Electrical and Mechanical Characteristics of Composites Consisting of Fractionated Poly(3-hexylthiophene) and Conducting Particles

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ABSTRACT: The dynamic viscoelasticity of fractionated poly(3-hexylthiophene)titanium carbide (P3HT/TiC) composites was examined with regard to their electrical characteristics. The elastic modulus (E') at 0°C [i.e., near the glass-transition temperature (T_g) of P3HT] increased with increasing TiC content of the composite. In particular, composites whose TiC content exceeded the threshold concentration showed a high E'. This was caused by the high E' of TiC and the strong interaction between TiC and P3HT. When the sample was heated above the T_g, E' decreased rapidly and an increase in the loss tangent appeared near the T_g of P3HT. Mechanical loss was caused by friction between TiC and P3HT. The change in mechanical characteristics affected the electrical conductivity. When the TiC content of the composite approximated to the threshold concentration, a significant change in mechanical characteristics took place, so that a large positive temperature coefficient (PTC) effect was observed near the T_g. To explain the PTC phenomenon, we propose a model of conductive pathway for P3HT/TiC. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 1429–1433, 2002

Key words: composites; conducting polymers; glass transition; inorganic materials; viscoelastic properties

INTRODUCTION

Conductive materials with positive temperature coefficient (PTC) characteristics are interesting and have been investigated by many researchers.[1–4] Conductive materials have been used for various purposes;[5,6] circuit protection devices, self-controlling heaters, and temperature sensors.

In a previous article, Liu et al. reported[7] that composites consisting of poly(3-alkylthiophene) and titanium carbide (TiC) showed a PTC effect near the glass-transition temperature (T_g). In particular, a significant PTC effect was observed with the highest average molecular weight of poly(3-hexylthiophene) (P3HT) prepared by fractionation.[8]

In this study, the dynamic viscoelasticity (DVE) of fractionated P3HT/TiC composites was examined, and the relationship between electrical and mechanical characteristics is discussed in this article.

Table I   Filler Content of P3HT/TiC or CB Composites and Their Resistivity

| Sample | Filler Content/Composite | | Resistivity[a] | | |
	Filler	wt %	R_0 (Ω cm)	R_{50} (Ω cm)	TC[b] (%)
T1	TiC	90	0.3	0.3	0
T2	TiC	70	1.5	4.8×10^2	32,000
T3	TiC	50	5.3×10^3	1.6×10^4	200
T4	TiC	30	3.6×10^4	1.3×10^4	−64
T5		0	5.5×10^4	1.7×10^4	−69
T6	CB	70	0.5	0.5	0
T7	CB	30	2.0	2.0	0

[a] R_0 and R_{50} are resistivities at 0 and 50°C, respectively.
[b] TC = $(R_{50} - R_0) \times 100/R_0$.

EXPERIMENTAL

Materials

TiC, with a particle size of 0.9–1.5 μm, was supplied by Furukawa Electric Co. (Tokyo, Japan), the carbon black (CB) (Furnace black, Asahi AG 300) was obtained from Asahi and Carbon Co. (Niigata, Japan) and had an average particle size of 0.02 μm. 3-Hexylthiophene was supplied by Tokyo Chemical Industry Co. (Tokyo, Japan); it was purified by distillation under reduced pressure prior to use. Synthetic-grade $FeCl_3$ from Merck (Darmastadt, Germany) was used without further purification. Other chemicals were guaranteed reagent-grade or analytical-grade commercial materials and were used without further purification.

Polymerization and Fractionation

P3HT was synthesized and fractionated as previously described.[8]

Preparation of P3HT/TiC Composites[8]

The fractionated P3HT was dissolved in toluene. After adding the solution with a given amount of TiC and stirring for more than 24 h, we poured methanol very slowly into the mixture to achieve uniform precipitation of P3HT on the surface of conductive particles. The precipitate was filtered off and dried under reduced pressure. Pellets 1 mm thick and 13 mm in diameter were prepared under 50 MPa for 1 min. They were cut into 4.0 × 8.0 mm samples for conductivity measurements and 4.0 × 6.0 mm pieces for DVE measurements.

