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Electrical properties of epoxy resin filled with carbon fibers

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The electrical properties of an epoxy resin filled with carbon fibers were studied. By discharging a high voltage through the composite it was found that the resistivity of the composite decreased. This effect was attributed to local dielectric breakdown of polymer layer between carbon fibers. The conduction mechanism of common and breakdown composites was studied by means of exploring of current-voltage characteristics and the frequency dependence of resistivity. A positive temperature coefficient (PTC) effect of resistivity behavior was observed both for common and breakdown samples. © *1999 Kluwer Academic Publishers*

1. Introduction

The electrical resistivity of polymer composites filled with carbon black (CB) or carbon fibers (CF) strongly depends on the filler content. Composite resistivity practically coincides with that of the polymer matrix at low concentrations of the filler. A sharp drop of resistivity occurs at some critical filler content and then the composite resistivity value strives toward that of the filler. This phenomenon can be explained in terms of the percolation theory as follows. Conductive particles agglomerate in the composite as clusters. As the size and number of the clusters increases with increasing filler content, at some critical content, that is called the percolation threshold, the cluster becomes infinite and the material becomes conductive. There are a few models that predict resistivity (or conductivity) behavior based upon filler content [1–3]. Most of them try to evaluate a fraction of filler which is involved in the infinite cluster and consequently makes a contribution to the composite conductivity.

One of the main features of composites filled with CB is that the agglomerates of particles in the infinite cluster are still separated by thin gaps of a polymer layer. It results in a variety of conduction mechanisms in such composites: tunneling, usually enhanced by thermal fluctuations of local field; dielectric breakdown, with significant increase of local temperature; internal field emission; overlap of wave functions, giving high conductivity across the gap; and graphitic conductance [4]. Variation of the filler content can also change a conduction mechanism within the infinite cluster of conductive particles. Because of this the former three mechanisms usually take place in composites with moderate filler content and the later two mechanisms in highly loaded composites.

Apart from the filler content there are other factors that can determine which mechanism will play a dominant role; primarily: size and shape of filler; temperature; and strength and frequency of an electrical field. A variation of any of these factors helps to reveal the mechanism governing the conductance within the composite under consideration. For instance, investigation of the current-voltage characteristics is widely employed for exploring of conduction mechanisms.

In the present work, the conduction mechanism of a composite consisting of an epoxy resin as a matrix and short carbon fibers as a conductive filler was studied by investigating current-voltage characteristics and resistivity dependence on the frequency of electrical field. Applying a high voltage was found to decrease irreversibly the resistivity of the composites studied. This effect was attributed to the dielectric breakdown in polymer layer between CF at the place of a contact. The conduction mechanism of the common samples was studied in comparison with that of breakdown samples.

2. Experimental

2.1. Composite preparation

Epoxy resin ACR R-1415 from Shinnittetsu Corporation was used in the study. The glass transition temperature of the fully cured epoxy resin (T_g^∞) was 100 ± 2 °C, as measured by DSC. It is worth noting that the resistivity of the epoxy resin cured without CF has a temperature dependence. Below the glass transition temperature it was constant and rather high. Above T_g^∞, the resistivity gradually decreases. Short carbon fibers (SCF) KUREHA M101 were used as a conductive filler. The fibers had an average length of 60 μm and diameter of 16 μm. The carbon fibers were degassed under vacuum for one hour at 120 °C before mixing with the epoxy resin. The epoxy resin was heated to 90 °C and then mixed up with carbon fibers for 10 min by hand. After mixing, the liquid composition was degassed under a vacuum for 10 min at 90 °C in order to remove air bubbles. Then the liquid composition was poured between glass plates separated by a 1 mm gap, and cured by one of the following schedules:

1. Cure at 150 °C for 1 h.
2. Cure at 120 °C for 2 h followed by curing at 150 °C for 1 h.

Both cure schedules ensured complete curing of the epoxy matrix, as confirmed by DSC. Most of the data were obtained for composites cured by the first schedule. Composite sample sheets were 1 mm thick.

2.2. Electrical measurements

Specimens in the form of squares 20×20 mm^2 were cut from the composite sheets. At least three samples with a total number of specimens equaling 6 were utilized for measuring the current-voltage characteristics of each CF content studied. The specimen surfaces were covered by a silver paste in order to ensure a good electrical contact with the copper electrodes. A voltage was applied through the specimen thickness. The specimen with the attached copper electrodes was placed in a special chamber where temperature was controlled in accordance with a desired program. The heating rate during the electrical measurements was equal to 4 °C/min. Picoammeter 487 from Keithley Instruments, Inc. equipped with a variable voltage source was employed for the measurements. Direct current was used to measure current-voltage characteristics. The measurements were made with temperature intervals of 1 °C at several voltage values simultaneously. The voltage values were from 0.001 to 500 V.

