Time dependence of electrical resistivity under uniaxial pressures for carbon black/polymer composites

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In the past several years, some composites containing dispersed conducting particles in an insulating polymer matrix have been studied for applications such as thermistor and pressure sensors [1–3]. The electrical resistivity of such a composite critically depends on the volume fraction of the conducting filler particles, which is well explained by the percolation theory [4]. For a composite near the critical threshold, we would expect to see a negative piezoresistive effect, below a critical pressure, as well as a positive temperature coefficient (PTC) effect, which has been already utilized for thermistors such as self-regulating heaters and overcurrent protection devices [5–7]. Recently, the time-dependent elastic properties of composites containing randomly dispersed particles in a polymer matrix have been widely studied [8, 9]. However, in the process of investigation, we found that the resistivity of carbon particles/polymer composites would decrease with time under an invariant uniaxial pressure, which is similar to a "resistivity creep" behavior. So, attention has been paid to this phenomenon in this paper.

Room temperature vulcanized (RTV) liquid silicone rubber (SR, QD231, Beijing Chem. Plant, China) was used as a polymer matrix in our experiment. Conductive carbon black (CB) powder with an average particle size 6 μm (SL10, Carbon Black R&D Institute, China) was dispersed, ranging in volume between 30 and 40%. Hexane was used as solvent to mix the fillers with the rubber. Mechanical stirring along with ultrasonic vibration was also used for better particle dispersion. After 4 hr of vigorous mixing, the solvent was evaporated by vacuum evaporator. The viscous mixture was molded into disks ($\Phi 6$ mm × 2 mm) at 45 °C for 16 hr. The compression apparatus used for measuring the resistance change with uniaxial pressure is described in Fig. 1. Two steel plates contacting the samples were used as electrodes. In some cases, pressure was applied in a direction parallel to the electrical current flow. The resistance was measured directly using a HP-3458A digital multimeter at room temperature. The compression deformations of the samples were obtained by measuring the displacement of the upper steel plate, using a digital dial indicator. A computer that had interfaces with the multimeter and dial indicator was used to record the data at preconcerted times. All the results reported here were obtained from fresh samples, i.e., samples exposed to the mechanical field first.

Fig. 2 shows the change of resistivity during a loading cycle under uniaxial pressure for CB (30 vol%) filled composite. When load is exerted, resistivity decreases with pressure, showing piezoresistivity. This piezoresistive effect can be illustrated as follows. The conducting filler particles are essentially not in contact in the composite just before the critical threshold, giving a high resistivity. As stress is applied on the composite, the elastic polymer matrix deforms to the extent that conducting filler particles are forced closer together to form conduction paths, resulting in reduction of resistivity.

The time dependence of resistivity and strain under 0.5 MPa and 1 MPa pressures is shown in Fig. 3. There exists molecular motion of the polymer matrix under uniaxial pressure, which results in strain creep behavior in the composite. Strain creep may gradually reduce the distance between adjacent fillers and the orientation of conductive paths along the stress direction. Then, the resistivity decreases with time under an invariant load, showing "resistivity creep" behavior. Although Qiang et al. have found this phenomenon, accurate data were first experimentally observed by the authors, in SR/CB composites.

Note that there exists a retardation time lag between resistivity creep (t_S) and strain creep (t_R) as shown in Fig. 3a and b. With the strain increasing, the CB conductive particles are forced closer together, forming a continuous conductive path, subsequently increasing the conductivity. However, the continuous conductive path forms not only because of direct contact between the filler particles dispersed in the rubber matrix, but is also because of it being easier for electrons to jump across the gap (tunnel effect) when the interparticle distances are reduced to a few nanometers. When the change of strain becomes stable, the movement of the conductive particles continues for a period of time. Although the fillers cannot contact with each other directly, the threshold value for the interparticle gap may be reached, so the resistivity of the composite still decreases. The retardation time of the resistivity creep is about double of that of the strain creep.

