Time Dependence of Piezoresistance for the Conductor-Filled Polymer Composites

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ABSTRACT: The piezoresistance and its time dependence of conductor-filled polymer composites have been investigated. To reveal the origin of the time dependence of piezoresistance, the creep of the polymer matrix is also studied. Based on the interparticle separation change under the applied stress, a model has been developed to predict the piezoresistance and its time dependence. By analyzing this model, the influences of applied stress, filler particle diameter, filler volume fraction, matrix compressive modulus, potential barrier height, and the matrix creep behavior on the piezoresistance and its time dependence are interpreted quantitatively. These predicted results are compared with the experimental data obtained on the polymer composites filled with conductor fillers, and good agreements were obtained. © 2000 John Wiley & Sons, Inc. J Polym Sci B: Polym Phys 38: 2739–2749, 2000

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INTRODUCTION

The electrically conducting composites composed of conducting filler into an insulating polymer matrix have attracted a great deal of scientific and industrial interest for many years.[1–5] The main advantage of these composites is the abrupt changes in the electrical conductivity caused by the change of either filler content or temperature. At a constant temperature, the composites undergo an insulator-to-conductor transition with the increase of filler content.[6] The insulator-to-conductor transition is usually very sharp, so that a critical volume fraction of conductive filler, the percolation threshold, can be well defined, and percolation effect has been adopted as a term to represent such a resistivity change. On the other hand, a composite with a certain volume fraction of conductive filler possesses itself of an intensive positive temperature coefficient effect, abbreviated PTC effect, in which the abrupt increase in resistivity results from temperature increase. The PTC transition temperature, which is defined as a temperature or a narrow temperature range where the sudden increase in resistivity is found, is usually near the melting point of the polymer matrix. Although both percolation effect and PTC effect are two different characteristics of conductive polymer composites, they can both be attributed to an intrinsic change in microstructures, or say more precisely, the separation of conductive filler particles. The interparticle separation is controlled by the filler content in percolation effect, while controlled by the thermal expansion of the polymer matrix in PTC effect.

Because the separation change between the adjacent filler particles is the intrinsic mechanism behind the abrupt changes in the resistance of conductive polymer composites, any process that can change the separations of conductive

filler particles can also change the resistivity. An application of stress to the conducting polymer composites changes the composite resistance, which has been primarily investigated. It has been reported that if the applied stress was a pressure, despite hydrostatic pressure or uniaxial pressure, the composite resistance reduced under the stress, and this effect has been named as the piezoresistance.[7–11] The main reason for the piezoresistance was thought to be the difference between the filler and matrix compressibilities. The application of stress thus leads to a change in the interparticle separation in composites. Many results showed that the piezoresistance depends on materials composition, pressure, and filler content.[7–11]

In the study of PTC effect, many researchers found that the resistance of conductive composites still changes with time when the temperature is fixed.[12,13] The reason for this is that the dispersion of conductive filler is altered during annealing, owing to the high surface energy of fillers, which reduces the effective interparticle separation. Similar to the PTC effect, the piezoresistance also changes with time under a fixed stress, which is the so-called time dependence of piezoresistance. Unlike the PTC effect, the origin of time dependence of piezoresistance is the creep of the polymer matrix. The interparticle separation reduces as the polymer matrix creeps under a fixed stress; thus, the composite resistance decreases with time. As the time dependence affects the reproducibility and stability of the piezoresistance, it will complicate or even baffle the application of piezoresistance. But little work has been focus on this topic.

Carmona[5] has developed a model to predict the piezoresistance of the conductor filled polymer composites close to threshold. Although his model can precisely fit the experimental data, it still has many disadvantages: (1) it is difficult to predict the effects of the influencing factors on the piezoresistance quantitatively, especially the effects of filler particle diameter, matrix compressive modulus, etc.; and (2) it cannot explain the time dependence of piezoresistance, etc.

The conductor-filled polymer composites, which exhibit a piezoresistance under the pressure, are widely used for various electronic applications such as tough control switches for televisions, cameras, watches, variable volume control elements for electronic organs, and as stress sensors for various applications.[10] For all these applications, the reproducibility and stability of the
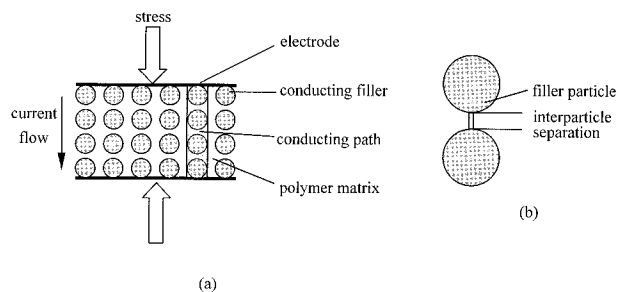

Figure 1. Schematic view of the piezoresistance measurement and microstructure of the conductor filled polymer composites.

piezoresistance, which is controlled by the time dependence, are very important but little studied. Therefore, we focus our work on the time dependence of piezoresistance, i.e., how to decrease the time dependence and improve the reproducibility and stability of piezoresistance.

