Nonlinear Surface Electrical Resistivity of Graphite–Polyurethane Composite Films

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ABSTRACT: In this article, we study the surface resistivity of graphite–polyurethane composites using voltage–current characteristics. The evolution of the percolation network of graphite in polyurethane is qualitatively studied using optical micrographs. As expected, the surface resistivity decreases as a function of graphite concentration. In particular, the surface resistivity of the 69% graphite–polyurethane composite is about four orders of magnitude lower than the surface resistivity of the 27% graphite–polyurethane composite. The electrical resistivity of the composite is found to be highly nonlinear with respect to an increasing voltage at a low graphite weight fraction. On the other hand, the nonlinearity is significantly milder at higher weight fractions. The reasons behind the nonlinearity are discussed. Very preliminary studies indicate that very low weight fractions of single wall carbon nanotubes (e.g. 2.5%) are sufficient to generate electrical conductivities comparable to much higher loading fractions ($\sim$ 60% and higher) of the heavier graphite particles. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 293–298, 2007

Key words: conductive filler composite; surface resistivity; graphite; polyurethane; CNT

INTRODUCTION

Historically, conductive polymers and their composites are of great research interest because of their wide range of applications in batteries, sensors, electronics, electromechanical actuators, drug delivery, etc.[1] Two common types of conductive polymers are inherently conducting polymers[1] and polymeric composites containing conductive fillers.[2] In the case of inherently conducting polymers, these are made electrically conductive by doping with anions or cations. On the other hand, the electrical conductivity in conductive polymeric composites is attained by the addition of conductive particles to a polymer matrix. The conductive particles form a percolation network within the polymeric matrix, resulting in a conductive composite. While inherently conducting polymers require a complex chemical process for its preparation, the conductive polymer composites can be easily prepared by a simple polymerization process or by mechanical mixing. Polyurethane is a commonly used electrically insulating polymer that has excellent properties like high load bearing capacity, superior impact resistance, light weight, and high elasticity.[3] These properties make this material an excellent alternative for metals in applications such as sleeve bearings, wear plates, sprockets, rollers, and various other parts. Significant benefits include weight reduction, noise abatement, and wear improvements.[3] Moreover, polyurethane has an outstanding resistance to oxygen, sunlight, and general weather conditions.[4] These properties make the polyurethane very useful as protective coatings for materials prone to environmental degradation, e.g., metals and alloys.

There is a long and rich history on conductive polymer composites. The relation between the dynamic percolation process and the surface state of carbon black was studied by Katada et al.[5] They have studied the effect of annealing temperature and filler concentrations on percolation time in carbon black-filled polymethyl-methacrylate (PMMA). The electrical properties of polymers filled with different types of conducting particles were studied by Xiao-Su et al.[6] Wang et al.[7] have studied the electrical conducting properties of carbon black-filled high density polyethylene (HDPE) composites. The observed conductivity was explained with three models, viz., conduction via nonohmic contacting chains, conduction via ohmic contacting chains, and a combination of these mechanisms based on the different loading fractions of carbon black. Also, electrical conductivity of carbon black-HDPE was studied by

Hiedo et al.[8] Conductive filler composites were studied in polymer blends as well. This leads to a double percolation effect, studied by Sumita et al.[9,10] Bigg[11] has studied the effect on the thermal, mechanical, and electrical properties of polymers due to loading of metal fibers. Higher is the aspect ratio of the fibers, lower is the concentration of fibers needed to get high electrical conductivity. The effect of carbon fillers on mechanical and electrical properties of polyurethane was studied by Furukawa et al.[12] They have used artificial graphite, carbon black, carbon fiber, $CuCl_2$, and graphite intercalation compound as conductive fillers. The interesting properties of graphite/inherently conducting polymer (ICP) composites were studied by Bourdo and Viswanathan.[2] They have synthesized graphite/polyaniline composite that may be used as electrodes for rechargeable batteries. They have also studied the effect on conductivity in these composites as a function of pH of Graphite/polyaniline.