Fig. 4 shows resistivity creep of composites with different volume fractions of CB fillers. The mixture rule [10] shows the upper and lower limits of the viscoelastic properties of a two-phase system. The upper and lower bounds are calculated from Equations 1 and 2 as

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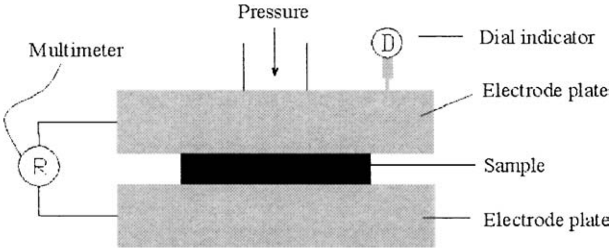

Figure 1 Scheme of resistance measurement under uniaxial pressure.

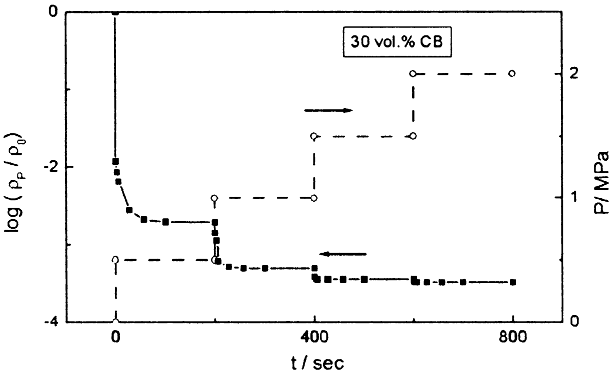

Figure 2 Change of resistivity (■) under various pressures (○) for the composite (CB, 30 vol%).

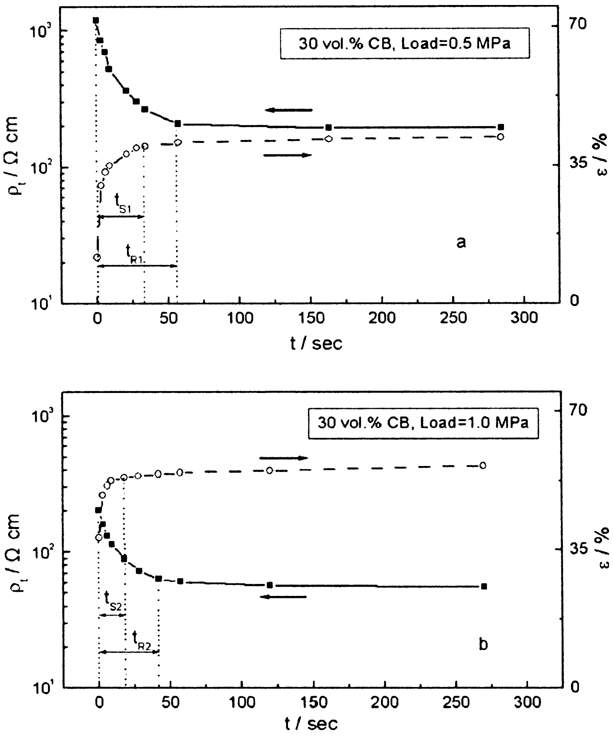

Figure 3 Time dependence of resistivity (■) and strain (○) under invariant pressures.

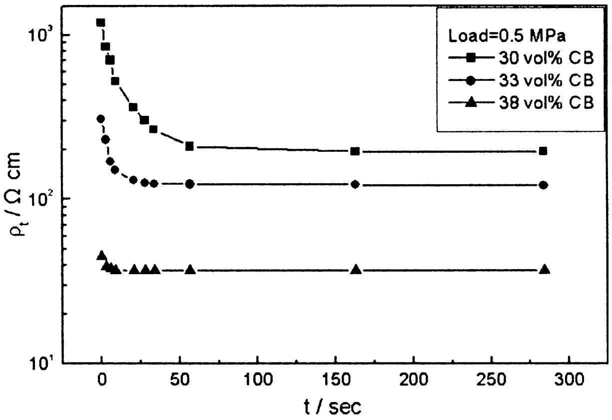

Figure 4 Resistivity creep of composites filled by 30 vol% (■), 33 vol% (●) and 38 vol% (▲) CB.

