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Effect of elongation on electric resistance of carbon–polymer systems [I]

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Abstract

Effects of elongation on the electric resistance of graphite–EVA(ethylene-acetate copolymer) systems were studied. It was found that a linear relation holds between the logarithm of electric resistance and elongation. We have made a simulation with tunneling junction-model. Namely, we have assumed that the system consists of many tunneling junctions which form series and parallel circuits through the system and that widths of tunneling potentials proportionally increase with elongation. The result of the simulation agrees with experiment: a linear relation holds between the logarithm of electric resistance and elongation. This implies that tunneling conduction plays an important role in carbon–polymer systems. However this result raises a new problem on the mechanism of switching which was thought to have been solved already.

Keywords: Elongation; Electric resistance; EVA(ethlene-acetate copolymer)

1. Introduction

It is known that crystalline polymer–carbon composites show switching behavior, namely their electric resistances are lower at lower temperatures but increase abruptly from certain temperatures (switching temperature). Ohe et al. have reported earlier the graphite–polyethylene–wax composite as a switching system and they ascribed the mechanism of switching not to thermal expansion of the bulk but to a small displacement of graphite grains [1]. Subsequently, Buche has reported switching systems and he has suggested that the mechanism of switching could be thermal expansion of the bulk polymer [2,3]. Since then ''thermal volume expansion'' seems to be believed as the mechanism of switching, although Meyer has raised a question about this [4]. On the other hand, an exceptional system has been reported where the mechanism of switching is neither thermal expansion nor tunneling [5–7]. However, the importance of the tunneling effect in carbon–polymer systems has been clearly demonstrated by Miyauchi et al. [8]. Unfortunately, in Ref. [8], no mechanism is described concerning switching.

Experimentally it is well known that crystalline polymers show switching when dispersed with carbon but that amorphous polymers do not. Thus, quick change in the density at the melting temperature seems necessary for switching. This seems to favor ''thermal expansion'' for the mechanism of switching. Therefore it would be interesting to see whether mechanical expansion could cause change in electric resistance as is seen in the case of thermal expansion. Unfortunately, no trial has been made hitherto to investigate the relation between the expansion and electric resistance. We will report here the relation between the elongation and electric resistance of a carbon–polymer system. The purpose of this research is not only to clarify the mechanism of the switching but also try to make strain sensors which can be applied to steel frames in buildings, ships, ''mega-floats'' and so on.

2. Experimental

2.1. Materials

Graphite (GC) was J-SP from Nihon Koku-en (average particle size 6 mm). Ethylene-vinyl acetate copolymer (EVA, polyethylene: 80%) from Toso was used.

2.2. Sample preparation

EVA was dissolved in toluene, mixed with the desired amount of graphite, and toluene was evaporated. This

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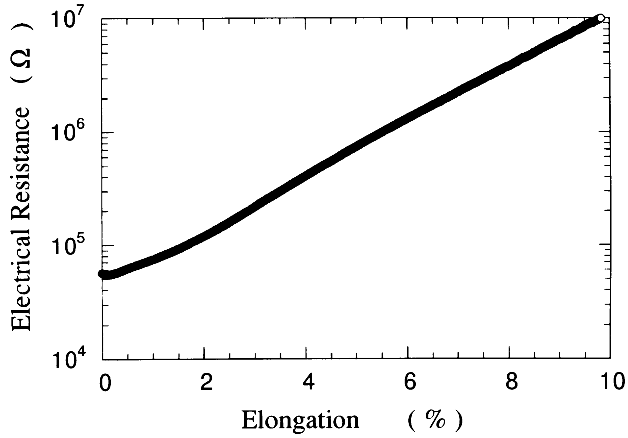

Fig. 1. Logarithm of electric resistance vs. elongation in the 30 wt% GC–EVA system.

composite was subjected to hot press and a sheet (100 × 100 × 1.5 mm) of the composite was obtained. Samples were obtained from this sheet by cutting into a dumbell shape and painting both ends with silver paint (Dodite D-551, Fujikura Kasei) as electrodes. The center part of the samples which were subjected to elongation was 10 mm in width and 25 mm in length.