The motivation for the present work arises from an application that is quite different from the one that has traditionally captured the attention of the polymers community. We have been working with thermally activated shape memory alloys (SMA) for sometime now. These materials undergo a solid–solid phase transformation that is sensitive to a change in temperature and mechanical loading, attended by significant reversible deformations. Used appropriately, the materials are capable of delivering high work densities and can thus be used as powerful actuators.[13] Thermal actuation of these materials is commonly done by joule heating of the SMA itself. Our recent work with a copper–nickel–aluminum (CuAlNi) single crystal shape memory alloy has indicated that the material has an electrical resistivity low enough so that targeted actuation temperatures of around 150–200°C are difficult to achieve by joule heating of the material. We have then explored the use of graphite–polyurethane composites as coatings on electrically insulating Kapton tape wrapped on SMA wires, and have demonstrated actuation at temperatures of about 150°C. Recently, we have characterized the different modes of heat transfer, electrical power consumption, and the transient thermal response of graphite–polyurethane composite-coated nichrome (nickel and chromium) wires under different environmental pressures.[14] Nichrome was chosen as the substrate as it does not undergo phase transformation and provides a stable substrate with which the thermal response of the coatings was tested. A substrate, such as the SMA, that undergoes significant reversible deformations will introduce the added effect of mechanical deformations on the coating and affect its thermal response; this work is underway now.

In this article, we present a study of the surface electrical resistivity of different loading fractions of graphite in polyurethane. Optical microscopy is used to study the nature of the percolation networks of graphite in the polyurethane. With a view toward the specific applications we are interested in, the surface resistivity is determined from voltage–current characteristics of the coatings. This is different from the traditional approach where the surface resistivity is determined from direct resistivity measurements. The voltage–current characteristics reveal an interesting nonlinear effect on the surface resistivity; this phenomenon seems to have largely gone unnoticed in the literature on conductive polymer composites possibly because the use of the composites as resistors were not a strong focus as far as applications are concerned. We also discuss the possible reasons as to why the nonlinear resistive effects arise. Finally, we also report very preliminary work on a dramatic effect of carbon nanotubes as a conductive filler in polyurethane.

THE EXPERIMENTAL PROCEDURE

The polyurethane used in this study was Permax 200 (a water-borne polyurethane) obtained from Noveon Chemicals (Cleveland, OH). The solid content of polyurethane is 40% by weight per gram of the solution. This is a highly electrically insulating polymer. The graphite was SureCoat 1530 obtained from Superior Graphites Inc. (Chicago, IL). This is an aqueous dispersion of graphite particles with 30% by weight per gram of colloidal solution. The average particle size of the graphite is about 15 μm.

The graphite–polyurethane composite was prepared by mixing the graphite solution in polyurethane. In the present study, we have used five different loading fractions of graphite in polyurethane. The graphite–polyurethane loading ratios used were 3 : 1, 2.5 : 1, 2 : 1, 1 : 1, and 0.5 : 1. These loading fractions correspond to 69.23, 65.2, 60, 42.85, and 27.27% by weight of solid graphite in polyurethane, respectively. After preparing the solutions, a thick film of each solution was prepared on a glass substrate. The glass substrates were cleaned with acetone and sonicated in ethyl alcohol to remove any impurities on the substrate. The graphite–polyurethane solution was poured on the substrate and drawn into a film using a draw-down bar. The films were dried first in the air and then at an elevated temperature of about 100°C in an oven for 5 min. Two samples of each concentration were prepared. The thicknesses of the films were measured using a Permascope (D211, Fischer Scientific). The average thickness of the films was about 3 mils (75 μm).

