

Viscoelastic and Conductive Characteristics of Titanium Carbide/Polyethylene Composites in Relation to Their Structural Parameters

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ABSTRACT: Titanium carbide (TiC)/polyethylene (PE) composite is a candidate for a positive-temperature coefficient resistor, which is used for a self-recoverable element that provides protection from overcurrents in many kinds of electrical devices. In the present study, the PE-based composites containing various volume fractions (ϕ) of TiC were prepared, after which their viscoelastic characteristics were investigated compared against their electric conductivity as a function of temperature. When the value of ϕ exceeded 0.39, the resistivities of the sample decreased steeply with increasing TiC content. The resistivity of the specimen maintained a constant value of about 0.1 Ωcm in the range of ϕ

values > 0.52 . Alternatively, the changes in the storage moduli at room temperature with various ϕ values of the samples could be expressed by a modified Kerner equation with the maximum ϕ value of 0.67. Melting behaviors of the samples were also examined and discussed in terms of their morphological features. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3134–3139, 2004

Key words: fillers; composites; structure–property relations; electrical conductivity; positive-temperature coefficient (PTC)

INTRODUCTION

During the past few decades, many investigations have been carried out to obtain polymer composites with excellent positive-temperature coefficient (PTC) resistors.^{1–8} Materials with PTC characteristics are reliably used as self-recoverable devices for overcurrent protection in electrical circuits. Among the satisfactory materials having PTC resistor characteristics are composites made of polyolefin and powders with excellent electrical conductivity like ceramic particles.^{9,10}

When we mix polyethylene (PE) as matrix material and titanium carbide (TiC) as a conducting filler, the TiC/PE composites obtained are characterized by the complex structures composed of TiC networks within PE fine structures, having the specific fusion temperature of PE crystallites. Once PE crystallites melt out, the conductive networks of TiC in the composites will be broken down, accompanied by disconnection of the TiC chain.

On the other hand, based on the concept of percolation, the fillers from a continuous chain thereby drastically decrease the composite resistivity, at a critical volume fraction of conducting fillers in an insulating poly-

mer matrix. To apply the percolation theory to those composite materials, it is important to clear the physical mechanism of the appearing function. In this study, dynamic viscoelasticity and electric resistance of composites that contain various volume fractions of TiC were measured in parallel. On the basis of those measurements, the relationship between the dispersion condition of the conductive filler and electric properties was discussed to determine the influence of composite on electrical conductivity internal structures.

EXPERIMENTAL

Sample preparation

The TiC powder used in this study had an average particle diameter of about 1.5 μm . Both TiC (TiC-M; Japan New Metals Co., Japan) and PE (MODIC-AP H503; Mitsubishi Chemical Co., Japan) samples were weighed for the desired compositions corresponding to the total volume of 50 cm^3 . They were then mixed by use of a plastomill (Toyo Seiki Co., 30C-150 type) under 30 rpm at 160°C for 20 min. The resulting mixtures were successively hot-pressed into plates of 300 μm thickness at 160°C for 15 min under a pressure of 200 kgf/cm^2 (Fig. 1).

Measurements

The specimens for electric resistivity measurements were prepared by pressing the mixture, which was

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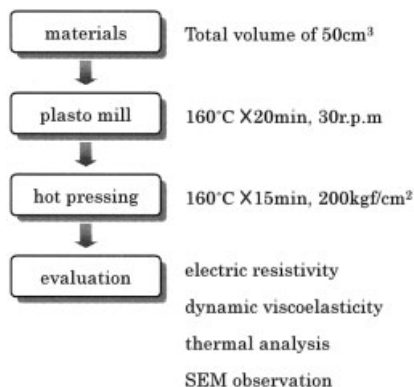


Figure 1 Schematic diagram of experimental procedure.

inserted between electrolytic nickel foils at 200°C for 10 min. After being cooled to room temperature, they were cut into discs of 9 mm diameter. In cases of resistivity ranges < 10 MΩ, sample resistivity was measured using an LCR meter (HP 4263B) by means of a four-terminal method under the condition of R_{dc} Mode. In ranges > 10 MΩ, the resistivity was measured using a digital Super Mega ohmmeter (DSM-8103; Toa Co., Japan) by means of a two-terminal method.