The purpose of this article is to present the results of our recent studies on the evolution of piezoresistance and its time dependence based on several different conductor-filled polymer systems. The tin–lead alloy powder, copper powder, and aluminum powder have been used as the conducting fillers, and the polyethylene, polystyrene, and epoxy as polymer matrices. In this article, a model based on the separation change is also developed to predict the piezoresistance and its time dependence of the conductor-filled polymer composites. By analyzing this model, the influences of applied stress, filler particle diameter, filler volume fraction, matrix compressive modulus, and matrix creep behavior on the piezoresistance and its time dependence are interpreted quantitatively, and the way to decrease the time dependence of piezoresistance is obtained.

DERIVATION OF THE MODEL

In conducting composites the total resistance is a function of both the resistance through each conducting particle and the polymer matrix. Assuming that the resistance of the matrix is constant everywhere, the resistance of the paths perpendicular to the current flow may be neglected, and, thus, the number of conducting particles between electrodes becomes a factor in this relationship, as well as the number of conducting paths [see Fig. 1(a)]. The total resistance can then be described by[14]

$$R = \frac{(L-1)R_m + LR_c}{S} \approx \frac{L(R_m + R_c)}{S} \quad (1)$$

where R is the composite resistance, R_m the resistance between two adjacent particles, R_c the resistance across one particle, L the number of particles forming one conducting path, and S the number of conducting paths.

When the interparticle separation is very large, no current flows through the interparticle separation. But if the separation is quite little, the tunneling current may flow through the separation.[15] According to the analyses of Simmons,[16–19] the tunneling current J at low applied voltage is given by

$$J = \frac{3\sqrt{2m\varphi}}{2s}\left(\frac{e}{h}\right)^2 V \exp\left(-\frac{4\pi s}{h}\sqrt{2m\varphi}\right) \quad (2)$$

where m and e are the electron mass and charge respectively, h Plank's constant, V the applied voltage, s the thickness of the insulating film, and ϕ the height of the potential barrier between the adjacent particles that can be gained by the subtraction of polymer's work function from the conductor's. Because the electron tunneling probability depends on the insulating barrier thickness, it is considered that practically all the tunneling occurs within the small surface areas.[20] Thus, as shown in Figure 1(b), s in eq. (2) equals the separation between the surfaces of two adjacent particles, which is the least distance between the particles.

Assuming that a^2 is the effective cross-sectional area, where the tunneling occurs [see Fig. 1(b)], then the resistance R_m is given as follows:

$$R_m = \frac{V}{a^2 J} = \frac{8\pi h s}{3a^2 \gamma e^2}\exp(\gamma s) \quad (3)$$

where

$$\gamma = \frac{4\pi}{h}\sqrt{2m\varphi}$$

As the conductivity of the conducting particle is very large compared with that of the polymer matrix, the resistance across the particle can be neglected ($R_c \sim 0$). Then substituting eq. (3) into eq. (1) gives

$$R = \frac{L}{S}\left[\frac{8\pi h s}{3a^2 \gamma e^2}\exp(\gamma s)\right] \quad (4)$$

By this equation, the composite resistance can be calculated theoretically.

Piezoresistance of Composites

If a stress is applied to the sample, the resistance will be altered due to the change of interparticle separation, which is caused by the compressibility difference between the filler particle and matrix. Assumed that the interparticle separation changes from s_0 to s under the applied stress, the relative resistance (R/R_0) can then be calculated by

$$\frac{R}{R_0} = \frac{s}{s_0}\exp[-\gamma(s_0 - s)] \quad (5)$$

where R_0 is the original resistance, and s_0 the original interparticle separation.

As the compressive modulus of the polymer matrix is much lower than that of conducting particle, the deformation of conducting particle under stress can be neglected. As a result, the change of interparticle separation along the conducting path is only due to the deformation of the polymer matrix. Therefore, if the applied stress is uniaxial press, the separation s under the applied stress can be calculated as

$$s = s_0(1 - \varepsilon) = s_0\left(1 - \frac{\sigma}{M}\right) \quad (6)$$

where ϵ is the strain of the polymer matrix, σ the applied stress, and M the compressive modulus of the polymer matrix.

To simplify the arithmetic during the estimating of s_0, the conducting particles are assumed to be spherical, of the same size, and arranged in a cubic lattice. Then the interparticle separation s_0 is given by[21]

$$s_0 = D\left[\left(\frac{\pi}{6}\right)^{1/3}\theta^{-1/3} - 1\right] \quad (7)$$

where D is the particle diameter, and θ the filler volume fraction.

Substituting eqs. (6) and (7) into eq. (5) gives

$$\frac{R}{R_0} = \left(1 - \frac{\sigma}{M}\right)\exp\left\{-\gamma D\left[\left(\frac{\pi}{6}\right)^{1/3}\theta^{-1/3} - 1\right]\frac{\sigma}{M}\right\}$$

$$= f(\sigma, M, D, \theta, \varphi) \qquad (8)$$

The relative resistance, the most important parameter for the piezoresistance, can then be predicted by eq. (8). By analyzing this equation, the influence of applied stress (σ), matrix compressive modulus (M), filler particle diameter (D), filler volume fraction (θ), and potential barrier height (ϕ) on the piezoresistance can also be interpreted quantitatively.

Time Dependence of Piezoresistance

Besides the stress, the interparticle separation change of the polymer matrix is also a function of time, which can be interpreted by the creep of polymer.[22] As a result, the piezoresistance of composites varies with time during the test.