In further discussion, terms "common" and "breakdown" samples will appear. A common sample is one that was prepared after a cure schedule. A breakdown sample is a common sample that was subjected to high voltage before making the electrical measurements. The high voltage was equal to 500 V, and it was applied to the sample for a very short period of time of less than one second.

The frequency dependence of the resistivity was obtained at room temperature by means of device 4192 LF Impedance Analyzer from Hewlett Packard.

3. Results and discussion

How applying a high voltage can irreversibly decrease resistivity will be discussed first. As was mentioned above, a polymer layer exists between filler particles and/or their agglomerates. Therefore an electrical current usually flows in the composite through the agglomerates separated by the polymer gaps. It should be noted that voltage across the gap is expected to be higher than the macroscopic voltage, V, by a factor, M, equal to the ratio of the average size of the conducting aggregate to the average gap width [5]. If the factor M or voltage V are large enough, dielectric breakdown can take place. This phenomenon was observed for polymer composites filled with carbon black [5, 6]. The average size of the conductive agglomerates in these composites was approximately 1 μm.

There is a distribution of the inter-fiber contacts by the gap width as was discussed in literature [7, 8]. Some of the fibers are in direct contact with each other whereas others are separated. "Direct contact" means that there are no polymer gaps between adjacent fibers. Because the fiber diameter is one order of magnitude greater than the agglomerate size in composites with CB, a larger voltage can exist across the gap in composites with CF. If this voltage is great enough it can result in local dielectric breakdown of the polymer layer in the gap. During dielectric breakdown, an irreversible damage in the form of carbonization of the polymer occurs which usually gives rise to the formation of a conducting pathway [9, 10]. It is interesting that the decrease in resistivity after the application of high voltage, was not observed for composite filled with Ketjen Black (KB) in our study. So, it is most possible that the large diameter of the fibers is the main reason why local dielectric breakdown takes place in composite with carbon fibers, but not so with KB.

Fig. 1 shows that the resistivity of the studied composites exhibits a percolation behavior with increasing CF content. Breakdown has little influence on the percolation threshold value. The threshold takes place at 5% of CF for breakdown samples and at 6% for the common ones. A difference in the resistivity values for these two samples, however, is rather significant just above threshold and gradually diminishes with increasing CF content. Such behavior can be explained qualitatively as follows: in composites with a high content of CF, most of the fibers are in direct contact with each other and, because of this, breakdown does not decrease the resistivity value significantly. In the composite with moderate CF content, breakdown is more effective since a lot of the fibers are separated and breakdown generates the contacts between them.

In order to clarify the type of the conduction mechanism, the current-voltage characteristics were studied

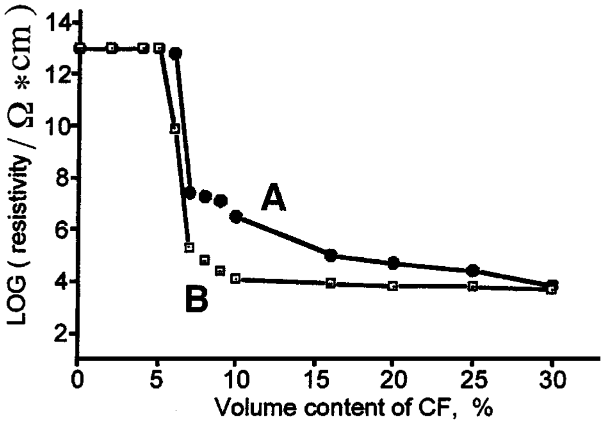
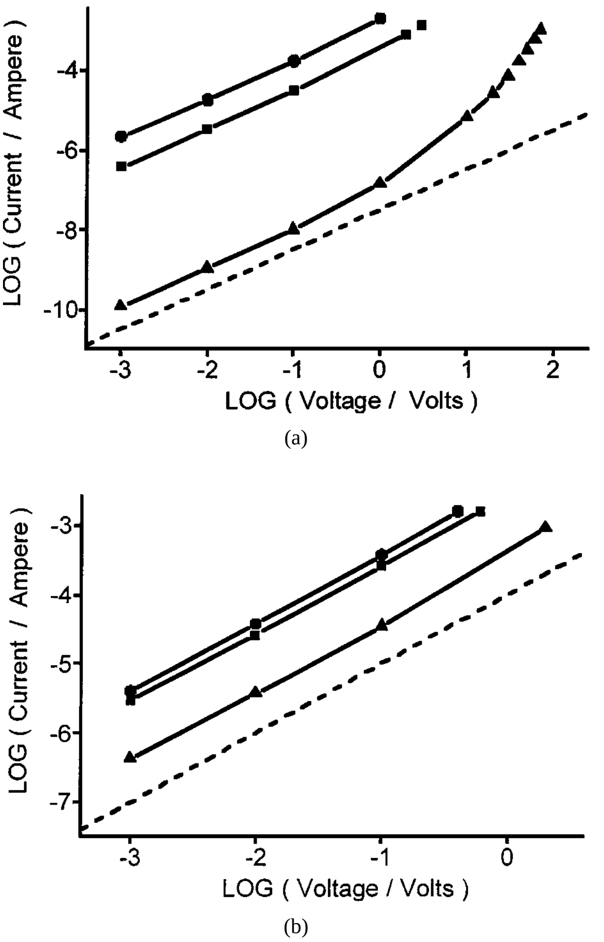


