Imaging of Conductive Filler Networks in Heterogeneous Materials by Scanning Kelvin Microscopy

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ABSTRACT: This article reports a novel application of scanning Kelvin microscopy for exclusively revealing the distribution of a percolated conductive filler network in heterogeneous materials. The materials under investigation are carbon black and carbon nanotube-filled epoxies with a highly inhomogeneous conductivity distribution due to their fabrication. The Kelvin method is demonstrated to be especially suitable for resolving the resistive particle network in these kinds of composite materials with sample resistance levels in the megaohm range. Transmission optical microscopy reveals matches between the scanning Kelvin images and the sample morphologies, whereas the percolating backbone cannot be distinguished in the optical micrographs. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 3381–3386, 2001

Key words: scanning Kelvin microscopy; heterogeneous materials; conductive filler network; carbon black; carbon nanotubes; nondestructive investigation; percolation; composite materials

INTRODUCTION

The vibrating capacitor or Kelvin[1,2] method is a well-established experimental technique for measuring the contact potential difference (CPD) or the work function of metal[3] and semiconductor surfaces.[4,5] In addition, the method can be applied to other classes of materials such as polymers[6] and carbon black (CB).[7] Here, the sensitivity of the CPD to the appearance of electronic surface states and surface charges is used. For CB, it is possible to estimate the degree of surface oxidation. Scanning Kelvin microscopy (SKM) allows for the mapping of the two-dimensional CPD distribution on sample areas of 1 cm^2 with a micrometer resolution without extensive experimental requirements.[8]

In this article, we report the application of SKM for the investigation of heterogeneous insulating materials filled with a conductive component such as CB and carbon nanotubes (CNTs) in a polymeric matrix. These composites are suitable for antistatic[9] and electromagnetic shielding[10] applications and exhibit an inherent inhomogeneity in their filler particle distribution. This inhomogeneity can be controlled by the manufacturing process of the materials and has a strong influence on the resulting electrical properties.[11] Therefore, a nondestructive investigation method for revealing the distribution of the conductive network in the polymeric host is necessary. We show that SKM enables selective mapping of the filler particles participating in the percolating network, whereas isolated particles or clusters not connected to the network are not resolved. This is a considerable advantage with respect to conventional transmission optical and transmission electron microscopy, which also re-

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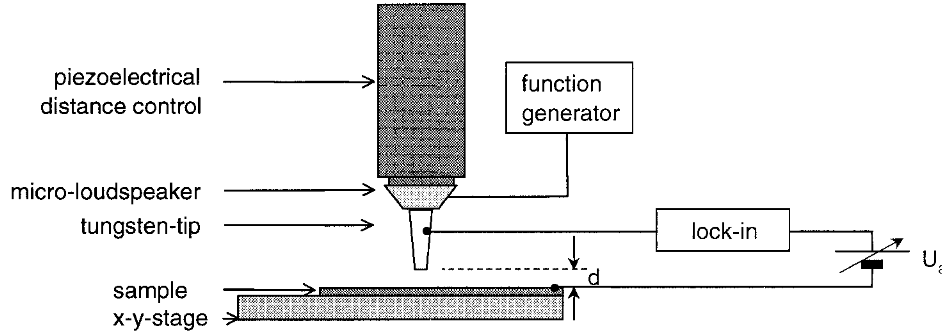


Figure 1 Kelvin setup used for the analysis of the conductivity distribution in heterogeneous materials. The sample is mounted on an x–y translation stage, above which an oscillating tungsten tip is positioned, which is leveled before the scan. The applied external voltage (U_E) is fixed, and the induced Kelvin current is measured at each position with a lock-in amplifier.

quires greater efforts in terms of sample preparation.