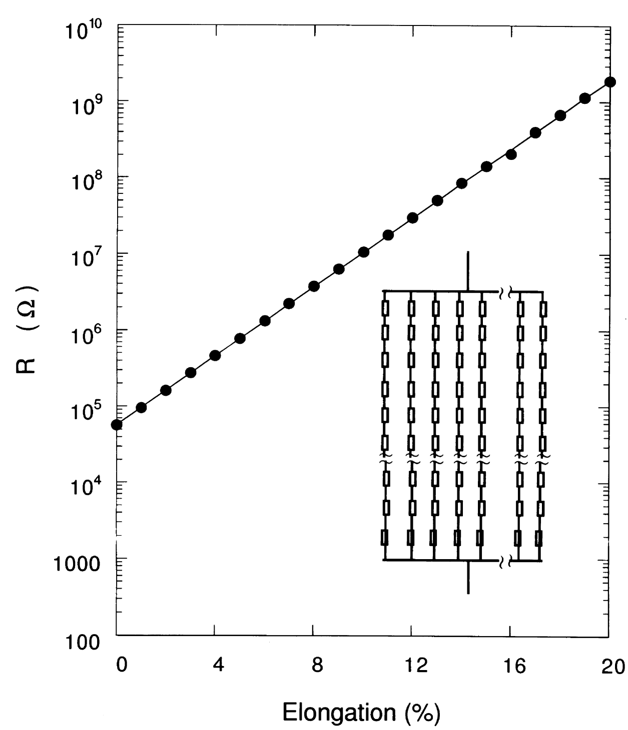

Fig. 2. The calculated value of the logarithm of electric resistance vs. elongation. The number of parallel circuits (*N*) and junctions in a series circuit (*M*) are 100 and 20, respectively. The values of standard deviations, σ_p and σ_{si}, are 0.2μ and $0.1\mu_{pi}$, respectively. The inset shows the equivalent circuit, where –□– shows a tunneling junction.

2.3. Measurement of elongation and electric resistance

Apparatus for the measurement of elongation and electric resistance was order-made (hardware: Kawachi Tekkou, Kasugai; software: Step-One, Nagoya). Elongation power was generated by a pulse motor which was computer-controlled. Elongation was measured by a digital gauge (LY41, Sony) with a sensor (DE30R). Electric resistance was measured by a digital multimeter (Advantest R6452A). Both signals from the gauge and the multimeter were taken simultaneously into a computer (NEC PC-9821 V16). Precision of elongation was 1 μm and the speed of elongation was 3 μm/s.

3. Results and discussion

Fig. 1 shows logarithm of electric resistance as a function of elongation in the 30 wt% GC–EVA system. As is shown in Fig. 1, a linearity is seen in the relation between the logarithm of the electric resistance and the elongation. In order to explain this relation, a theory of tunneling effect can be applicable. Simmons [9] has derived an equation of tunneling current density at the low voltage region as,

$$J = [3(2m\varphi)^{1/2}/2s](e/h)^2 V\cdot\exp[-(4\pi s/h)(2m\varphi)^{1/2}] \quad (1)$$

where m, e and h are the electron mass, charge on an electron and Planck's constant, respectively, and φ, s, V are the height of tunnel potential barrier, the barrier width and the voltage applied across the barrier, respectively. From Eq. (1) resistivity can be derived and the logarithm of the resistivity (ρ) is expressed as a function of the width of the tunneling barrier (s) as,

$$\log(\rho) = (4\pi/h)(2m\varphi)^{1/2}s - \log[\{3(2m\varphi)^{1/2}/2\}(e/h)^2] \quad (2)$$

This shows that the logarithm of the resistivity of tunneling junction is a linear function of the potential width. If a sample is composed of a single tunneling junction and the potential width of the junction increases proportionally with elongation, then the relation between the logarithm of the resistivity and the elongation is linear. However, since an enormous number of carbon grains are dispersed in a sample, there exist many tunneling junctions composed of gaps between GC grains. In order to see whether the linearity between the logarithm of resistance and elongation as shown in Fig. 1 is explicable by the tunneling mechanism, a simulation was performed taking many tunneling junctions into consideration.