the series and parallel models, respectively:

$$E_c = E_f v_f + E_m v_m \tag{1}$$

$$E_c = \left(\frac{v_f}{E_f} + \frac{v_m}{E_m}\right)^{-1} \tag{2}$$

where E_c, E_f, and E_m represent viscoelastic moduli for composite, filler, and matrix, while v_f and v_m are the volume fractions of filler and matrix, respectively. As is well known, the retardation time of CB is far less than that of polymers under the same pressure. Thus, increasing the volume fraction of CB may reduce the retardation time of the SR/CB composite. This predication is consistent with experimental data in Fig. 4. However, according to the percolation theory and general effective media equation [11], the piezoresistivity of the composite can be affected by the increase of the CB fraction.

To overcome the resistivity creep independently, we succeeded to disperse 1.0–2.0 vol% of nano-sized SiO_x (20–30 nm) fillers prepared by vapor phase process into the rubber composite. The experimental results observed are shown in Fig. 5. This suggests that the presence of nano-sized SiO_x controlled the microstructure and physical properties of the composites. On the surface of SiO_x particles, there exists abundant under-stable Si—O structure because the oxygen atoms run out. The value of x is in the range of 1.2–1.6. In the process of vulcanization, the Si—O—Si bond, as shown in Fig. 6, may be formed from the dealcoholization

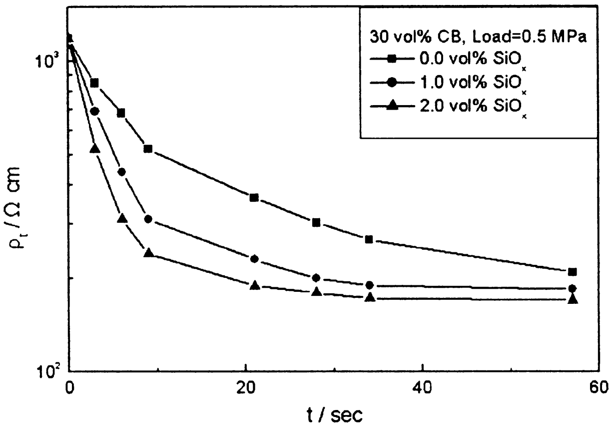

Figure 5 Resistivity creep of composites filled by 0 vol% (■), 0.5 vol% (●) and 1.0 vol% (▲) SiO_x.

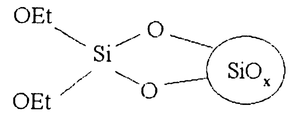

Figure 6 Chemical bonds between vulcanizator and SiO_x.

reaction taking place between vulcanizator and SiO_x. This chemical bond structure can make cross-linked action more sufficient for the silicone rubber. Moreover, nano-sized SiO_x particles can adsorb near the silicone rubber molecules because of their high surface energy and binding energy. And then, nano-sized SiO_x acts as a kind of strengthening filler, which may not only form the effective chemical bonds but also result in physical sorption. In the experiment, mechanical properties of these composites were found to be improved significantly, which would overcome the resistivity creep effectively. It was found that nano-sized SiO_x fillers could also improve the piezoresistivity of the composite. The in-depth research for the effect of nano-sized SiO_x fillers in the piezoreisitive composites will be published shortly.

In conclusion, the time dependence of resistivity is mainly due to the viscoelastic properties of the polymer matrix for the piezoreisitive composites filled by CB. However, the retardation time of the resistivity creep is longer because of the electron tunnelling effect. Although increasing the CB fraction can reduce the retardation time of resistivity, the piezoresistivity of the composites is also weakened to a certain extent. As a result of these experiments, a novel route has been developed to overcome resistivity creep by dispersing homogeneously nano-sized SiO_x fillers into the composites.

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