EXPERIMENTAL

Measurement Principle

The experimental setup for SKM is shown in Figure 1. The sensing element is a tungsten tip about 50 μm in diameter positioned at a distance of 10 μm above the sample surface. A piezoelectric height control allows the adjustment of a constant mean distance between the tip and the sample before the scan. The sample is mounted on an x–y stage for mapping the induced Kelvin current across the sample with a step width of 50 μm. The distance between the tungsten tip and the sample is modulated sinusoidal with a frequency f of 1 kHz and an amplitude of about 2 μm by means of a microresonator. With the resulting capacitor approximated by parallel plates, the current I induced in the external circuit is given by

$$I = \frac{\Delta\Phi + U_E}{Z_0} \tag{1}$$

with

$$Z_0 = \frac{[d_0 + d_1 \cos(\omega t)]^2}{\varepsilon_0 \varepsilon_r A d_1 \omega \sin(\omega t)}$$

where $\Delta\Phi$ denotes the CPD between the tip and the sample, U_E is the external voltage, and Z_0 is a constant with the unit of an impedance. A stands for the surface area of the tip, and ϵ_0 and ϵ_r are the permittivities of the free space and the medium between the electrodes, respectively. The parameters d_0 and d_1 are the mean distance and modulation amplitude of the tungsten tip, respectively. In the measurement mode used, the external voltage was fixed, and the Kelvin current was measured as a function of the tip position with a lock-in amplifier.

In the samples investigated, the current is modified by an additional serial impedance due to the resistance of the fillers and the polymeric matrix. The modified current I^* can be evaluated if we take into account a reduced external voltage $U_E \rightarrow (U_E - U_Z)$. Here, U_Z denotes the voltage drop across this serial impedance and is given by $U_Z = I^*Z$, where Z is the magnitude of the impedance. Modifying eq. (1), we obtain the following after a straightforward calculation:

$$\frac{I^*}{I} = \frac{1}{1 + Z/Z_0} \tag{2}$$

An estimation of the minimum value for Z_0 in the measurement setup used results in 500 MΩ. For values of $Z \geq Z_0$, the Kelvin current is considerably lowered. This occurs when the tip scans insulating areas on the sample or conductive clusters that are isolated from the percolated backbone. Therefore, this value of Z_0 can be seen as the measurement resolution for the conductive areas. A calibration measurement shows that this value of the serial impedance corresponds to a Kelvin current of about 5.0 pA. In addition to this, the Kelvin current provides information on the depth distribution of the particle network and the

capacitive conductivity between branched clusters.