Before outlining the surface resistivity measurements, it is useful to give the connection between the surface resistivity and volumetric resistivity. Consider the flow of electrical current, in a material with dimensions—L, W, and T—as shown in Figure 1. The electri-

cal resistance of the material in the direction of current flow is

$$R = \rho \frac{L}{WT}, \qquad (1)$$

where "ρ" is the volumetric electrical resistivity of the material. To determine "ρ" from resistivity measurements, the geometrical parameters of the material are necessary. If the material happens to be a coating (i.e., $T \ll W, L$), a more convenient property to measure is the well-known surface resistivity, $\rho_{surface}$. Its definition as well as its relation to the electrical resistivity [eq. (1)] is given as

$$\rho_{surface} = \frac{\rho}{T} \quad \Rightarrow \quad R = \rho_{surface} \frac{L}{W}. \qquad (2)$$

For the measurement of surface resistivity of the films, silver paste pads were deposited on the two ends of the glass substrates. The schematic of the film and contact pad configuration are shown in Figure 2. The contacts pads were deposited such that 1×1 in.^{2} of the film was exposed for the measurement of the surface resistivity. Based on these dimensions and the latter of eq. (2), the surface resistivity turns out to be

$$\rho_{surface} = \frac{V}{I}, \qquad (3)$$

where "V" is the voltage and "I_s" is the surface current. Voltage–surface current characteristics of the films were studied using a Keithley 2400 Sourcemeter. The V–I characteristics were studied in the voltage range of 0–35 V. Also, microstructural studies of the films were carried out using optical microscope attached to MEMS probe station (PM8, SUSS Microtech).

RESULTS AND DISCUSSION

In this section, we begin with a study of voltage–current characteristics of the graphite–polyurethane composite films with different graphite loading fractions. This is given in Figure 3. For every run, the voltage is the input and the current is the quantity that is measured 5 s after the voltage is applied. The measurement at a given voltage was repeated on two separate
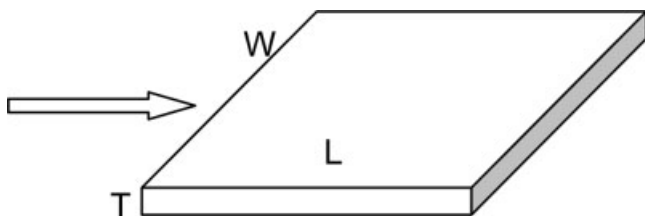

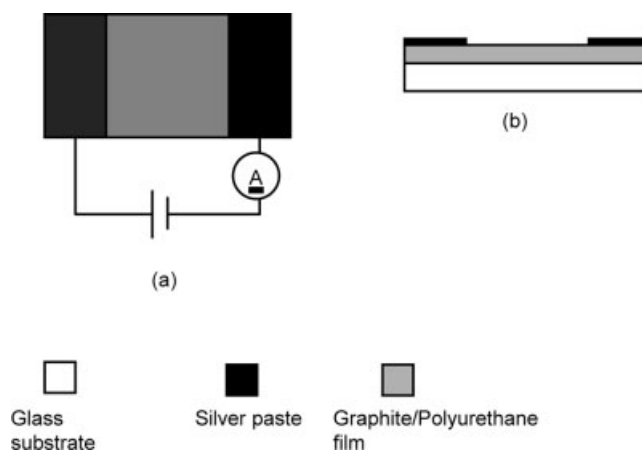**Figure 1** A schematic to define the surface resistivity of a coating.

Figure 2 Schematic of V–I_s measurement of graphite/polyurethane composite films: (a) top view and (b) side view.

samples of same nominal composition. The difference between the measured values from the two repetitions was negligible ($<1\%$). The mean value of two readings were used to plot V–I_s in Figure 3. Also, we allowed a cooling time of 2 min between two consecutive applications of voltage. As shown in the figure, V–I_s curves are almost linear for concentrations of graphite at 60% and above. The resistivity for lower concentrations of graphite is too high, forcing their corresponding V–I_s curves to almost touch the horizontal axis. For that reason, those V–I_s curves are redrawn on a different scale, and given as an inset to Figure 3. The nonlinear V–I_s response at the two concentrations of graphite, 43 and 27%, is now clear. For these concentrations, a critical voltage of about 10 V is required before a measurable surface current is registered. However, even above 10 V, the amount of surface current measured is very small and is 0.005 mA for the 27% graphite and 0.5 mA for the 43% graphite.