The deformation of the matrix can be perfectly described by the famous Nutting equation:[22,23]

$$\varepsilon(t) = \varepsilon_0 + \psi\sigma^{\beta}t^n = \varepsilon_0 + \psi\sigma t^n \qquad (9)$$

where ϵ_0 is the original strain under the applied stress, ψ, β, and n are constants. As β is rather close to unit for most polymers, the creep behavior over an extended time interval is completely characterized by the two constants ψ and n.[22]

The time dependence of interparticle separation under the fixed stress can then be calculated as

$$s(t) = s_0[1 - \varepsilon(t)] \qquad (10)$$

Combining eqs. (7), (9), and (10) with eq. (4), the relative resistance of composites at the time of t under the fixed stress can be expressed as

$$\frac{R}{R_0} = \frac{R(t)}{R_0} = \frac{1 - \varepsilon(t)}{1 - \varepsilon_0}\exp\{-\gamma s_0[\varepsilon(t) - \varepsilon_0]\}$$

$$= \left(1 - \frac{\psi\sigma t^n}{1 - \varepsilon_0}\right)$$

$$\times \exp\left\{-\gamma\psi\sigma D\left[\left(\frac{\pi}{6}\right)^{1/3}\theta^{-1/3} - 1\right]t^n\right\}$$

$$= f(\sigma, D, \theta, \varphi, \varepsilon_0, \psi, n) \qquad (11)$$

One issue, which must be clarified, is that the physical meaning of R_0 in eq. (11) is different from that in eqs. (5) and (7). The R_0 in eqs. (5) and (7) is original resistance without applied stress; however, the R_0 in eq. (11) is the instant original resistance just upon the application of stress.

From eq. (11), it is seen that the relative resistance decreases with the time under a fixed stress. This behavior is further influenced by the applied stress (σ), filler particle diameter (D), filler volume fraction (θ), potential barrier height (ϕ), and the creep behaviors (ϵ_0, ψ, and n) of the polymer matrix. If these factors are fixed, the time dependence of piezoresistance is determined.

MATERIALS AND EXPERIMENTS

Materials Studied

The conducting fillers used were tin–lead (Sn–Pb) alloy powder, copper (Cu) powder, and aluminum (Al) powder. Two classes of Sn–Pb were used in our study: one was powdered solder of composition 60 wt % Sn, 40 wt % Pb provided by the Institute of Powder Metallurgy in Zhongnan Technology University of China, whose number mean particle diameter was about 0.1 μm. Another Sn–Pb was ground from the commercial bulked solder provided by Yun-Nan Tin Ye Co. of China, which has the same composition but larger particle diameter (0.5 μm). The Cu used in our study was purchased from the Shanghai Dier Smelting Plant, and has a diameter of 0.2 μm. The Al used, from the Assembling Factory of Shanghai Chemical Reagent Station, is a powder with the diameter of 0.7 μm.

Polyethylene (PE), polystyrene (PS), and epoxy were used as polymer matrices. The PE used in our study was the high-density polyethylene supplied by Maoming Petrochemicals Co. of China; The PS used was obtained from Yan-Shan Petrochemicals Co. of China. Three epoxies were used in our study, all of them were the diglycidyl ether of bisphenol A (Wujiang Xuelian Resin Factory) hardened with diethylene triamine (Shanghai Hongxin Chemical Reagent Plant). The difference of these three epoxies was that: the first one (epoxy00) did not contain any additive, while the other two epoxies, which were named as epoxy10 and epoxy20 in this article, were respectively modified by adding 10 wt % and 20 wt % dibutyl phthalate (Hangzhou Double-Forest Chemical

Table I. Compressive Modulus of the Polymer Matrixes

Polymer Matrixes	Compressive Modulus (GPa)
PE	0.67
PS	3.45
Epoxy00	2.91
Epoxy10	1.87
Epoxy20	0.97

Reagent Plant). The addition of this additive in our study was to decrease the compressive modulus of epoxy.

For the samples of Sn–Pb/PE, Cu/PE, Al/PE, Sn–Pb/PS, Cu/PS, and Al/PS, the conducting filler and polymer powder mixtures were mixed in a satellite ball mill (QM-1SP) at 200 rpm for 11 h, then the powder mixtures were compression molded in a matched metal die at 170 °C for 20 min to form the 4 mm-thick sheets. For the epoxy matrix samples, the epoxies (added with the hardener and additive) were mixed with the conducting fillers for 10 min by hand, and then cured at 90 °C for 3 h.

Mechanical Measurement

The compressive modulus was measured on a Multifunctional Electronic Mechanical Testing Apparatus (WSM-2000, Changchun Testing Instrument Institute of China) according to ASTM D 695. The head-moving rate was 1.3 mm/min. The samples were cut into cylinders with a diameter of 12 mm and a height of 30 mm. The compressive moduli of the materials studied were listed in Table I.

The creep behavior was also measured on the Multifunctional Electronic Mechanical Testing System. The samples were cut into cylinders with a diameter of 12 mm and a height of 40 mm. Just as the fixed stress was reached, the heights of the samples were detected and transformed into strains by the apparatus. The creep behavior was then obtained.

Resistance Measurements under Pressure

All these samples were cut into dimension of 40 × 40 × 4-mm sheets, except for the epoxy matrix samples whose dimension was 40 × 40 × 1 mm. To get excellent conductive contact and for the convenience of the piezoresistance measurement,

brass electrodes of 1 cm^2 were adhered at each side by silver paste. The reason to adopt much less area of electrodes than that of samples was to avoid the transverse movement of the composites under high stress and ensure that the applied stress is a uniaxial press.