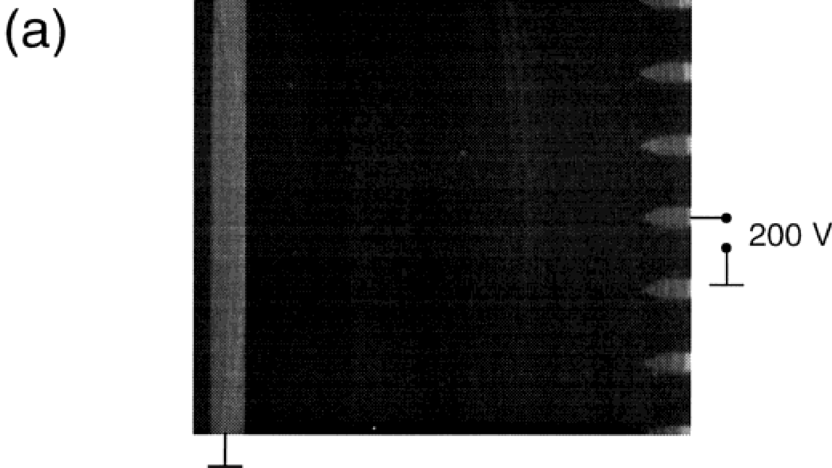
Materials

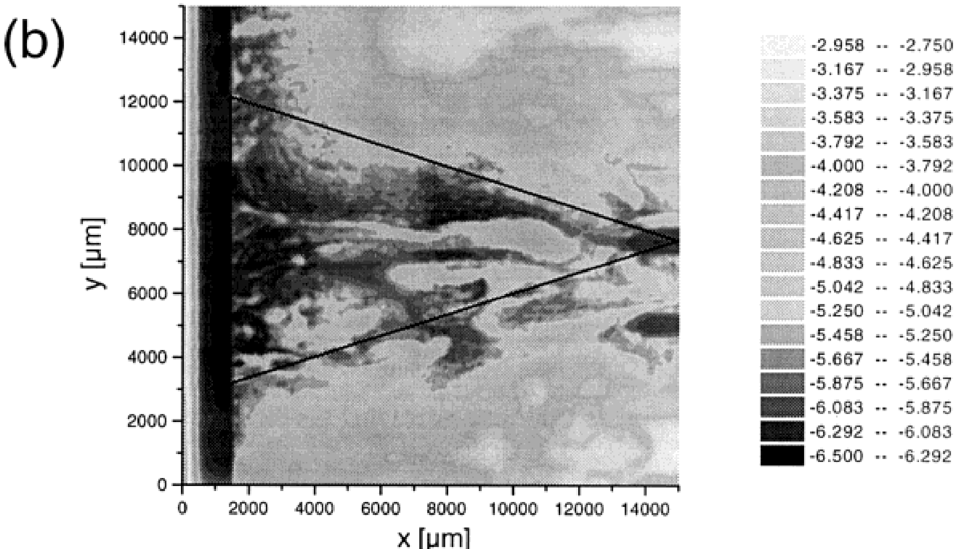
The materials investigated in this study were epoxy polymers with CB and CNTs as filler particles. The polymeric matrix was an epoxy polymer based on a bisphenol A resin (Araldite LY556, Novartis, Basel, Switzerland) and an aromatic amine hardener (Araldite LY932). Applying an intense stirring process, 0.6 wt % CB (Printex XE2, Degussa–Hüls AG, Düsseldorf, Germany) was dispersed in the epoxy resin. A mean size of the isolated CB aggregates of 500 nm was revealed by transmission electron microscopy. An inhomogeneous conductivity distribution in the composite was realized with the method of electrically induced agglomeration of CB; it is described in detail elsewhere.[12] Figure 2(a) shows a photograph of the cross section of the cured sample. Visible are the brass ground electrode on the left-hand side and seven tip electrodes on the right. During the curing of the epoxy resin, a voltage of 200 V was applied between the central tip electrode and the ground electrode, corresponding to an electric field strength of 180 V/cm. The field was sufficient to form a conductive network of CB particles between these electrodes, whereas the CB aggregates in the outer regions remained isolated. We verified this by measuring the DC resistance between the tip and the ground electrodes, showing a resistance of 7 MΩ for the central tip and values above 1 GΩ for the outer ones. After the hardening, we fabricated a polished cross section in the electrode plane to perform the SKM. The sample was contacted at the ground electrode with the Kelvin circuit. For the transmission optical microscopy, the sample was abraded and polished from the backside to a thickness of 80 μm. The CNTs used in this study were nonoxidized multiwall tubes with a mean diameter of 10 nm. These nanotubes showed an entangled appearance in the as-received state consisting of aggregates in the micrometer range. The dispersion procedure for 0.022 wt % CNT in the epoxy resin was similar to that of the CB materials and is described in detail elsewhere.[13] After the epoxy was cured for 8 h at 140°C, we cut a film 200 μm thick to achieve a transparent specimen. In a transmission optical micrograph [Fig. 3(a)], the formation of a macroscopic network of CNTs is visible. To put this network in contact with the external Kelvin circuit, we sputtered a palladium electrode on top of the specimen with a window of 7×8 mm^2.