Conductivity Measurements

The conductivities were measured in a vertical direction with a digital multimeter (Hewlett-Packard Co. Ltd. (Palo Alto, CA), HP34401A). Gold electrodes were used, and the ohmic contact was confirmed for each sample.

DVE Measurements

DVE was measured with dynamic viscoelasticimetory (TA Instruments Co. (New Castle, DE), DMA980) at a heating rate of 5°C/min; the measuring frequency was 10 Hz.

Scanning Electron Microscopy (SEM)

Scanning electron micrographs were obtained with an electron microscope (Topcon Co. (Tokyo, Japan), Alpha-30A) fitted with a temperature controller at the sample holder.
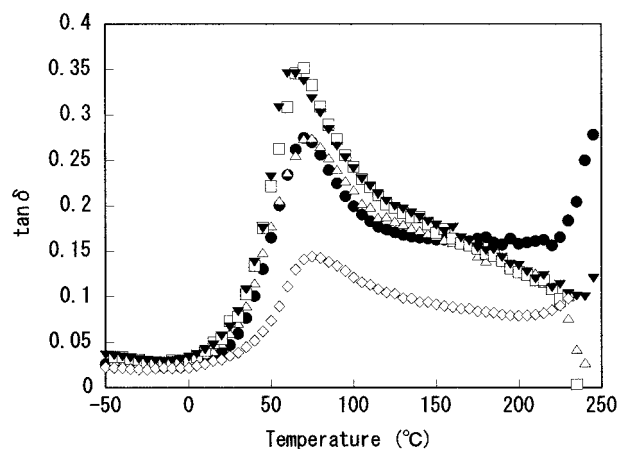
RESULTS AND DISCUSSION

Characteristics of Composites Consisting of Fractionated P3HT and TiC

The TiC contents of the P3HT/TiC composites that were used and their electrical properties are shown in Table I, where the temperature coefficient (TC) of the composites is represented by $(R_{50} - R_0) \times 100/R_0$. Although the electrical properties of T1, containing 90 wt % of TiC were similar to TiC (i.e., resistivity at 0°C, = 0.3 Ω cm and TC = 0%), those of T4 and T5 with TiC contents less than 50 wt % were similar to P3HT (i.e., resistivity at 0°C was higher than 10^4 Ω cm and TC was negative.[8] T2, containing 70 wt % of TiC near the percolation threshold, exhibited a PTC effect in the vicinity of the room temperature (i.e., TC = 32,000%).[8] To compare the electrical properties with the mechanical ones, we mea-
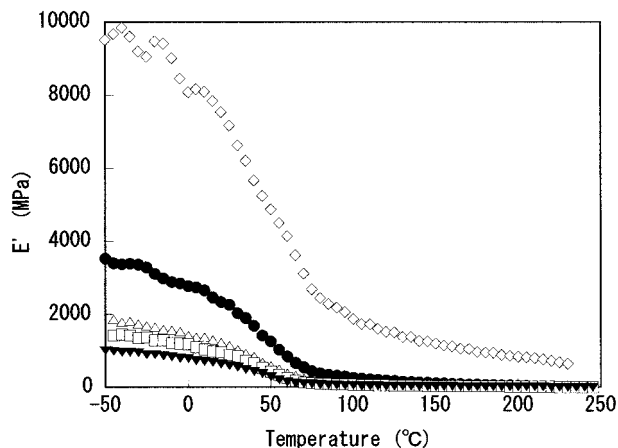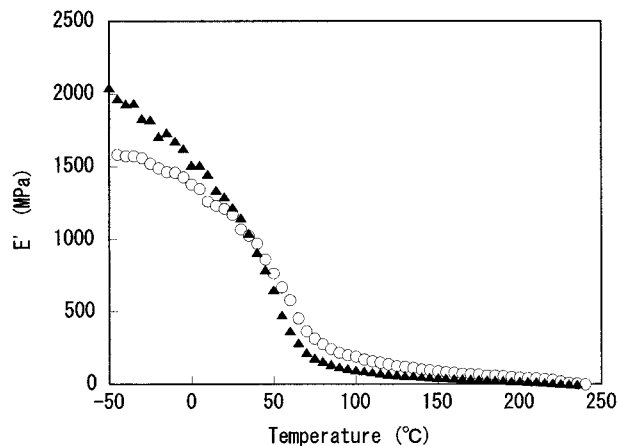
Figure 1 Temperature dependence of E' for TiC/P3HT composites: (◇) 90 wt % TiC, (●) 70 wt % TiC, (△) 50 wt % TiC, (□) 70 wt % TiC, and (▼) 0 wt % TiC.

