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Influence of the pressure-dependent contact area between electrode and composite surface on the electrical conductivity

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ABSTRACT

In this work, the influence of the pressure-dependent contact area between electrodes and surfaces of the composite samples on the electrical conductivity of polymer/carbon black composites was investigated. It was found that the electrical conductivity depended on the pressure (P) applied by the testing device and the carbon black concentration (ϕ). Meanwhile, the logarithm of electrical conductivity exhibited a linear relationship with $\phi^{-1/3}$ regardless of the pressures. Furthermore, it was found that the electrical conductivity σ showed a specific relationship ($\log\sigma(P) = kP^{-1} + \log b$) in the pressure range investigated regardless of the concentration. Based on this correlation, the maximum (true) electrical conductivity of the composite samples at a given concentration for infinite pressure can be revealed by extrapolation. Thus, a novel approach is given to eliminate strong variations in electrical conductivity measurements on composites due to imperfect contacts.

1. Introduction

The incorporation of conductive fillers, such as carbon black (CB), carbon fibers or carbon nanotube, into polymer matrix has the potential to create conductive polymer composites (CPCs) with enhanced thermal, electrical, and other physical properties [1–8]. The electrical conductivity of the CPCs has been well demonstrated a sharp increase at a critical volume fraction of the conductive filler, which is referred to as the electrical percolation threshold corresponding to the formation of a conductive filler network in the polymer host.

Up to now, various models have been proposed to describe the percolation phenomena at critical conductive filler levels and predict the electrical conductivity behavior of composites based on numerous factors [3–5,9–14]. The widely used theory includes the classical percolation theory and tunneling conduction theory. The classical percolation theory has been recognized both theoretically and experimentally, and a model that follows the power-law equation was proposed [9,10]:

$$\sigma = \sigma_o(\phi - \phi_c)^t \quad \text{for } \phi > \phi_c \tag{1}$$

where σ_o is the intrinsic conductivity of the filler, ϕ is the conductive filler concentration, ϕ_c is the critical concentration of fillers, i.e., percolation threshold and t represents the critical exponent which depends on the dimensionality of the percolated network. The following simple correlation of the tunneling conduction model was proposed [11–14]:

$$\sigma \propto \exp(-Ad) \tag{2}$$

In Eq. (2), A and d represent the tunnel parameter and tunnel distance, respectively. Herein, it is assumed that the distribution of conductive fillers in insulating polymer matrix is homogeneous, so the average tunnel distance d among conductive particles in the composites higher than the percolation threshold depends on the ϕ value with the relation:

$$d \propto \phi^{-1/3} \tag{3}$$

Thus, the value of $\log\sigma$ should be directly proportional to $\phi^{-1/3}$ as shown in Eq. (4):

$$\log\sigma \propto \phi^{-1/3} \tag{4}$$

The mechanism of electrical conduction in a composite is dependent on the formation of conductive network throughout the polymer matrix [15–17]. In CPCs, the total electrical resistance is a function of that through each conductive particle and the polymer matrix [15]. Accordingly, one assuming that the electrical resistance of the matrix is constant everywhere, and the electrical resistance of the conductive pathways perpendicular to the current flow is neglected [15]. Furthermore, since the electrical resistance of the conductive particle is very small in comparison with that

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of the polymer matrix, the electrical resistance across the conductive particle can be neglected. Accordingly, the total electrical resistance R can then be described as [15–17]:

$$R = \left\{ \sum_{j=1}^{m} \mu(j) \times \left[\sum_{i=1}^{n(j)} R_c(i,j) \right]^{-1} \right\}^{-1} \quad (5)$$

where n is the number of conductive particles forming one effective conductive pathway, m is the effective conductive pathways in a composite, $n(j)$ is the number of the conductive particle in the jth effective conductive pathways, $R_c(i,j)$ is the electrical resistance between the ith and $(i+1)$th conductive particle in the jth effective conductive pathway, $\mu(j)$ is the switch of the jth effective conductive pathway.

For the electrical resistance measurements, silver paste is commonly used and coated onto the surface of the composite samples for good contacts. The electrical properties measured from these experiments are integral values including contributions of all effective conductive pathways in the given composite [1–6]. However, on the one hand, the expensive silver paste will increase costs; on the other hand, as expected in Fig. 1(b), the surface of composite sample is usually rough. In our previous work [6–8], an electrode made from alumina foil and foamed rubber was used to measure the electrical resistance (Fig. 1(a)). In this device, a constant pressure P was used to minimize the contact resistance between the electrodes and surfaces of the sample. The materials of electrodes in our case are much cheaper than the silver paste and it could also successfully test the electrical resistance. The setup not only avoids the use of silver paste and destructive samples, but also reduces the cost. Nevertheless, a disadvantage of this setup is that, these electrodes can work only under a certain pressure.