As a first step we have used a series circuit model where the sample was expressed as a single circuit of series tunneling junctions. Then the resistance of the series circuit was calculated as a function of elongation of tunneling widths, assuming that widths of potential barriers increase proportionally with elongation. Since GC grains are randomly dispersed in a sample, it would be better to consider some distribution for grain gaps, namely widths of tunneling potential barriers. A Gaussian function was used for the distribution of potential widths of tunneling barriers. Namely, expressing the number of tunneling junctions as N_s, the distribution of the potential widths (x_1, x_2, …, x_n) can be expressed by a Gaussian function with the mean value (μ) and the standard deviation (σ_s). Values of N_s and σ_s are set as parameters then the value of μ was selected in order to obtain the best fit between the calculation and the experiment, where the ratio of the resistance without elongation (R_o) to that with 10% elongation (R_{10}) was calculated and compared with the experimental value, which was obtained from Fig. 1 to be 5.1754×10^{-3}. Calculation was performed using several values for N_s and σ_s. In every case it was found that linearity holds between the logarithm of resistance and the elongation. It was also found that only a very few numbers of junctions of the distribution edge (the narrowest width edge) determine the resistance of the series circuit. This fact lead us to the next step.

The series circuit described above is inadequate to express the real sample. Therefore a parallel equivalent circuit is used. This is shown as an inset to Fig. 2. A contradiction may be raised that junctions must be combined horizontally across parallel circuit to form a check (or grid) pattern. We think this is not necessary: In a grid circuit, a net horizontal current is zero. Thus, microscopically, a path of current could be a dendrite (tree) shape or a combination of those. From the view point of an electric circuit a circuit of dendrite shape can be expressed as a parallel circuit. Another contradiction may be that an equivalent circuit should be three dimensional. However, a three dimensional parallel circuit can be expressed by a combination of two dimensional circuits. From the view point of an electric circuit, both are the same. Therefore the parallel circuit shown in Fig. 2 could be used for the present purpose. The important point is that a diversity of potential widths must be fully taken into account.

In order to take the diversity of potential widths of tunneling junctions, the equivalent circuit shown in Fig. 2 was used, where series circuits, numbered as 1, 2, …, i, …, and N_p, are connected in parallel. Each circuit consists of N_s junctions connected in series. Now let the mean potential width through the system be μ and the mean potential width in ith circuit be μ_i, where i is 1, 2, …, N_p. Namely, the mean value for μ_1, μ_2, …, and μ_{Np} is μ. Let the standard deviation for μ_1, μ_2, …, and μ_{Np} be σ_p. We set the values of μ_1, μ_2, …, and μ_{Np} as $\mu - 3\sigma_p$, $\mu - 3\sigma_p + (6\sigma_p/N_p)$, $\mu - 3 + 2(6\sigma_p/N_p)$, …, $\mu - 3 + (i-1)\cdot(6\sigma_p/N_p)$, …, and $\mu + 3\sigma_p$, respectively. This means that the mean values of parallel circuits distribute from $\mu - 3\sigma_p$ to $\mu + 3\sigma_p$ depending on Gaussian. Now let potential widths of ith series circuit be x_{i1}, x_{i2}, …, x_{ij}, …, and x_{iNs}, respectively. Since the mean value for x_{i1}, x_{i2}, …, x_{ij}, and x_{iNs} is μ_i, these potential widths are set to be $\mu_i - \sigma_{si}$, $\mu_i - \sigma_{si} + (2\sigma_{si}/N_s)$,…, $\mu_i - \sigma s_i + (j-1)\cdot(2\sigma_{si},/N_s)$, …, and $\mu_i + \sigma_{si}$, respectively, where σ_{si} is the standard deviation of potential widths in the ith circuit. By the procedure described above the diversity of potential widths of tunneling junctions is satisfied.

The conductivity of ith parallel circuit (Y_i) is given as follows,

$$Y_i = \Sigma[(A/\sigma_s)\exp[-(\mu_i - x_{ij})^2/2\sigma_{si}^2]\exp\{-(4\pi\mu_{sj}/h) \times (2m\varphi)^{1/2}\}] \quad (3)$$

where φ is assumed to be 5 eV and A is a constant, which disappears in the final stage. The net conductance (Y_{tot}) is given from the summation of Eq. (3).

$$Y_{tot} = \sum[1/\{(2\pi)^{1/2}\sigma_p\}]\exp[-(\mu - \mu_i)^2/2\sigma_p^2]Y_i \quad (4)$$

In both equations Gaussian distribution is taken into account.