sured the dynamic viscoelasticity of T1–T5 in the −50 to 250°C range. The temperature dependence of the elastic modulus (E') is shown in Figure 1. E' at 0°C increased with an increased TiC content in the composites. For T5, T4, T3, T2, and T1 (TiC content = 0–90%), E' was about 700, 1000, 1200, 3000, and 8000 MPa, respectively. The increase in E' seemed to arise from the high E' of TiC and the strong interaction between TiC and P3HT as described by Tang et al.[9] It was found that E' increased rapidly just as the conductivity when the TiC content exceeded the percolation threshold. This indicates that formation of TiC aggregates above the threshold content was not related only to the occurrence of electrical paths but also to the reinforcement of the mechanical modulus. For each composite, E' de-
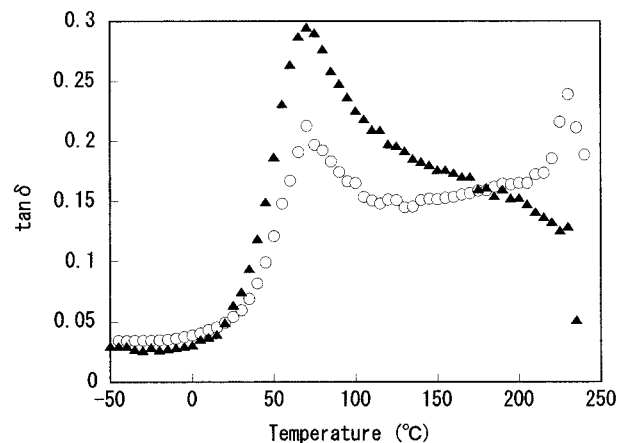

Figure 3 Temperature dependence of E' for TiC/CB composites: (○) 70 wt % CB and (▲) 30 wt % CB.

creased with increasing temperature in the 0–50°C range. In particular, the changes in T1 and T2 were pronounced; that is, for T1, the difference in E' from 0 to 50°C was about 4000 MPa, and for T2, it was about 1900 MPa. The value of T1 at 50°C, however, was still much higher than that of T3, T4, or T5 at 0°C. This indicates that at this stage, no breakdown took place in the electrical paths of T1. As a result, the resistivity of T1 did not change in the temperature range. For T2, E' at 50°C was almost similar to that of composites with low TiC contents (T3–T5), so that a PTC characteristic appeared in the 0–50°C range because of the decline of electrical paths. The temperature dependence of the loss tangent (δ) of the composites is shown in Figure 2. For each composite, the increase in tan δ started at about 0°C, and the maximum appeared around 50–60°C. We assumed that the mechanical loss was caused by

Figure 2 Temperature dependence of tan δ for TiC/P3HT composites: (◇) 90 wt % TiC, (●) wt % TiC, (△) 50 wt % TiC, (□) 70 wt % TiC, and (▼) 0 wt % TiC.


Figure 4 Temperature dependence of tan δ for TiC/CB composites: (○) 70 wt % CB and (▲) 30 wt % CB.

friction between TiC and P3HT and changed the conductive paths. Although the mechanical loss of T1 was lowest and the resistivity did not change, that of T2 was more pronounced than that of T1, leading to the PTC effect.