The piezoresistance measurements were performed under uniaxial presses that were produced by a steel pole with a cross-sectional area of 1 cm^2. The resistances of the samples were measured by a digital multimeter (M890D, Shenzhen Fulid Electron Co. of China) along the compress direction after the current leveled off.

In this study, the resistance of samples studied has been measured as a function of the applied stress, and the time dependence of resistance change under the fixed stress was also measured. In all the measurements, the stress was always applied in a direction parallel to the electrical current flow.

RESULTS AND DISCUSSION

Piezoresistance of Composites

Figure 2(a) shows the resistance of the samples of Al/PE, Al/PS, Cu/PE, Cu/PS, and Sn–Pb/PS with the same filler volume fraction of 30%. The resistance of these samples decreases from Al/PS, Al/PE, Cu/PS, and Cu/PE to Sn–Pb/PS, which results from different particle diameters of fillers and different crystallizability of polymer matrices. It can also be seen that the resistance of all the samples decreases after a compressive stress is applied.

In the application of piezoresistance, most attention is focused on the relative resistance (R/R_0), instead of resistance.[2,8] At the same time, the model developed in this article only predicts the evolution of R/R_0. Therefore, to investigate the essence of piezoresistance, the R/R_0 of these samples are calculated and shown in Figure 2(b), where the R_0 is the original resistance before the pressure stress is applied. It can be seen that the R/R_0 also decreases monotonously with an increase of applied stress; furthermore, the decrease of R/R_0 becomes weaker from Al/PE, Al/PS, Cu/PE, and Cu/PS to Sn–Pb/PS.

As shown in eq. (6), the interparticle separation decreases with an increase of applied stress. As a result, the electrical conduction through the conducting paths becomes easier under stress [see eq. (2)], and the R/R_0 decreases. By analyzing
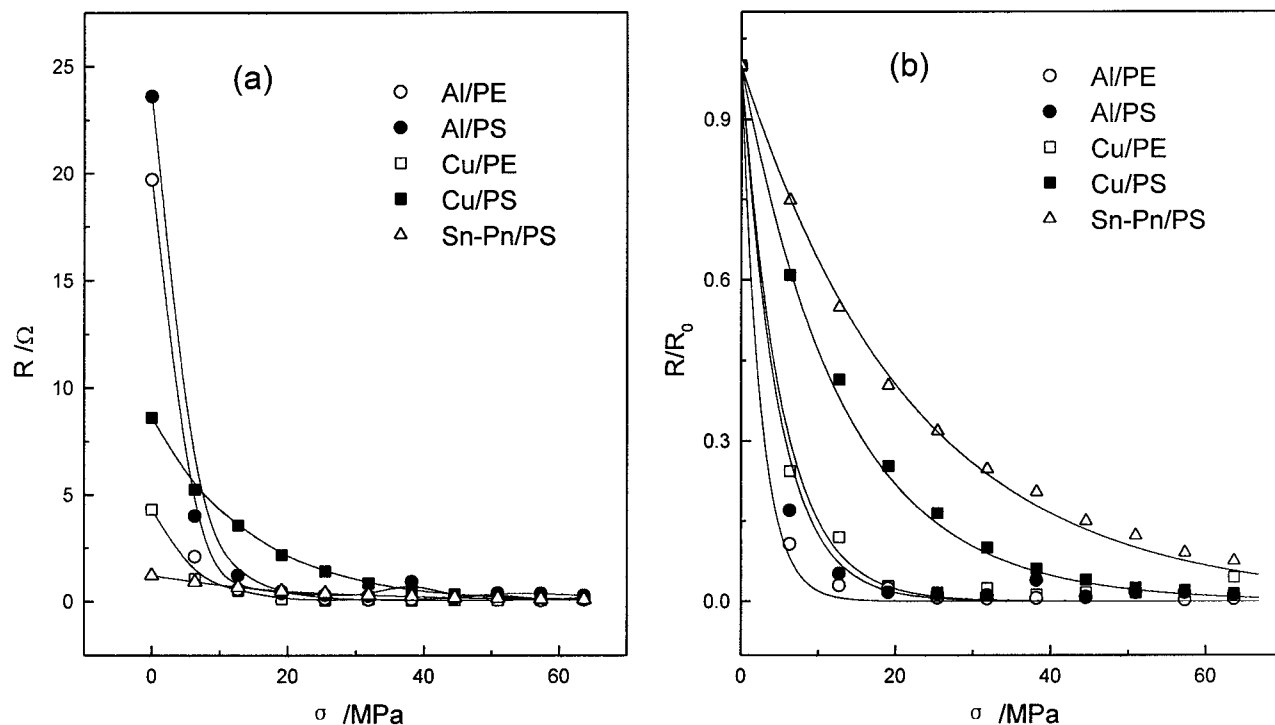
Figure 2. Resistance (a) and relative resistance (b) of the samples ($\theta = 30\%$) of Al/PE, Al/PS, Cu/PE, Cu/PS, and Sn–Pb/PS as a function of applied stress. Full lines are the theoretical data.

eq. (8), where the R/R_0 is expressed as a function of applied stress, the piezoresistance of conductor-filled polymer composites can be predicted quantitatively. The values of filler particle diameter (D), filler volume fraction (θ), matrix compressive modulus (M), and potential barrier height (ϕ) are needed in the theoretically calculation of R/R_0. Among them, the values of θ, M, and ϕ are already known when the composites is fixed, but that of ϕ needs to be calculated by ourselves.