The Figure 4 shows the variation of the surface resistivity, $\rho_{surface}^0$, with the graphite concentration in the composite at an applied voltage of 5 V. As seen in the Figure 4, the composite with 27% graphite concentration has very high surface resistivity of 8196 kΩ/square. Surface resistivity decreases with increasing graphite concentration and reaches to 344 kΩ/square for the graphite concentration of 43%. It reaches as low as 0.371 kΩ/square for the graphite concentration of 69%. To study the relative effects of a change in resistivity at voltages higher than 5 V, we have given the normalized surface resistivity, $\rho_{surface}/\rho_{surface}^0$, in Figure 5. As seen in the figure, the normalized resistivity undergoes a much smaller decrease at graphite concentration of 60% and higher, as compared to the lower graphite concentrations.

Figures 6(a–c) show the optical micrographs of composite films with graphite concentration of 27, 60, and 69% by weight, respectively. These pictures were taken with $\times 200$, and show the evolution of the percolation
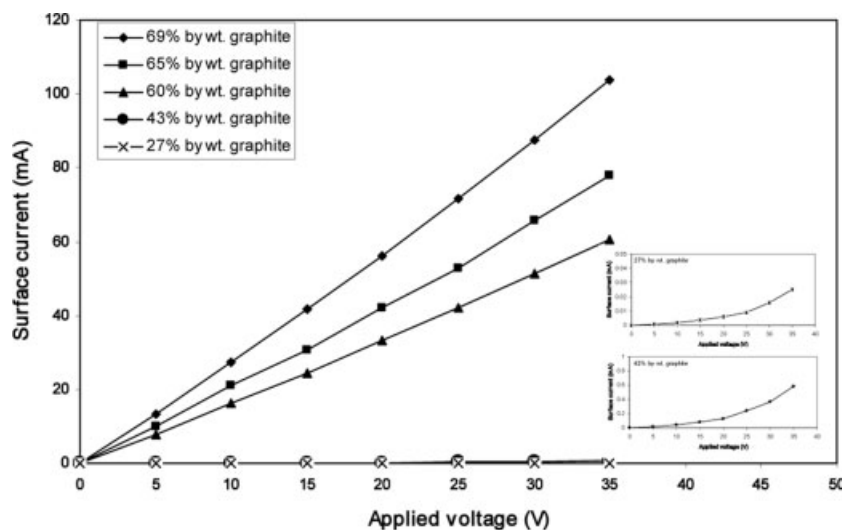
Figure 3 Voltage–surface current curves of graphite/polyurethane composite films for different graphite loading fractions.

network of graphite in the polyurethane. As seen in Figure 6(a), the small graphite concentration translates into large observable gaps between the graphite particles. Inspite of the absence of widespread connectivity, it is interesting to note that such a microstructure allows for measurable current flow at voltages higher than 10 V. An obvious increase in connectivity can be seen in in Figures 6(b and c) for the graphite concentrations of 60 and 69%, respectively.

Despite the weak conductive network seen in Figure 6(a) for the 27% graphite, measurable currents at different voltages (recall the inset in Fig. 3) implies that besides whatever connectivity there may be in the percolation network, another possible mechanism could be quantum mechanical tunneling.[15] In this phenomenon, there is a charge jump between two conductive particles in close proximity and separated by a nonconductive material. Confirmation of this hypothesis as well as the relative contributions of the tunneling effect and the connectivity in the percolation network will have to be con-

clusively established. At graphite concentrations 60% and higher, the high connectivity in the percolation network is believed to be the over-riding factor impacting on the electrical conductivity of the composite. The mild nonlinearity of the normalized surface resistivity with respect to the voltage (Fig. 5) may be attributed to thermal effects. The coefficient of thermal expansion (CTE) of polyurethane is about two orders of magnitude higher than graphite.[16] This CTE mismatch results in much higher thermal expansion in the polyurethane than in the graphite; the magnitude of this mismatch should increase with higher voltages (as that will trigger higher temperatures). We hypothesize that this phenomenon results in better contact between the graphite particles, leading to a somewhat lower resistivity.