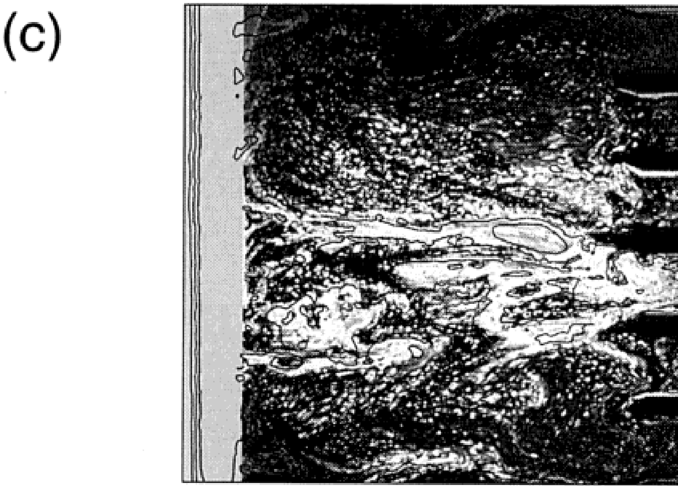
RESULTS AND DISCUSSION

Figure 2 shows an SKM image [Fig. 2(b)] in comparison with a photograph [Fig. 2(a)] and a transmission optical micrograph [Fig. 2(c)] for the CB/epoxy specimen. The photograph reveals the electrode configuration used with the CB-filled polymer in between. The sample appears homogeneously black on this macroscopic scale. In the SKM image, the electrodes remain visible, the current is below 5 pA for the outer tip electrodes, indicating that these electrodes are not connected to the conductive CB network. Between the central tip electrode and the opposite ground electrode, a triangular area with currents above 5 pA is denoted, showing the formation of a percolated network. The visible current distribution in this region can be explained by the three-dimensional arrangement of the particles in the network. Outside the triangle, the current remains low, corresponding to insulating areas of the polymer and isolated CB clusters with an impedance exceeding 500 MΩ. Figure 2(c) shows the morphology of the sample in a transmission optical micrograph. Visible is the inhomogeneous distribution of the filler particles in the triangular area. The bright regions in this area are impoverished by CB and can be explained by the concentration of the particles in the conductive pathways. A more even distribution of CB is visible outside this area, and any existing inhomogeneities are due to convection of CB during the curing process. Additionally plotted is a contour of the SKM image to show the matching of both pictures. Obviously, optical microscopy is not suitable for distinguishing conductive and insulating regions within the sample.

Figure 3 shows a transmission optical micrograph [Fig. 3(a)] and the corresponding SKM image [Fig. 3(b)] for the CNT-filled sample. Visible in the micrograph is the cluster of nanotubes spanning the sample. The formation of such types of macroscopic clusters and the vanishing of isolated particles is typical for the investigated nonoxidized CNTs embedded in the epoxy polymer.[13] SKM gives evidence that the CNTs form an electrically conductive particle network. The gaps in the Kelvin current appearing in the SKM image [see circles in Fig. 3(b)] can be explained by a network depth above the scan depth resolution of


(a)
200 V


(b)
14000
12000
10000
8000
6000
4000
2000
0
y [µm]
0
2000
4000
6000
8000
10000
12000
14000
x [µm]
-2.958 -- -2.750
-3.167 -- -2.958
-3.375 -- -3.167
-3.583 -- -3.375
-3.792 -- -3.583
-4.000 -- -3.792
-4.208 -- -4.000
-4.417 -- -4.208
-4.625 -- -4.417
-4.833 -- -4.625
-5.042 -- -4.833
-5.250 -- -5.042
-5.458 -- -5.250
-5.667 -- -5.458
-5.875 -- -5.667
-6.083 -- -5.875
-6.292 -- -6.083
-6.500 -- -6.292


(c)