The ϕ between the adjacent particles in composites can be obtained by subtracting the polymer and conductor work functions.[15] Some of the work functions of the materials used in our study are shown in Table II. The ϕ between the filler particles in Cu/PS and Al/PS can then be obtained as 0.39 and 0.55 eV, respectively. It is also can be observed in Table I that the compressive modulus of PS is 3.45 GPa. Substituting these values into eq. (8), the R/R_0 for the Cu/PS and Al/PS at any applied stress is then obtained. The calculated R/R_0 are shown in Figure 2, exhibiting a good agreement with the experimental data.

Unfortunately, the work functions of PE and Sn–Pb alloy are not available, so the ϕ of the composites containing PE or Sn–Pb cannot be

calculated simply by subtracting the work functions. Therefore, the experimental data of the piezoresistance is fitted with eq. (8) by computer, and the ϕ of the composites is gained at the same time. The fitted results of Cu/PE, Al/PE, and Sn–Pb/PS are also shown in Figure 2. The ϕ of these

Table II. Work Function of the Materials Used and Potential Barrier Height between the Adjacent Particles in the Composites Studied

Materials	Work Function (eV)	Composites	Potential Barrier Height (eV)
PS[a]	4.8	Cu/PS	0.39[c]
Epoxy[a]	4.0	Al/PS	0.55[c]
Cu[b]	4.41 ± 0.02	Sn-Pb/PS	0.57[d]
Al[b]	4.25	Cu/PE	0.09[d]
Sn[b]	4.38	Al/PE	0.07[d]
Pb[b]	4.0	Sn-Pb/PE	0.09[d]
Sn-Pb[d]	4.23	Sn-Pb/epoxy	0.23[d]

[a] See. Ref. 25.
[b] See. Ref. 26.
[c] Calculated from the data of work function.
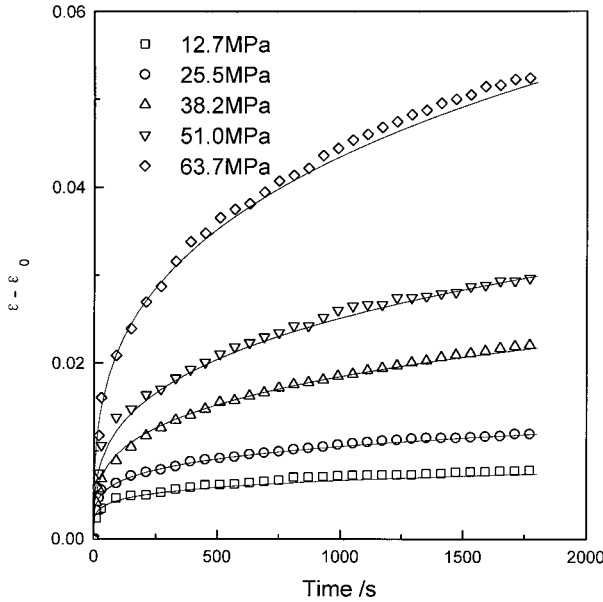[d] Fitted by the experimental data.

Figure 3. Deformation–time curves of PE under various stresses.

Table III. ε_0, ψ, and n of PE as a Function of the Applied Stress

Applied Stress (MPa)	ε_0	ψ	n
12.7	0.018	1.48×10^{-10}	0.183
25.5	0.037	9.41×10^{-11}	0.214
38.2	0.057	7.23×10^{-11}	0.275
51.0	0.077	6.27×10^{-11}	0.298
63.7	0.096	8.46×10^{-11}	0.302

The creep curves of PE, PS, epoxy00, epoxy10, and epoxy20 under the stress of 38.2 MPa are shown in Figure 4. The creep of PE is the greatest among these five polymers, while that of PS is the feeblest. It can also be seen that the creeps of epoxies become larger from epoxy00, epoxy10 to epoxy20. The ϵ_0, ψ, and n of these polymers under the stress of 38.2 MPa are shown in Table IV. The ϵ_0, ψ, and n of PE are the highest, while those of PS are the lowest. The ϵ_0, ψ, and n of epoxy increase with the increasing amount of additive added.

three composites thus obtained are 0.09, 0.07, and 0.57 eV, respectively. At the same time, the work functions of PE and Sn–Pb is calculated as 4.32 and 4.23 eV. As shown in Table II, the value of the Sn–Pb work function agrees with the weight average of the Sn and Pb work functions. Therefore, the fitting treatment is believable in the precision range of our study. All the values of work functions and potential barrier heights used can then be obtained and are shown in Table II.

Creep of Polymer Matrix

The relative resistance of conductor-filled polymer composites further decreases with time under a fixed stress. The basic reason is the creep of the polymer matrix, which has been put forward during the derivation of the model. From eq. (11) it can be seen that the parameters (ϵ_0, ψ, and n) describing the polymer creep characteristics are needed in the application this model. So the creep behavior of the polymers used are studied at first.

Figure 3 shows the creep behavior of PE under various stresses. The deformation increases with time, and the larger applied stress makes the increment larger. Fitting these experimental data with the Nutting equation, the ϵ_0, ψ, and n under various stresses are obtained and shown in Table III. It can be seen that the ϵ_0 and n increase with increasing stress, while the ψ changes more complicatedly.