Before closing, we would like to mention some very preliminary work using single walled carbon nanotubes (SWCNT) as conductive fillers. Carbon nanotubes have been extensively used in various polymers to generate a percolation network.[17,18] Our future in-
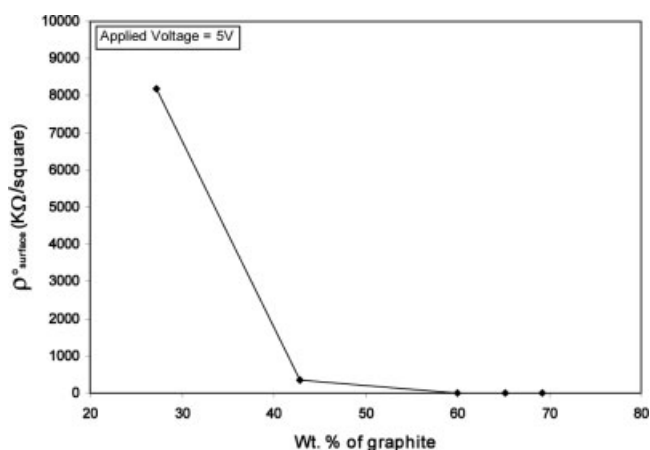

Figure 4 Variation of surface resistivity with graphite concentration at 5 V.
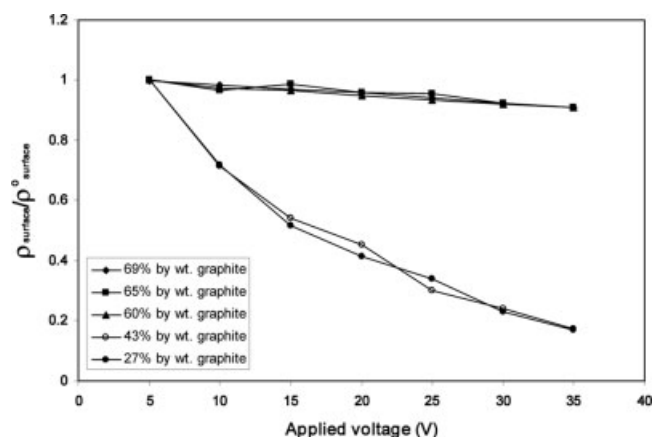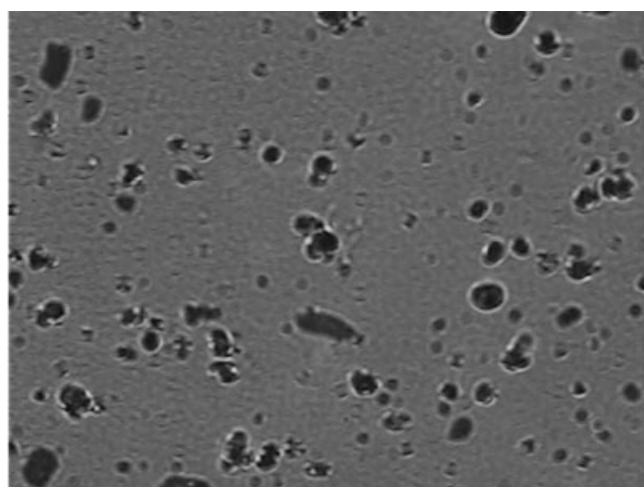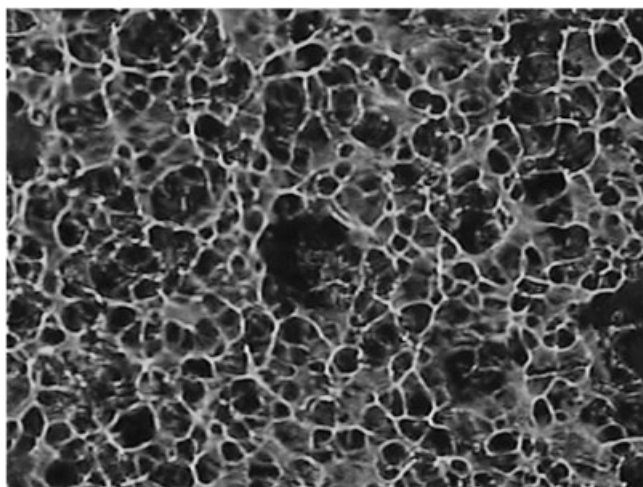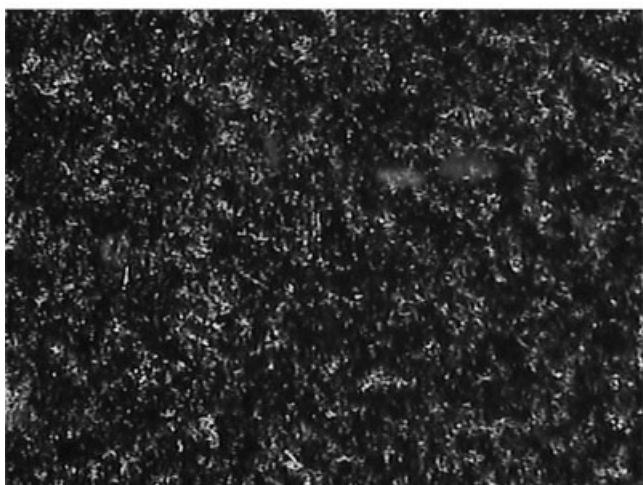