Characteristics of Composites Consisting of Fractionated P3HT and CB

As for P3HT/CB composites, the percolation threshold appeared at low concentrations because
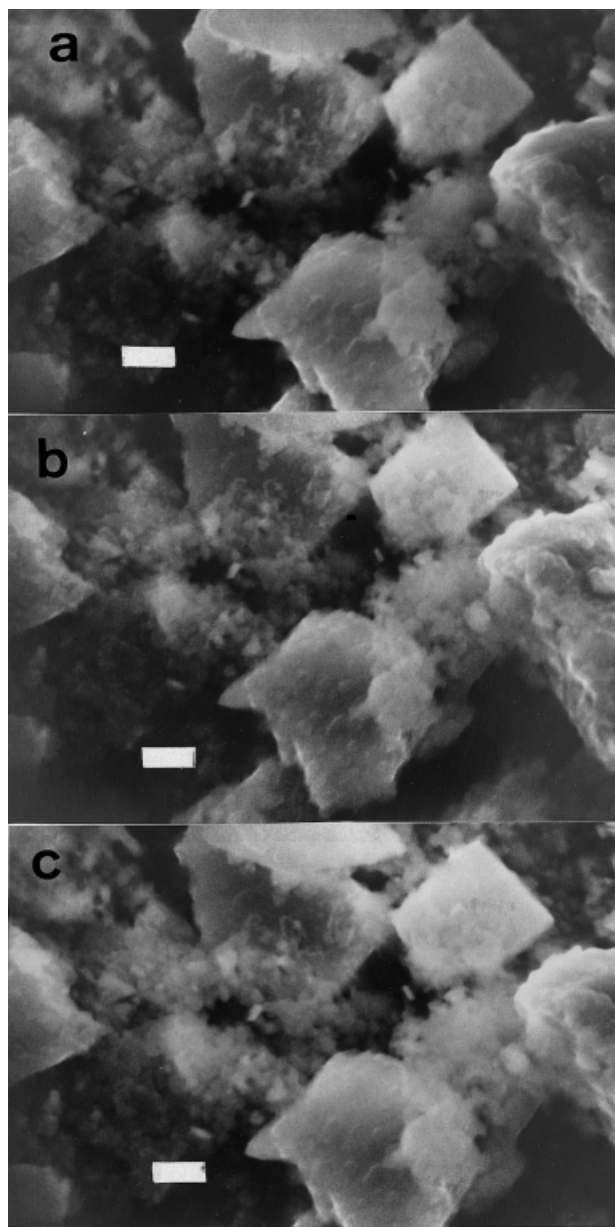
Figure 5 SEM photographs of TiC/P3HT (30 wt % TiC) at various temperatures: (a) 10°C, (b) 20°C, and (c) 50°C. Scale bars = 1 μm.
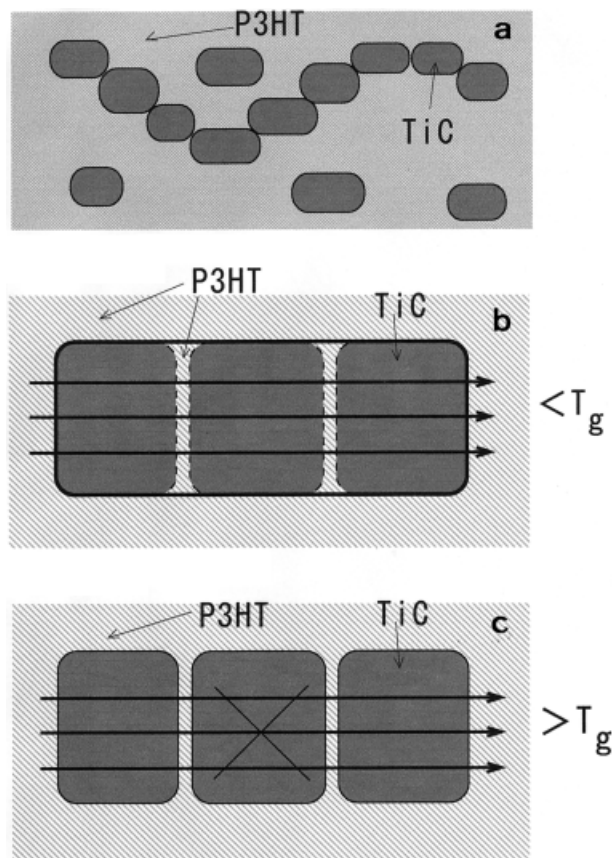
Figure 6 Conductive model for TiC/P3HT composites (30 wt % TiC): (a) conductive path near percolation, (b) below T_g, and (c) above T_g.