In viscoelastic measurements, the composite plates of 300 μm thickness were cut into sheets of 5 × 20 mm size. The temperature dependency of storage modulus (E'), loss modulus (E''), and loss tangent ($\tan \delta$) were measured using a dynamic viscoelastic analyzer (DVE-V4; Rheology Co.) in dry air from 20 to 160°C at the applied mechanical frequency of 1 Hz.

The dispersed states of the filler were examined using a scanning electron microscope (JSM-5300; JEOL, Tokyo, Japan) to observe the fractured surfaces of the composites. For this observation, the fracture surfaces of the composites were obtained using tweezers after dipping the sample in liquid nitrogen, followed by Au sputtering with an ion-sputtering device (JFC-1100E; JEOL).

RESULTS AND DISCUSSION

Effect of mixing torque during sample preparation

Figure 2 shows the influence of volume fraction (ϕ) on the mixing torque detected by a strain gauge. In general, it is difficult to obtain a composite with high filler content ($\phi > 0.5$) because of poor wettability between the matrix polymer and the filler surfaces. The torque increased with increasing ϕ value, then decreased rapidly in the range of ϕ values > 0.52. This can be explained that, in the range of very high filler content where fillers are packed densely, the frictional force among the particles caused by a small amount of PE becomes lower, thus leading to the decrease in torque.

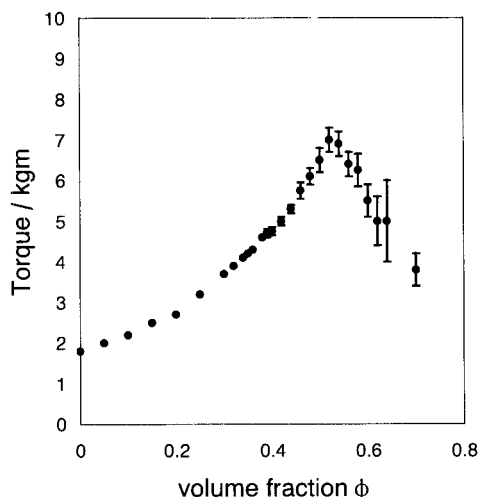


Figure 2 Changes in the torque detected in the mixing process as a function of TiC volume fraction ϕ .

Figure 2 also indicates that the fluctuation of the torque above $\phi = 0.4$ appears to be remarkable as the result of slippage among TiC particles.

Electric resistivity of TiC/PE composites

Figure 3 illustrates that the electric resistivities (ρ) of the composites at room temperature depend on the ϕ value. The values of ρ gradually decrease in the range from $\phi = 0$ to $\phi = 0.39$, then begin to change downward at $\phi = 0.43$. This characteristic corresponds to the percolation behavior in a dispersed particle system. The resistivity changes by 15 orders of magnitudes from 10^{13} to 10^{-2} Ωcm accompanied by TiC volume fraction. Especially in the range of $\phi = 0.39$ –0.5, the change reaches 14 orders of magnitude. Above $\phi = 0.52$, the resistivity decreases gradually with in-

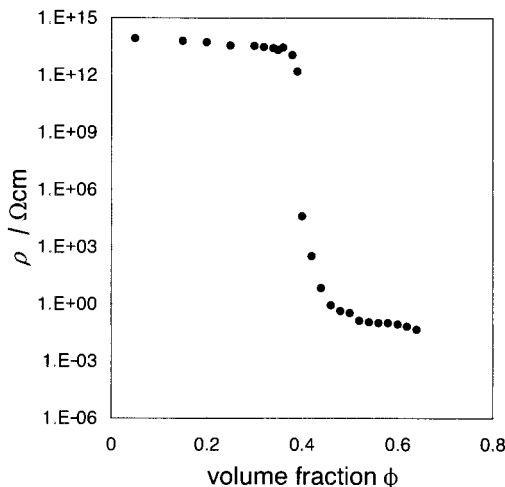


Figure 3 Changes in the ρ values as a function of ϕ at room temperature.