Figure 5 Variation of normalized resistivity with the applied voltage for different graphite concentrations.

(a)

(b)

(c)

Figure 6 Optical micrographs of graphite/polyurethane composite films with different graphite loading fractions: (a) 27%, (b) 60%, and (c) 69% (by weight). Magnification is ×200. The light areas in the above micrographs represent the polyurethane and the dark areas are the graphite.

terest is to synthesize CNT–polyurethane composite films and characterize their electrical and mechanical properties. We are presenting here some very preliminary results of SWCNT–polyurethane composite films. We have prepared three films with SWCNT loading fraction of 0.0085, 1.25, and 2.5% by weight following the same procedure that was followed for the graphite–polyurethane composites. While the 0.0085% CNT-based composite showed a small measurable current of the order of μA, the films with CNT loading of 2.5% by weight showed a fairly high current of 8 mA at 35 V. Recall that currents of the order of mA was seen for a graphite concentration of 60% by weight and higher (Fig. 3). This is probably due to the fact that the low density of SWCNT translates into a percolation network with good connectivity, allowing for conductivities that are comparable with a much higher loading fraction of the heavier graphite particles. Having said that, we alert the readers to interpret the data of the CNT–polyurethane composites with a degree of caution as the tests need to be repeated. With that cautionary note, we have decided to communicate the preliminary results as the measured currents are far higher than the instrumentation errors.

CONCLUSIONS

The surface resistivity of graphite/polyurethane composites were studied using voltage–current characteristics. The surface resistivity turned out to be highly nonlinear for low weight fractions (43 and 27%) of graphite in polyurethane, whereas the nonlinearity was significantly milder at higher concentrations of graphite (60, 65, and 69%). Possible reasons for such nonlinearities were discussed. The evolution of the percolation network of graphite in the polyurethane was also qualitatively analyzed using optical micrographs. Very preliminary studies indicate that very low weight fractions of single wall carbon nanotubes (e.g. 2.5%) are sufficient to generate electrical conductivities comparable to much higher loading fractions (∼60% and higher) of the heavier graphite particles.

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