Therefore, assuming that there is only partial contact between the electrode and the surface of the composite sample under a small pressure, and the contact area will increases as the pressure increases (Fig. 1(b)). Accordingly, based on Eq. (5), the electrical resistance $R(P)$ between electrodes under the pressure P can be described by:

$$R(P) = \{ m(P) \times [nR_c]^{-1} \}^{-1} \quad (6)$$

where $m(P)$ the number of effective conductive pathway at a given pressure P. Herein, the number of effective conductive pathway increases as the pressure increase due to the increase of contact area, leading to the decrease of electrical resistance. Thus, the electrical conductivity increases as the pressure increase. Accordingly, in this work, the influence of the pressure-dependent contact area between the electrode and composite surface on the electrical conductivity of polymethylmethacrylate (PMMA)/CB composites was investigated.

2. Experimental

2.1. Materials

The PMMA Plexiglas 7N used as the matrix material was from Evonik Röhm GmbH (Germany). The weight-average molar mass and polydispersity index are 92 kg/mol and 1.9, respectively. Carbon black (CB) as the conductive filler was Printex XE2 from Evonik. The specific surface area of CB is 900 m^2/g as measured by the BET-method.

2.2. Sample preparation

An internal mixer (Haake polyDrive, Thermo Scientific, Germany) was used to prepare the composites. The conditions are as follows: 200 °C for 2 min at 20 rpm for introduction of materials and then further 8 min at 60 rpm. Subsequently, the samples were compression molded to 2 mm thick disk-like plates with a diameter of 25 mm. Pre-heating at 200 °C for 5 min under vacuum, followed by hot pressing at 100 bars for 2 min and then quenched to room temperature for 10 min. The materials were dried at 80 °C under vacuum for at least 24 h before mixing in internal mixer and compression molding.

2.3. Electrical resistance measurements

A simple experimental setup was built in Erlangen and used for room temperature electrical resistance testing [6–8]. According to the schematic in Fig. 1(a), a foamed rubber which was covered with alumina foil was used to create a sufficient contact between the electrodes and the surfaces of the sample. The sample with two electrodes is placed between the stainless steels and then compressed from the zero-pressure to a certain pressure. The pressure values were recorded by an ohm gauge and then calibrated by a tensile testing machine Zwick Z050. In this study, the pressure range was between 2.0 MPa and 5.1 MPa. The pure PMMA has a Young's modulus E between 1.8 and 3.1 GPa (data sheet). Therefore, the maximum strain ε of pure PMMA sample is 0.0028 according to $E = P/\varepsilon$. On the other hand, the Young's modulus of CB is 100 GPa [18]. Therefore, the Young's modulus of polymer composites is dependent on the content of the filler [19,20]. That is, Young's modulus of PMMA/CB composites is greatly enhanced by the addition of CB particles. Thus, the maximum strain of

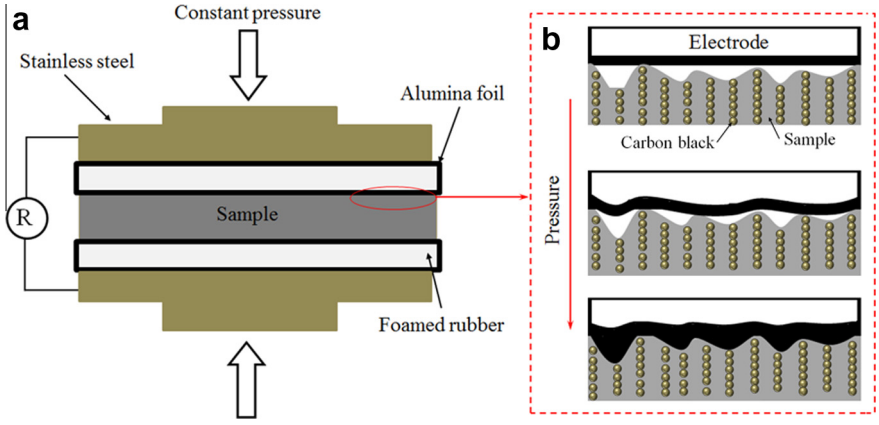

Fig. 1. Schematic view of (a) experimental setup for electrical resistance measurement as well as (b) the interface between electrode and surface of the composite sample under increased pressure.