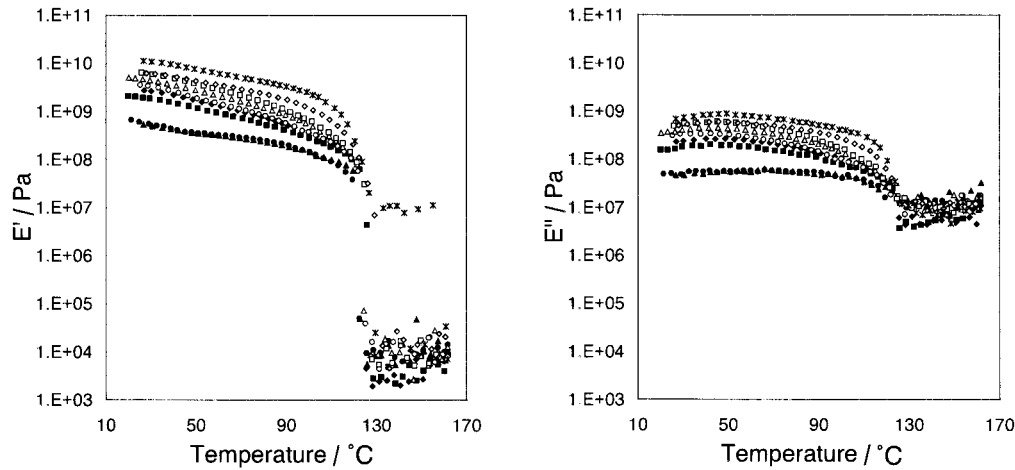


Figure 4 Temperature dependency of storage and loss moduli for TiC/PE composites at 1 Hz. The symbols indicated are: 0 (●); 0.1 (▲); 0.2 (■); 0.3 (◆); 0.4 (○); 0.42 (△); 0.48 (□); 0.54 (◇); 0.60 (*).

creasing TiC volume fraction. By the simple assumption that the conduction originates from the number of the contacts among fillers, this drastic change of resistivity can be explained as follows: when the TiC volume fraction is about 0.39, TiC particles begin to come into contact and the conduction network is effectively constructed. As a result, the electrical property changes from that of an insulator to that of a conductor. When the TiC volume fraction reaches $\phi = 0.52$, the conduction network probably forms completely within the composites. This speculation is derived from the fact that the resistivity maintains an almost constant value of $0.1 \Omega\text{cm}$ above that content.

TiC/PE composite materials are discussed rheologically in the following, with regard to each TiC volume range, respectively, where resistivity is high, changes drastically, and decreases gradually, as an insulation range, a penetration range, and a high conductivity limiting range.

Dynamic mechanical properties

In Figure 4, the sample with higher TiC volume fraction exhibits higher storage modulus (E'), which decreases rapidly close to the melting point of PE.

The temperature dependency of the modulus as a function of ϕ is negligible for the sample with higher TiC volume fraction.

As shown in Figure 5, the volume fraction dependency of $\tan \delta$ at the softening temperature (ST, 105°C) decreases rapidly from the $\tan \delta$ value of $\phi = 0.52$ volume fraction. This rapid change in the viscoelastic behavior at 0.52 could be explained given that the contact area among TiC particles is greater than that between PE and TiC particles.

The TiC volume fraction dependency of the relative elastic modulus E'/E'_1 (E'_1 : charged elastic modulus of

matrix that contains no filler), examined by the modified Kerner equation, is proposed as follows:

$$\frac{E'}{E'_1} = \frac{1 + AB\phi}{1 - B\phi} \quad (1)$$

where

$$A = \frac{7 - 5\nu_1}{8 - 10\nu_1}$$

$$B = \frac{(E'_2/E'_1) - 1}{(E'_2/E'_1) + A} \quad \psi = 1 + \left(\frac{1 - \phi_m}{\phi_m^2} \right) \phi$$

in which ν_1 is Poisson's ratio of matrix, E'_2 is the elastic modulus of filler, ϕ is the volume fraction of filler, and ϕ_m is the maximum volume fraction of filler.