Time Dependence of Piezoresistance

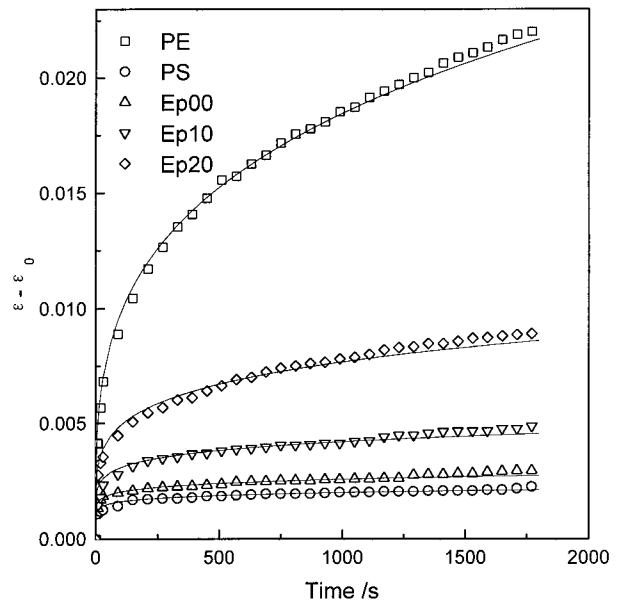The original interparticle separation of the fillers in composites are calculated from the data of D

**Figure 4.** Deformation–time curves of PE, PS, epoxy00, expoy10, and epoxy20 under the stress of 38.2 Mpa.

Table IV. ε_0, ψ and n of the Polymer Matrix Used

Materials	ε_0	ψ	n
PS	0.011	2.70×10^{-11}	0.096
PE	0.057	7.23×10^{-11}	0.275
Epoxy00	0.013	3.30×10^{-11}	0.103
Epoxy10	0.020	4.29×10^{-11}	0.136
Epoxy20	0.039	5.26×10^{-11}	0.194

and θ with eq. (7), and are shown in Table V. It can be seen that the separations are small and comparable with the data of ref. 25. By the results of above section and eq. (10), the interparticle separation in composites will further decrease with time under the fixed stress as a result of the creep of the polymer matrix, which is the origin of the time dependence of piezoresistance.

Figure 5 shows the time dependence of piezoresistance (R/R_0) for Al/PE, Cu/PE, Al/PS, and Cu/PS samples with the same filler volume fraction of 30%, where the R_0 is the original resistance just upon the application of stress, i.e., the data in Figure 2(a). As shown in Figure 5, the R/R_0 decreases sharply at the starting period of the test, and then tends to form a relatively fixed value. The fixed values of the Al-filled composites are lower than those of the Cu-filled composites, and the values of the PE matrix composites are lower than those of the PS matrix composites. The evolution of R/R_0 with time can be predicted by eq. (11), where the R/R_0 is expressed as a function of time. Substituting the corresponding value from Tables I, II, and IV into eq. (11), the theoretical time-dependence curves of piezoresistance for these samples are obtained and shown in Figure 5. It can be seen that the theoretical data agree with the experimental ones very well.

By analyzing eq. (11), the influence of applied stress (σ), filler particle diameter (D), filler vol-
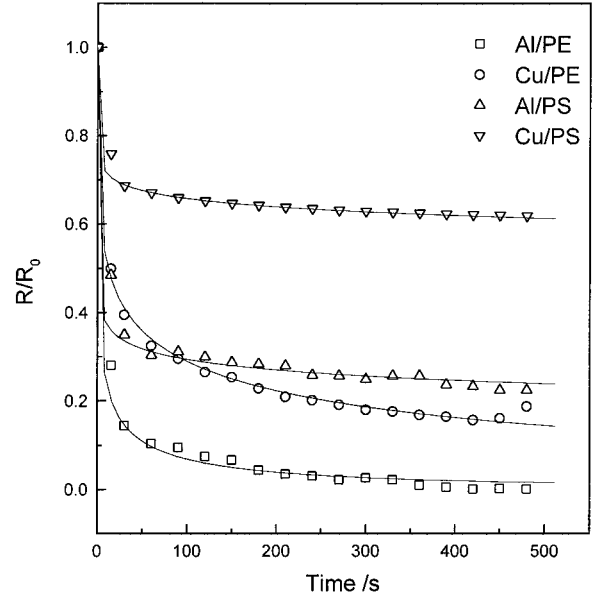
Figure 5.   Time dependence of piezoresistance for the samples $(\theta = 30\%)$ of Al/PE, Cu/PE, Al/PS, and Cu/PS under the stress of 38.2 MPa. Full lines are the theoretical data.

ume fraction (θ), matrix compressive modulus (M), potential barrier height (ϕ), and the polymer creep behaviors $(\epsilon_0, \psi,$ and $n)$ on the time dependence of piezoresistance can also be predicted.

