paths increases with increasing Ni content. Therefore, with increasing Ni content, it becomes more difficult to disconnect a conductive path by increasing the specific volume of the composite. To disconnect a conductive path, a greater increase in the specific volume of the composite is necessary. Thus, we conclude that the onset of the PTC effect occurs later with increasing Ni content because the specific volume of the composite increases at higher temperatures. For details, refer to our previous works.[8–10]

Table 1 indicates ρ_L, ρ_H and the order of PTC intensity for various composites. When the Ni content was 20 vol.%, the ρ_H of PMMA/Ni composites was comparable to that of PVDF/Ni composites, whereas the ρ_L of PMMA/Ni composites was higher than that of PVDF/Ni composites. Therefore, the PTC intensity of PMMA/Ni composites was less than that of PVDF/Ni composites. The crystalline polymer crystallizes, excluding extraneous materials such as filler. As a result,
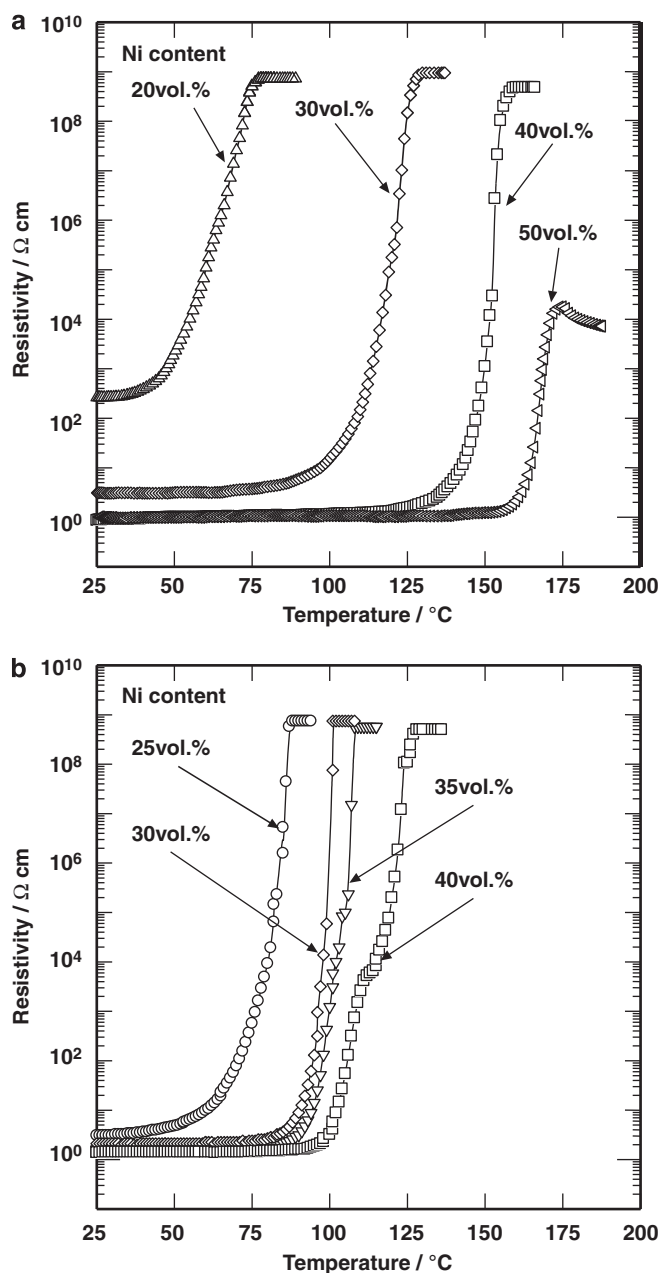
Figure 5 PTC curves of (a) PVDF/Ni composites and (b) LLDPE/Ni composites with various Ni contents.

This PTC intensity is comparable to those of PVDF/Ni and LLDPE/Ni composites. It is assumed that the Ni content of 25 vol.% in PMMA/Ni composites strikes a balance between development of conductive paths and disconnection of conductive paths by a slight volume expansion. These results indicate that the most important factor for the onset of the PTC effect in PMMA/Ni composites is Ni content.