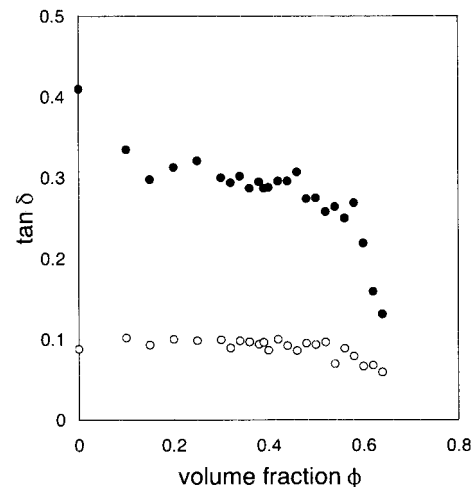


Figure 5 Volume fraction dependency of $\tan \delta$: room temperature (○); 105°C (●).

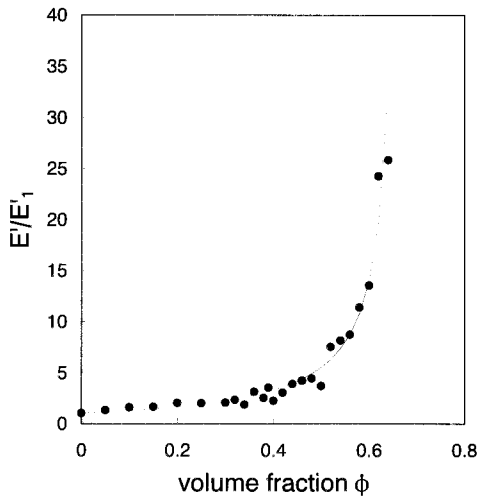


Figure 6 Changes in relative elastic moduli as a function of ϕ at 105°C. The line indicated was obtained by the modified Kerner equation with $\nu_1 = 0.5$, $B = 1.0$, and $\phi_m = 0.67$.

Figure 6 shows that the solid circles and the solid line indicate the TiC volume fraction dependency of the relative elastic moduli, E' and E'_1 , obtained from experimental measurement and calculated using the modified Kerner equation of $\phi_m = 0.67$, respectively. The curve agrees with the plot irrespective of the volume fraction of filler. This result suggests that the maximum filler content in the TiC/PE composite is 0.67 and that the type of packing is a random structure, which is most densely packed (Table I).

Melting and crystalline behavior

In Figure 7, it may be observed from DSC measurement for the TiC/PE composite that the peak associated with the melting is around 130°C, and the temperature is independent of TiC volume fraction. Also enthalpy was found to decrease with increasing TiC volume fraction. These findings are interpreted that the melting peak in heating is attributed to the melting.

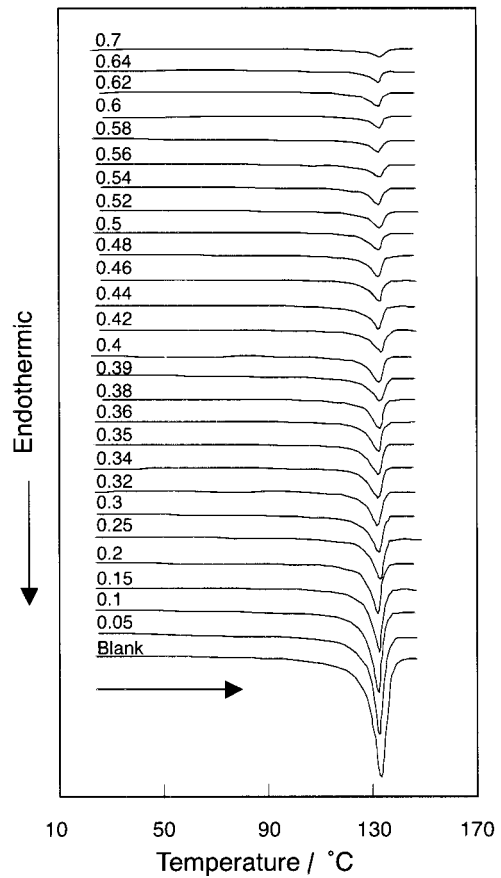


Figure 7 DSC traces for TiC/PE composites of various ϕ values, indicated respectively by different numerals.