The simulation was carried out as follows. Instead of the conductance in Eq. (4), the ratio of the resistance without elongation to that with 10% elongation was concerned. The resistance without elongation $(R_o)_{calc}$ is given by the inverse of Eq. (4). The resistance of 10% elongation $(R_{0.1})_{calc}$ is given by the same procedure by multiplying, μ, σ_{si} and σ_p by 1.1. In the calculation, σ_{si} and σ_p are given by $\sigma_{si} = f_s\mu_i$ and $\sigma_p = f_p\mu$. We set values of N_s, N_p, f_s and f_p as parameters. Then μ is the only unknown value in Eq. (4). Therefore the ratio, $\gamma_{calc} = [(R)_0/(R)_{0.1}]_{calc}$, includes only one unknown value of μ. Thus, μ can be obtained by solving the equation below, where the left side of Eq. (5) is the experimental value, $\gamma_{expl} = 5.1754 \times 10^{-3}$ as described already.

$$[R_o/R_{0.1}]_{calc} = 5.1754 \times 10^{-3} \quad (5)$$

The solution was obtained by computational work. In this calculation $|(\gamma_{calc} - \gamma_{expl})/\gamma_{expl}|$ was less than 10^{-15}, which means that Eq. (5) is actually satisfied. Using the selected μ electric resistances are calculated as a function of elongation. One of the results is shown in Fig. 2 where numbers of tunneling junctions (N_s and N_p) are 20 and 100, respectively, and standard deviations, σ_p and σ_{si}, are 0.2μ and $0.1\mu_{pi}$, respectively. As is seen in Fig. 2, the linear relation holds between the logarithm of electric resistance and elongation in the equivalent circuit which consists of many tunneling junctions. The calculations were performed using various values of N_s, N_p, f_p and f_{si}. In all cases the linear relation between logarithm of electric resistance and elongation was always obtained.

The detail of the calculation was reviewed. It was found that in a circuit, which consists of barriers connected in series, barriers with widths which are close to the widest determine the electric resistance of the series circuit and that parallel circuits of which mean barrier widths are close to the minimum determine the electric resistance of the total system. In the calculation in Fig. 2 the mean potential width in the system (μ) was obtained to be 5.4 nm. However, it was found that junctions with the barrier width of ~ 2 nm actually determine the electric resistance of the system. Calculation was done using various values of σ_p (f_p).

Although μ changes depending on σ_p, barrier widths responsible for the electric resistance of the system are always ~ 2 nm. This implies that tunneling barrier widths which determine the electric resistance of the present system could be ~ 2 nm. This corresponds to the values suggested by Ohe (0.5–2.5 nm) [1].

As is described already, in an equivalent circuit as shown in Fig. 2 parallel circuits of which resistances are close to the minimum actually determine the resistance of the total system. Electric current flows through paths of low resistance (narrow potential width). At the same time, the resistance of a single path composed of series electric resistances is determined by high resistance (wide potential width). This means that potential widths (gaps between carbon particles) which determine the resistance of the total system are far from the mean value. Namely, in the Gaussian distribution curve, only the edge part contributes to the electric conduction and the main part around the mean value does not. This indicates that the electric resistance of such systems cannot be discussed from a view point of ''average''. Generally it is frequently noticed that a property of a material system reflects mean values of components. If a property of a system is related directly to a mean value of components, the determination of parameters, μ and σ, would be useful and meaningful. Unfortunately, in the present case it would be difficult to obtain values of μ and σ for gaps between particles, although it is possible to obtain μ and σ for particle sizes. However, in the present situation μ does not seem important for electric conduction. The purpose of the calculation described above is to demonstrate that a linearity holds between the logarithm of the electric resistance and the elongation. The linearity was confirmed for systems with variety of σ.

In the case of thermal expansion, it is reported that a linear relation holds between the logarithm of electric resistance and the increment of the volume [10]. This seems similar to our results. We have also measured the electric resistance of 30 wt% GC–EVA systems as a function of temperature and found the ratio of the electric resistances at the switching temperatures to that at room temperature was 3.84×10^5. Volume expansion at the switching temperature could be at most $\sim 20\%$ which results in linear expansion of 6–7%. However, the ratio of electric resistances at 7% and 0% expansion is obtained from Fig. 1 to be 43. So the difference between thermal and mechanical expansion is about four orders of magnitude. As is described already, in an earlier stage thermal expansion was rejected [1] or thought to be suspicious for the mechanism of switching [4]. The difference in electric resistance ratios between thermal and mechanical expansion raises here a new problem. The mechanism of switching may not be thermal expansion. Or, all gaps between GC grains may not expand proportionally with elongation. At present, no answer is available on these points. Further studies are necessary to clarify these.

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