the size of conductive particles was small, and therefore, energy accumulation was significant, as previously reported.[8] Two samples (T6 and T7) with CB contents above the percolation concentration were examined.

Their resistivities were 0.5 and 2 Ω cm at 0°C, respectively, and they were unaffected by temperature rise. The electrical paths seemed to be relatively stable because of the energy buildup.

The DVE of P3HT/CB composites (T6, T7) was measured in the -50 to 250°C temperature range, and the results are shown in Figures 3 and 4. For T6 (CB content = 70%) and T7 (CB content = 30%), with contents above the percolation concentration, E' values at 0°C were 1450 and 1550 MPa, respectively; they were small if compared with the E' values of T1 and T2 at 0°C with a similar resistivity. This was due to the low E' of CB and the weak interaction between P3HT and CB. Although E' rapidly decreased with increasing temperature, tan δ increased; the resistivity, however, was unaffected by the temperature rise.

The mechanical characteristics as a function of the temperature did not affect the electrical ones because the interaction between P3HT and CB was weak, and the energy buildup of CB was high.

Morphological Study of Composites Consisting of Fractionated P3HT and TiC

The PTC effects of conductive polymer composites result from a trade-off between the network structure of conductive particles and the large thermal expansion of the polymer matrix.[10,11] In particular, a large PTC switching of polyethylene/CB composites was confirmed at the melting point on account of the expansion of the polymer matrix.[12,13] PTC effects were also observed near T_g of the polymer matrix.[14,15] In this case, the influence of the polymer expansion would be less than at the melting point. SEM for P3HT/TiC with a PTC effect was used at -10, 20, and 50°C and is shown in Figure 5. Comparison of the photographs taken at each temperature showed that the morphology of the composite was practically unaffected.

The mechanical and morphological results led to a model of conductive pathways for P3HT/TiC, which is shown in Figure 6. The electrical pathways would be completed by islands consisting of conductive particles at the percolation concentration, as shown in Figure 6(a). The islands would be pictured as shown in Figure 6(b,c), where TiC is aggregated through thin P3HT films. When the interaction between the conductive fillers and polymer matrix was strong (in the temperature range below T_g), an electrical current was assumed to flow through the thin film through a tunneling effect [Fig. 6(b)].[16] In the temperature range above T_g, however, there was hardly any current [Fig. 6(c)] due to the weaker interaction between TiC and P3HT. It was concluded, therefore, that the PTC effect appeared near the T_g of P3HT.

CONCLUSIONS

The DVE of P3HT/TiC composites was examined. The E' at 0°C rapidly increased from a TiC content approximating the threshold when the TiC content rose. This change corresponded to the change in resistivity. Both the temperature dependence of E' and that of the resistivity started near the T_g. For each composite, the increase in

tan δ also started near the T_g of P3HT. The mechanical loss was caused by in friction between TiC and P3HT and affected the conducting paths. On the other hand, E' at 0°C of the P3HT/CB composites (T6 and T7) was lower than that of T1 and T2 with a similar resistivity. In this case, the resistivity was not affected by a temperature rise, although E' rapidly decreased as the temperature rose and tan δ increased. To picture the PTC phenomenon, a model of conductive pathways for P3HT/TiC was proposed. The islands in the conductive pathways consisted of TiC aggregated through thin P3HT films. When the interaction between conductive fillers and polymer matrix was strong (in the temperature range below T_g), an electrical current, produced by the tunneling effect, flowed through the thin film, whereas in the temperature range above T_g, there was hardly any current due to the weaker interaction between TiC and P3HT.

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