If the melting peak temperatures in DSC measurement depend only on PE, the enthalpy normalized by PE volume fraction has to be constant. However, $\Delta H / \Delta H_0(1 - \phi)$ obtained from the experimental measurement decreases gradually, as shown in Figure 8. This

TABLE I
 ϕ_m Values for Various Lattices

Particle	Packing mode	ϕ_m
Spheres	Hexagonal closest	0.7405
	Face-centered cubic	0.7405
	Body-centered cubic	0.6
	Primitive cubic	0.5236
	Random closest	0.637
	Random diffuse	0.601
Rods	Parallel-hexagonal	0.907
	Parallel-square	0.785
	Parallel-random	0.82
	Random	0.52(?)

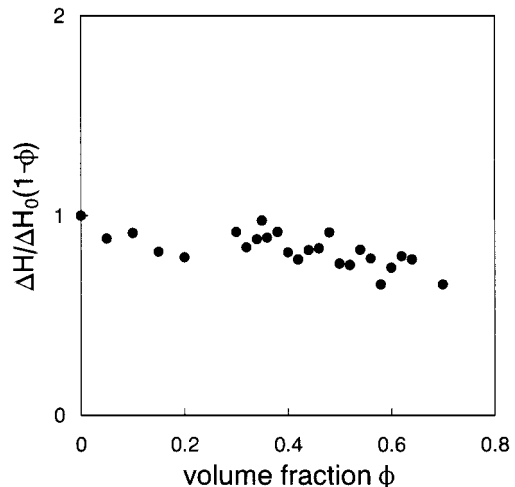


Figure 8 TiC volume fraction dependency of relative $\Delta H / \Delta H_0(1 - \phi)$.

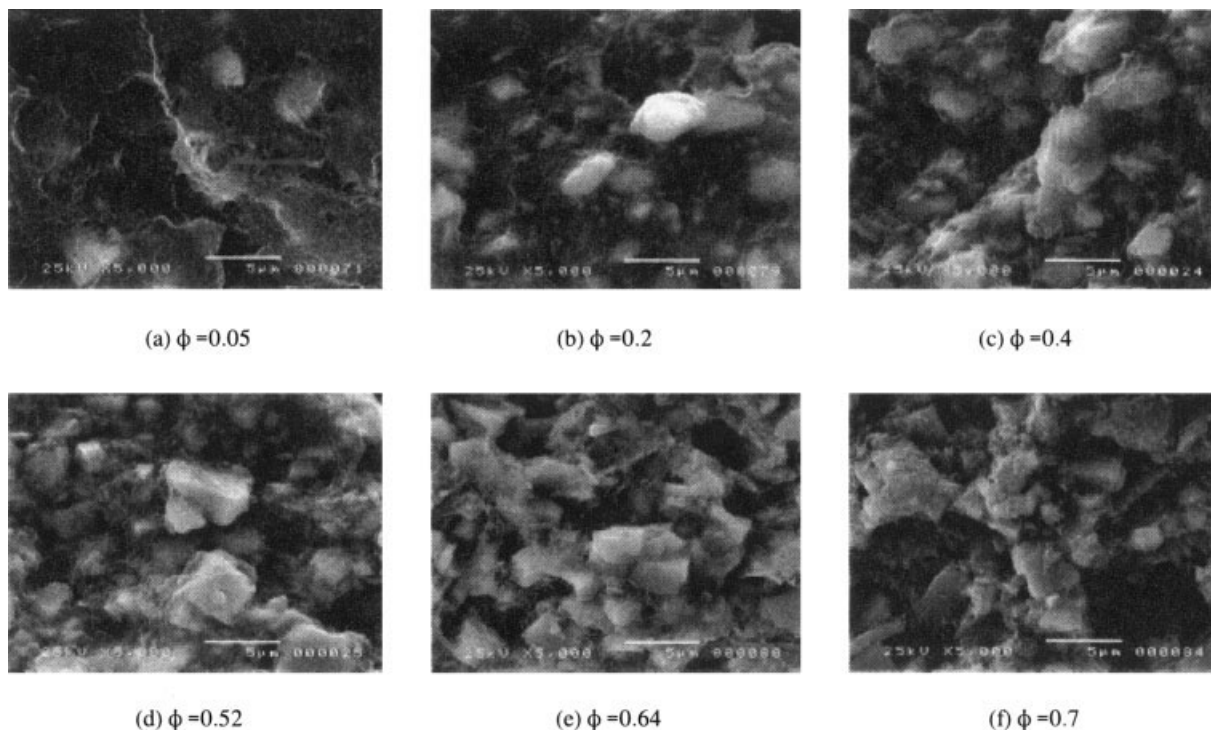


Figure 9 SEM micrographs of the fracture surface of the TiC/PE composite with various ϕ values.

result indicates that crystallinity of PE is lower than the theoretical value because the added TiC particles resist lamellar growth.