Until now, carbon black was generally used as a filler for composites.[1–5] It is assumed that carbon black particles adhere strongly to each other because the carbon black surface has microasperity. Therefore, it would be difficult to disconnect conductive paths in polymer/carbon black composites, and so it may well be that composites composed of amorphous polymers with only a slight volume expansion did not exhibit the PTC effect in previous studies.[2] Moreover, both the coefficient of volume expansion and the glass transition point of amorphous polymers should be noted. If the coefficient of volume expansion is small, composites should not exhibit the PTC effect. In addition, the shape of the PTC curve is affected by the glass transition point, that is, the temperature at the maximum of the PTC curve might change. These results indicate that if the kinds of polymer, filler and filler content are optimized, composites composed of amorphous polymer, which do not have the melting phenomenon, can be expected to exhibit a PTC effect comparable to that of composites composed of crystalline polymer.

CONCLUSIONS

We investigated the influence of Ni content on the PTC effect of Ni particle dispersed PMMA composites. PMMA/Ni composites with Ni contents of 20 and 25 vol.% exhibit the PTC effect, whereas PMMA/Ni composites with Ni contents of 30, 35 and 40 vol.% do not exhibit the PTC effect. The PTC intensity of a composite with a Ni content of 25 vol.% was equivalent to that of composites composed of crystalline polymer (for example, PVDF and LLDPE). In composites with Ni contents of 20 and 25 vol.%, there was little contact between Ni particles, so a gap between Ni particles was generated even with slight volume expansion of PMMA and the PTC effect occurred. However, in composites with Ni contents of 30, 35 and 40 vol.%, the contact between Ni particles was strong, and so no gap was generated between Ni particles with a slight volume expansion of PMMA. Previously, it was assumed that composites composed of amorphous polymer, which do not exhibit

it is assumed that the fillers are concentrated spatially with crystallization of the matrix polymer; thus, the conductive path connects easily.[9,10] However, in the composites composed of amorphous polymer, fillers are dispersed uniformly in the matrix polymer; thus, development of conductive paths becomes difficult. These factors lead to high ρ_L following low PTC intensity in the PMMA/Ni composites. However, when the Ni content was from 30 to 40 vol.%, the ρ_L of PMMA/Ni composites was comparable to

that of PVDF/Ni and LLDPE/Ni composites, whereas the ρ_H of PMMA/Ni composites was smaller than that of PVDF/Ni and LLDPE/Ni composites. Therefore, PTC intensity for PMMA/Ni composites was less than that for PVDF/Ni and LLDPE/Ni composites because the volume expansion of PMMA, which does not exhibit melting, is less than that of PVDF and LLDPE. Table 1 indicates that PMMA/Ni composites exhibit a PTC intensity of 10^8 or more when the Ni content is 25 vol.%.

Table 1 ρ_L, ρ_H and PTC intensity of various composites

Composite	Ni content (vol.%)	ρ_L (Ωcm)	ρ_H (Ωcm)	Order of PTC intensity
PMMA/Ni	20	40 000	>10[9a]	>10[4]
	25	7.8	>10[9a]	>10[8]
	30	2.7	5000[b]	10[3]
	35	2.8	100[b]	10
	40	1	5.4[b]	1
PVDF/Ni	20	270	>10[9a]	>10[6]
	30	3.2	>10[9a]	>10[8]
	40	1.1	>10[9a]	>10[8]
	50	1.1	20 000	10[4]
LLDPE/Ni	25	3.2	>10[9a]	>10[8]
	30	2.1	>10[9a]	>10[8]
	35	1.6	>10[9a]	>10[8]
	40	1.4	>10[9a]	>10[8]

Abbreviations: PMMA, poly(methylmethacrylate); PTC, positive temperature coefficient; PVDF, poly(vinylidene fluoride).
[a]Upper measurement limit of digital multimeter.
[b]Value at 150 °C.

melting, do not exhibit the PTC effect with high PTC intensity. We have provided the first conclusive evidence that the PTC effect of conductive polymer composites occurs even without polymer melting.

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