Figure 6 shows the change of relative resistance with time for the Sn–Pb/PE samples $(\theta = 30\%)$ under various stresses. The relative resistances decrease monotonously with time for all the samples, and the decrement of the samples under higher stresses is larger than that under lower stresses. The theoretical time-dependence curves of piezoresistance for the samples were calculated with eq. (11) and shown in Figure 6. It can be seen that the theoretical data agree with the experimental data fairly well. From Figure 3, the higher applied stress leads to the higher de-

Table V.   Original Interparticle Separation[a] (nm) for the Filler Particles in Composites under at Atmospheric Press

	Cu	Al	Sn-Pb $(D = 0.1\ \mu m)$	Sn-Pb $(D = 0.5\ \mu m)$	CB
20 vol %	75.6	264.7	37.8	189.1	15.9
25 vol %	55.8	195.6	27.9	139.7	11.7
30 vol %	40.7	142.7	20.4	101.9	8.6
35 vol %	28.7	100.5	14.4	71.8	6.0

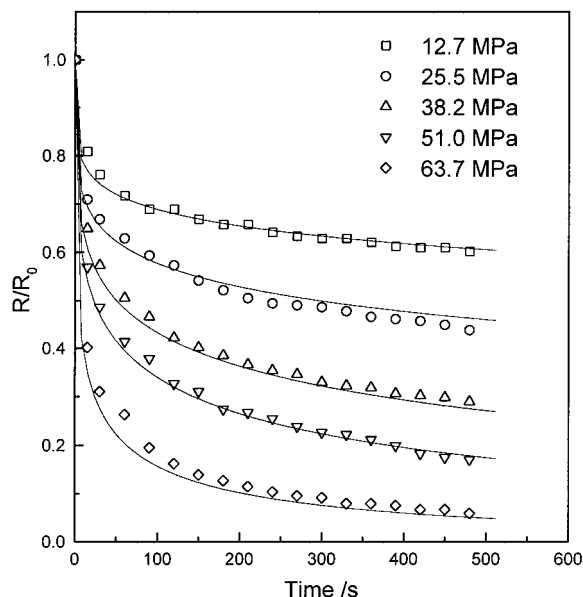[a] These data are calculated from the D and θ of fillers with eq. (7).

Figure 6. Time dependence of piezoresistance for the sample ($\theta = 30\%$) of Sn–Pb/PE under various stresses. Full lines are the theoretical data.
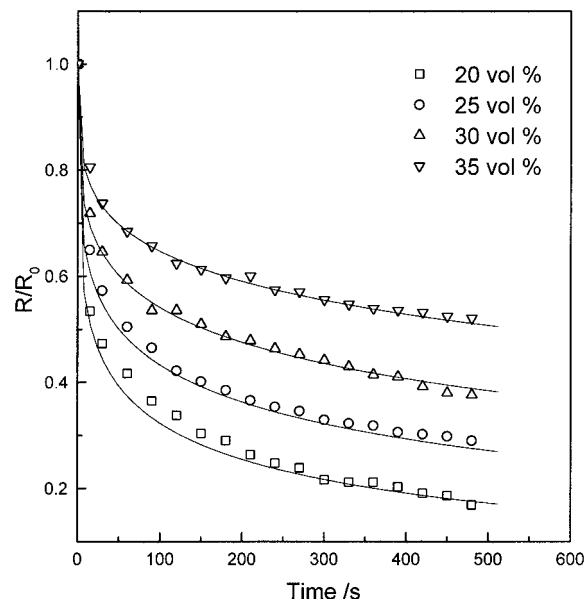

Figure 7. Time dependence of piezoresistance for the samples of Sn–Pb/PE with various filler volume fractions. Full lines are the theoretical data.

formation of the polymer matrix, which results in the larger change of interparticle separation [see eq. (10)]. As the interparticle separation change is the basic reason of the piezoresistance, the decrement of relative resistance is larger under the higher stress.

The relative resistance of the samples of Sn–Pb/PE with various filler volume fractions is plotted in Figure 7 as a function of time under the stress of 38.2 MPa. It can be seen that the relative resistance decreases slower for the samples with higher filler volume fractions. As shown in Table V, the original interparticle separation (s_0) decreases with the increasing θ. Therefore, the interparticle separation change (s_0–s) also decreases with the increasing θ [see eq. (6)]. As the R/R_0 rises by the separation change between the adjacent particles in composites [see eq. (4)], the R/R_0 then decreases slower at higher θ. This is the mechanism of the influence of θ on the time-dependence curve of the piezoresistance. The theoretical data of Sn–Pb/PE with various filler volume fractions are shown in Figure 7, displaying a fair agreement with the experimental data.

Figure 8 shows the time dependence of piezoresistance of two different Sn–Pb/PE samples ($\theta = 30\%$) under the stress of 38.2 Mpa. The difference is that the filler particle diameter of one sample is 0.1 μm and that of another one is 0.5 μm. As shown in Figure 8, the relative resistance

of the sample with large filler particles decreases sharply with time at the starting period of test, and then tends to become a relatively fixed value. The change tendency of the R/R_0 for the sample with small filler particles is similar, but the decrease is not as sharp as the first sample. Table V
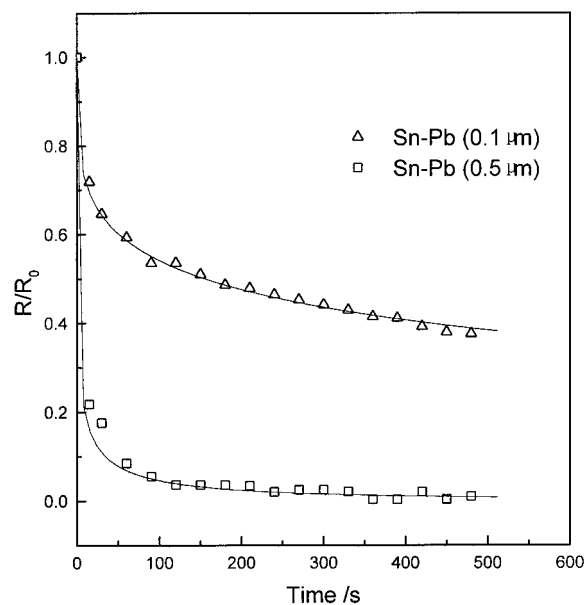