Morphology of composites

Figure 9 shows the SEM micrograph of the cross section under $\times 5000$ magnification. The white blocks correspond to TiC, which are surrounded by PE. Dispersed TiC increases with increasing TiC volume fraction. It may also be observed from the figure that TiC particles are dispersed separately among PE in the range of 0.05–0.36 volume fractions, and that TiC particles contact with each other above 0.39. Moreover, pores and naked TiC particles are observed below 0.7.

On the basis of the above discussion as shown in Figure 10, TiC particles exist separately when the resistivity of composite is almost the same as that of PE as in the insulation range. TiC particles begin to come into contact with each other to construct the conduc-

tion network in the penetration range. Above the filler content of 0.52, contacts between particles that control the electric conduction are completely within the high conductivity range.

Temperature dependency of resistivity

The associated PTC effect occurs because the elimination of particles forms continuous conductive paths by the expansion of PE. This expansion occurs near the melting point of the crystallites, resulting in an increase in the resistivity of the composite. Figure 11 shows that as the filler concentration was increased, a PTC effect was observed. The PTC effect level was found to be in the range 0.1 to $10^6 \Omega\text{cm}$. The transition temperature shifted higher with increasing filler content. At high loadings of TiC, the composites do not show the PTC effect. This behavior indicates that, although increasing the filler concentration decreased

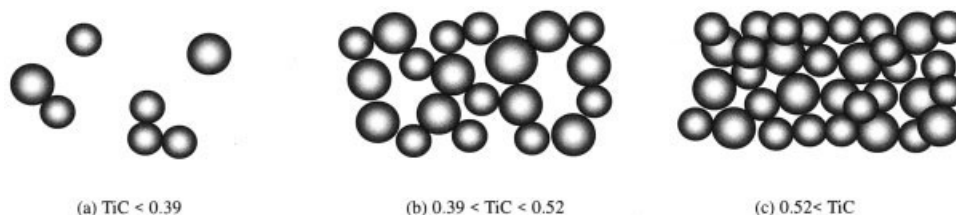


Figure 10 Changes of the cohesive form pictured schematically.

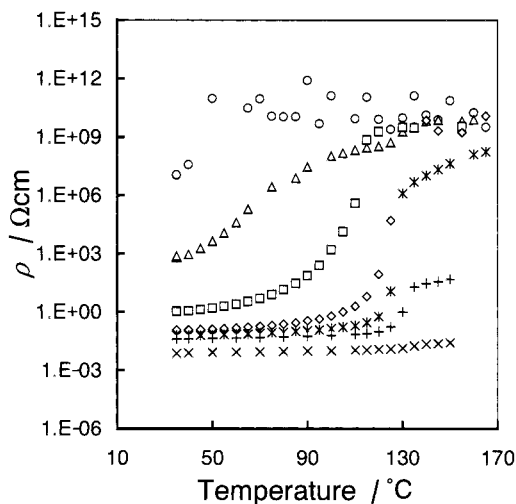


Figure 11 Changes in the ρ values of the TiC/PE composite as a function of temperature. The symbols indicated are: $\phi = 0.4$ (○); 0.42 (△); 0.48 (□); 0.54 (◇); 0.60 (*); 0.64 (+); 0.7 (×).

resistivity, it was nonetheless difficult to break down the TiC conductive networks in the composites.

CONCLUSIONS

When the TiC volume fraction was 0.05–0.36, the conduction network attributed to the contacts between

particles was not constructed to be in the insulation range. When it was about 0.39, contacts between particles increased. When it increased to 0.43, resistivity decreased drastically to that of a conductor. In the penetration range up to 0.52, the conduction network was constructed. Above the filler content of 0.52, it is the high conductivity range in which resistivity gradually decreased. Experimental results showed that the filler can be mixed up to 0.67.

It was clearly shown that TiC/PE composites exhibit a strong PTC effect.

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