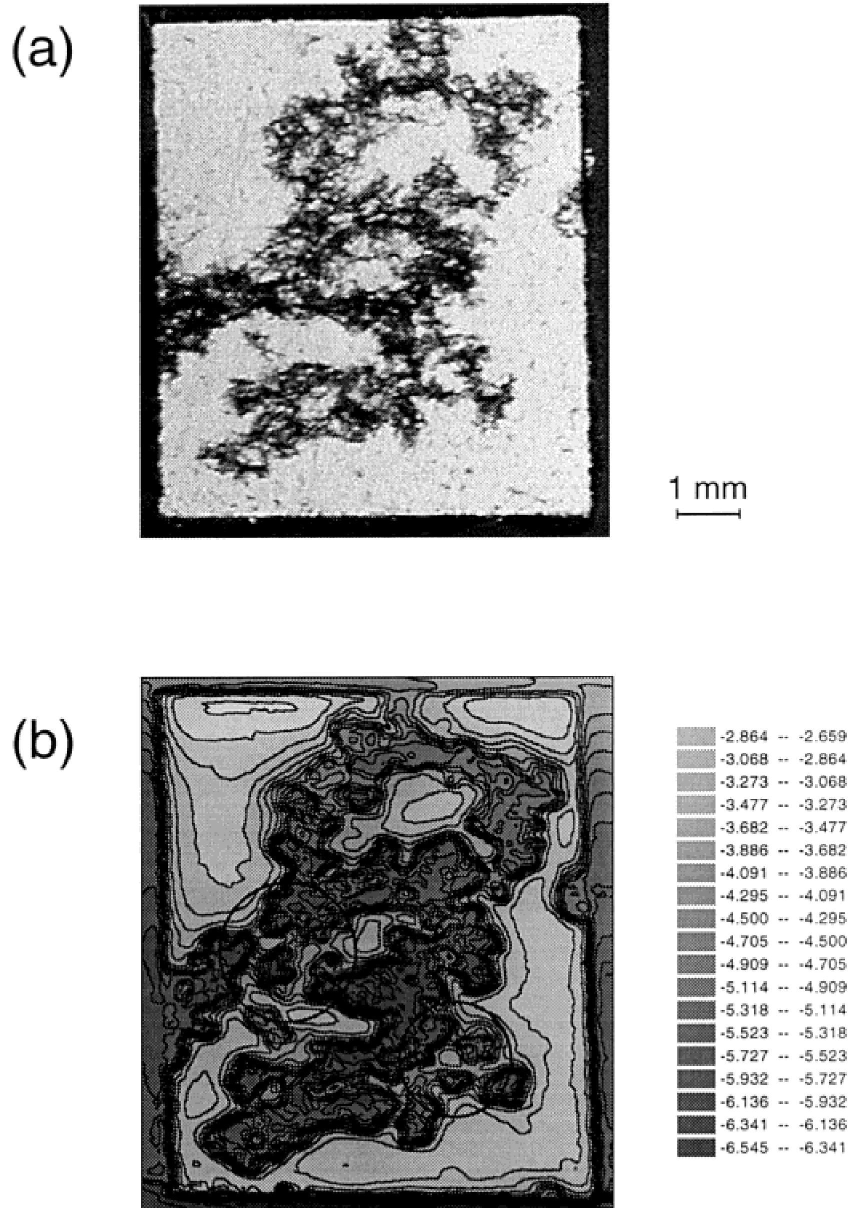


Figure 3 (a) Transmission optical micrograph of a CNT/epoxy sample and (b) SKM image of this specimen (the circles denote the gaps in the Kelvin current caused by the three-dimensional network structure).

the instrument ($<50\ \mu$m). Furthermore, the finite spatial resolution of the setup used (ca. 50 μm) results in a smoothing of the conductive CNT network structure in the SKM image.

CONCLUSION

In conclusion, a novel application of SKM for the imaging of conductivity distributions in heteroge-

Figure 2 (a) Photograph of the cross section of a CB/epoxy specimen [the ground electrode (left-hand side) and agglomeration electrode (middle tip on the right-hand side), with an applied agglomeration voltage of 200 V, are denoted], (b) SKM image of the current distribution in this sample [the gray scale is in picoamperes; the triangle denotes the area of the agglomerated CB particles], and (c) transmission optical micrograph of the cross section [a contour of the SKM image in Fig. 2(b) is plotted as well].

neous materials with percolated conductive fillers has been reported. In contrast with optical microscopy and other methods, Kelvin microscopy reveals solely the percolated network in the sample, whereas insulating areas and finite clusters of the conductive fillers give no signal. The Kelvin method in the setup used is especially suitable for imaging high-resistance networks with resistances of up to 500 MΩ. For interpretation of the SKM images, the finite spatial and depth resolution has to be taken into account.

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