Figure 8. Time dependence of piezoresistance for the samples ($\theta = 30\%$) of Sn–Pb/PE with different filler particle diameters. Full lines are the theoretical data.
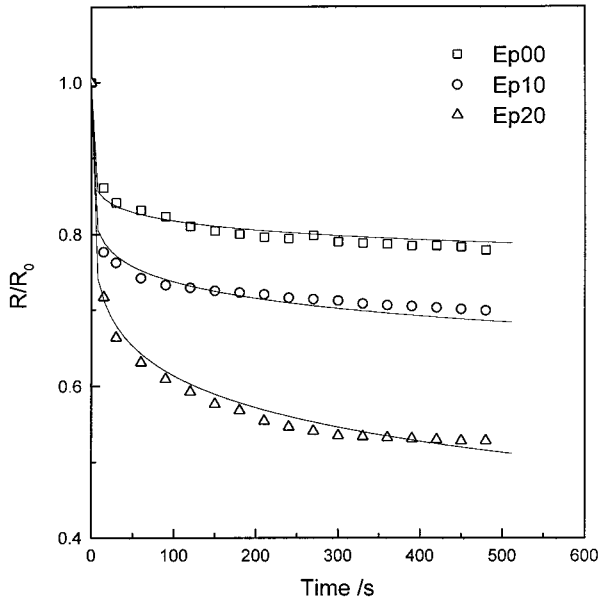
Figure 9. Time dependence of piezoresistance for the samples ($\theta = 30\%$) of Sn–Pb/epoxy00, Sn-Pb/epoxy10, and Sn-Pb/epoxy20. Full lines are the theoretical data.

shows that the sample with smaller filler particles has a less interparticle separation (20.4 nm) than that with larger particles (101.9 nm), which is similar to the case of the sample with higher filler volume fraction. As a result, the mechanism of influence of particle diameter on the time dependence of piezoresistance is similar to that of the influence of the filler volume fraction. The theoretical data obtained from eq. (11) are shown in Figure 8, and good agreement with the experimental data is also obtained.

The influences of σ, θ, and D on the time dependence of piezoresistance have been discussed above. As it is hard to find samples with different ϕ but the same other parameters, the influence of ϕ is not discussed in this article. Then the last influence factor, the polymer creep behavior (ϵ_0, ψ, and n), is investigated below. Figure 9 shows the time dependence of piezoresistance for three different Sn–Pb/epoxy samples with the same filler volume fraction of 30% under the stress of 38.2 MPa. The decrease of relative resistance becomes larger from epoxy00, epoxy10 to epoxy20. As shown in Figure 4, the deformation of epoxy becomes larger from epoxy00, epoxy10 to epoxy20 as the amount of additive added increases, the values of ϵ_0, ψ, and n in Table IV also increase. As the larger deformation of polymer matrix means a larger change of interparticle separation, the larger change of R/R_0 is gained when the epoxy

matrix composites are added with more additives. Again, the theoretical data by eq. (11) are shown in Figure 9, and agree with the experimental data fairly well. All the experimental and theoretical results mentioned above demonstrate the validity and reliability of our model.

SUMMARY

The piezoresistance and its time dependence of the electrically conducting composites composed of a conducting filler into an insulating polymer matrix have been investigated. To reveal the origin of the time dependence of piezoresistance, the creep of polymer matrix was studied also. It was found that the relative resistance decreases with an increase of applied stress. This process is affected by the applied stress, filler particle diameter, filler volume fraction, matrix compressive modulus, and potential barrier height. The deformation of polymer matrix under a fixed stress increases with the time, which is the basic reason of time dependence of piezoresistance. The results show that the increases of applied stress, filler particle diameter, and polymer matrix creep enhance the time dependence of piezoresistance, while the increase of filler volume fraction weakens it.

A model based on the interparticle separation change under the applied stress has been developed to interpret the piezoresistance and its time dependence. The theoretical data obtained from the model are found to agree with the experimental ones fairly well. By analyzing this model, it is concluded that the piezoresistance of composites is aroused by the separation change between the surface of adjacent particles, which is caused by the difference between the filler and matrix compressibilities. The time dependence of piezoresistance is aroused by the farther change of separation with time under the fixed stress, which is caused by the creep of polymer matrix.

The influences of applied stress, filler volume fraction, filler particle diameter, and polymer creep behavior on the time dependence of piezoresistance have also been discussed with this model. It was found that all these parameters influence the time dependence of piezoresistance by altering the change process of interparticle separation. Therefore, to decrease the time dependence of piezoresistance, which is important to improve the reproducibility and stability of piezoresistance, the change process of interparticle

separation should be controlled. Less stress, filler particle diameter, polymer matrix creep, and larger filler volume fraction are all the effective methods to decrease the time dependence of piezoresistance. However, as the resistance and piezoresistance of composites are also affected by these factors, syntheses of these two aspects would be taken and may be published in the future.

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