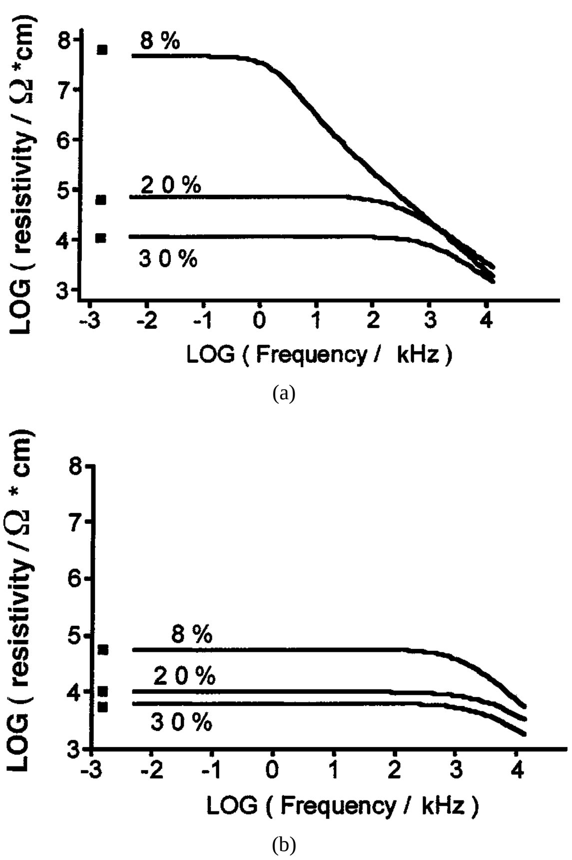
Figure 1 Dependence of direct current resistivity for common (A) and breakdown (B) samples on content of carbon fibers on semilog scale.



(a)

(b)

Figure 2 Current-voltage characteristics of (a) the common samples with different content of carbon fibers on log-log scale. Circles, 30% of CF, squares, 20%, triangles 8%. The dashed line indicates the slope expected for Ohm's law, (b) the breakdown samples with different content of carbon fibers on log-log scale. Circles, 30% of CF, squares, 20%, triangles, 8%. The dashed line indicates the slope expected for Ohm's law.



(a)

(b)

Figure 3 Dependencies of resistivity on the alternative current frequency of (a) the common samples with different content of carbon fibers on log-log scale. Black squares correspond to resistivity values of the same composites measured at direct current, (b) the breakdown samples with different content of carbon fibers on log-log scale. Black squares correspond to resistivity values of the same composites measured at direct current.

for the composites with different percent content of CF (Fig. 2). Ohmic behavior should be expected if the graphitic type of conductivity exists in the composite [4]. Only the common sample with eight percent of CF exhibited non-Ohmic behavior. So, only in this case is conductivity not graphitic. All other common and breakdown samples demonstrate Ohmic behavior. However, it is not possible to assert that in these samples graphitic-type conductivity is present since in some cases the resistivity of composites possessing the tunneling type of conductivity also obeys Ohm's law [4].

An investigation of the resistivity dependence on frequency can also help to clarify the conduction mechanism of the composite. If the conductive paths of the particles subsist in the composite little dependence of resistivity on frequency can be expected. On the other hand, if the agglomerates of CF are separated by gaps then the resistivity should depend on frequency [6, 11]. The former case is a typical one for composite with high loading of CF whereas the latter one is for composites with moderate content of CF.

Fig. 3a and b show that common samples demonstrate more pronounced dependence on frequency in comparison with the breakdown samples implying a non-graphitic mechanism of conduction. The resistivity of the breakdown samples also depends on frequency at high frequencies. It can be justified as even in the composites with high loadings of CF that there are contacts between fibers separated by gaps. These gaps make a contribution to the frequency dependence. Breakdown generates conductive paths between insulated fibers. However, all gaps can not be breakdown because of the existence of a limited size of the polymer layer thickness in the gap that can not be destroyed by a high

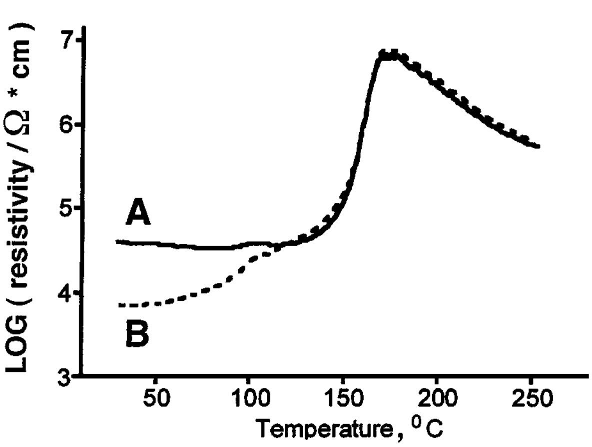
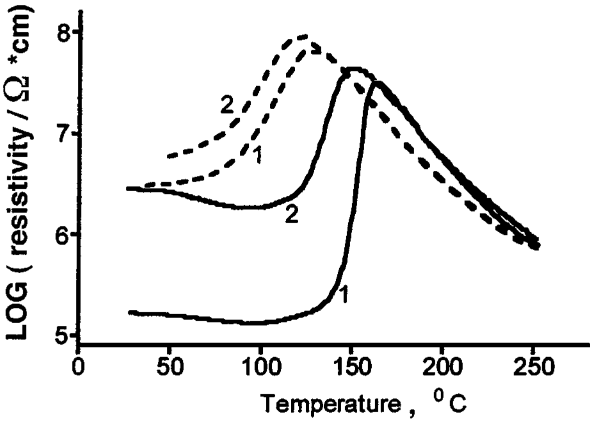
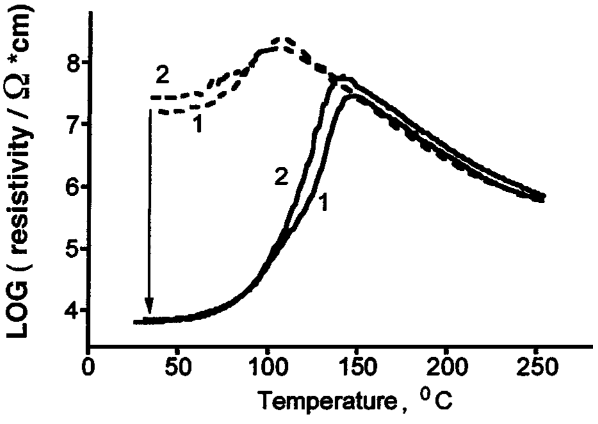


Figure 4 Logarithm of resistivity versus temperature for common (A) and breakdown (B) samples with 20% of carbon fibers. The composites were cured by the first cure schedule.



(a)



(b)

Figure 5 Logarithm of resistivity versus temperature for (a) common sample with 20% of carbon fibers through successive temperature runs. The composites were cured via the second cure schedule. Solid curves correspond to heating, dashed curves to cooling. Digits denote number of run, (b) breakdown sample with 20% of carbon fibers throughout successive temperature runs. The composite was cured by the second cure schedule. Solid curves correspond to heating, dashed curves to cooling. Digits denote number of run. A high voltage was also applied after the first run.

voltage. It is postulated that this is why the resistivity of all breakdown samples starts to diminish at the same value of frequency, about 10^3 kHz. In our opinion, this frequency should correspond to the limit size of the polymer layer thickness in the gap, which can not be breakdown by the particular high voltage value that we used.

The temperature dependence of resistivity is shown in Fig. 4. The resistivity of the common and breakdown samples exhibits positive temperature coefficient (PTC) behavior. Separation of CF with heating is the main reason of PTC effect [7]. Not all contacts are recovered during cooling, and resistivity values increases after temperature cycle (Fig. 5a). However breakdown can successfully be used both to decrease the initial value of resistivity at room temperature and to recover sample resistivity after temperature cycle (Fig. 5b).

4. Conclusions

Applying a high voltage was found to irreversibly decrease the resistivity of polymer composites filled with short carbon fibers. This effect was attributed to the formation of conductive pathways due to local dielectric breakdown at the place of inter-fiber contact. The tunneling mechanism of conduction can be unambiguously supposed only for common samples with a moderate content of carbon fibers. The common samples with a high content of CF, and all breakdown samples seem to conduct electrical current both through continuous paths of the fibers and through the paths with the gaps.

Breakdown does not influence the upper limit temperature of the PTC region, and can successfully be used to decrease initial value of resistivity at room temperature as well as to recover the sample resistivity after temperature cycle.

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