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Morphology of conducting filler-reinforced nitrile rubber composites by electrostatic force microscopy

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Abstract

An advanced technique of morphology observation of conducting filler-reinforced nitrile rubber composites by electrostatic force microscopy is reported. The composites were prepared by mixing carbon blacks and multi-walled carbon nanotubes with nitrile rubber. Increase in the voltage applied to the probe tip in electrostatic force microscopy enhanced clear visibility of carbon black particles and their distribution in the rubber matrix. The surface topography of the composite indicated the presence of carbon black aggregates having different size and structure depending on the type of carbon black. The electrostatic force microscopy images of carbon nanotube-filled composite clearly showed the presence of bundles of nanotubes embedded in the rubber matrix. The average diameter of nanotube bundles was found to be around 50 nm.

Keywords: Morphology; Rubber; Carbon nanotube; Carbon black; EFM

1. Introduction

The electrical properties of conducting carbon black (CB)-polymer composites have been acknowledged in antistatic, electromagnetic interference (EMI), current limiting resetable switches and electro-active pressure sensors and actuators applications [1]. Also, carbon nanotubes (CNT) have attracted significant interest in the development of electronic and automotive polymer components due to their unique performance even at relatively low concentration [2]. For instance, thorough dispersion of CNT in a polymer matrix can effectively provide the conducting pathway by forming an interconnecting structure leading to improved electrical conductivity [3]. The electrical conductivity of a polymer/conducting filler composite depends upon several factors, such as the nature of polymer matrix and the fillers having different size, shape, structure, and state of filler dispersion [4]. The structure and the morphology of polymer/CB composites at the microscopic level have been investigated by many analytical methods such as neutron and X-ray diffraction [5], electron microscopy [6], etc. However, the electrical conductivity of the composites could be tracked only if the nanoscale structural information of the conducting fillers in the matrix is available. Electrostatic force microscopy (EFM) is one of the important techniques to study the morphology of polymer composite containing electro-conductive fillers. Recently, the EFM technique was applied for the morphology study of CB dispersion in a soft rubber matrix [7] and in a hard thermoplastic matrix [8]. The technique was also applied for observing the morphology of CNT in a hard thermoset matrix [9], but to the best of our knowledge it has not been reported for CNT morphology in a soft rubber matrix. Recently, we successfully obtained clear EFM images for acrylonitrile-butadiene rubber (NBR)/CNT composites along with those of NBR/CB composites for comparison.

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2. Experimental

The NBR (acrylonitrile content 34%, Mooney viscosity [ML 1+4] at 100 °C: 41) was supplied by Kumho Petroleum Chemical Co., Korea. The carbon black (two types; HP 130 and N220) and the multi-walled carbon nanotube (MWNT, diameter: 15–30 nm, purity >95%) were obtained from Degussa, Germany and Nanotech Co., Korea, respectively. The NBR/CB composites were prepared in a Banbury type internal mixer (Hakke Rheocord 9000, Germany) at 130 °C with a rotor speed of 40 rpm and mixing time of 9 min, and then dicumyl peroxide (DCP, vulcanizing agent) was added on a two-roll mill. The compounds were cured in an electrically-heated compression press at 170 °C for optimum cure time determined from a cure rheometer (ODR, Alpha Technologies, USA). The NBR/CNT composite was prepared by a solution mixing method using acetone as a solvent. The NBR was first dissolved in acetone completely, and 11 phr of CNT was added to this solution and stirred continuously for 12 h with a magnetic stirrer. The solution was then ultrasonically agitated for another 2 h followed by drying in an air circulating oven at 40 °C for 24 h.

The morphology of cryogenically-fractured specimens was investigated using an atomic force microscope operated under normal and electrical mode (AFM, Nanoscope IV, Digital instrument Co.). The tip, a cobalt-chromium coated silicon cantilever having a radius of curvature less than 90 nm and height of approximately 15–20 μm, was used to probe the surface. First, surface topography was determined under tapping mode. Upon retrace over the same line, the electrical force was monitored under non-contact mode at a set lift height of about 37 nm from the sample surface. A dc bias voltage (1–7 V) was applied across the tip and grounded sample. The phase shift ($\Delta\phi$) of the oscillating cantilever at a frequency of 1 Hz was used to diagnose the change in the attractive force between the tip and the sample. The images obtained from EFM were then analyzed by SPIP image analysis software to get information about the particle size, interconnecting network and two- and three-dimensional topography.

3. Results and discussion

The EFM method measures local electrostatic interaction between a conductive tip and a sample through Coulomb forces. As the tip scans across the surface, a bias voltage is applied on the tip. Different areas of the surface may have different responses to the charged tip, depending on their local electrical properties. Such a variation in electrostatic forces can be detected in the change of oscillation amplitude and phase of the AFM probe. Because the electrostatic forces interact at greater distances than van der Waals forces, the electrical force information can be separated from surface topography of a flat surface simply by adjusting the tip-to-sample distance. Thus, the electrical features can be resolved from topography features. Fig. 1 shows EFM images of NBR/CB composites containing 30 phr ($\phi_{CB}=0.145$) of HP130. The topographic image of the sample was plain and devoid of any identifiable features of the morphology of the composite without voltage application (Fig. 1a). However, when voltage was increased to 3 and 5 V (Fig. 1b and c), the morphology became more clear with the appearance of bright parts representing the carbon black particles distributed uniformly in the NBR matrix. The appearance of bright parts implied that the current is flowing through the areas at a higher rate, where the CB formed a conducting path between the tip and the sample through electrostatic attraction. Close examination of the sample revealed the presence of circular CB particles having average particle size of about 60 nm connected with many other particles to form an aggregated structure. Application of very high voltage was limited due to electrical damage of the sample, which may destroy

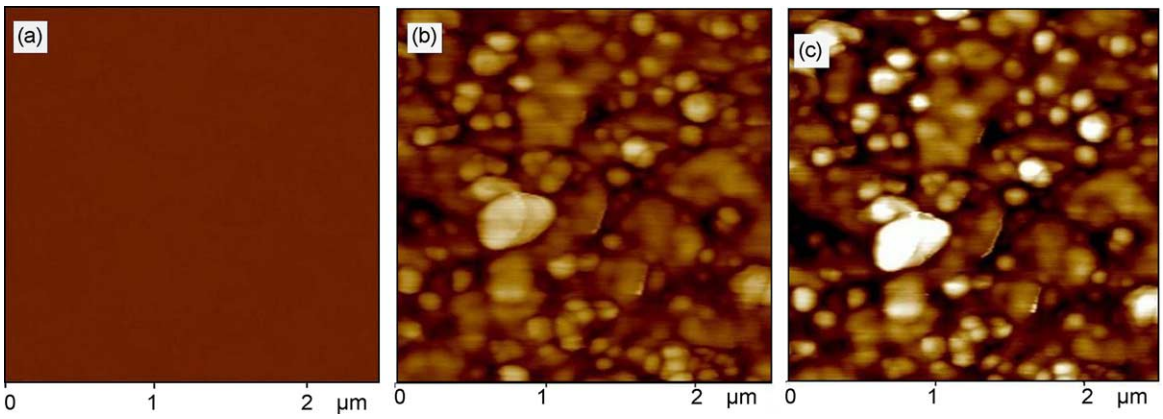

Fig. 1. Effect of tip voltage on EFM phase images of a NBR/CB (30 phr of HP130) composites: (a) 0 V; (b) 5 V; and (c) 7 V.

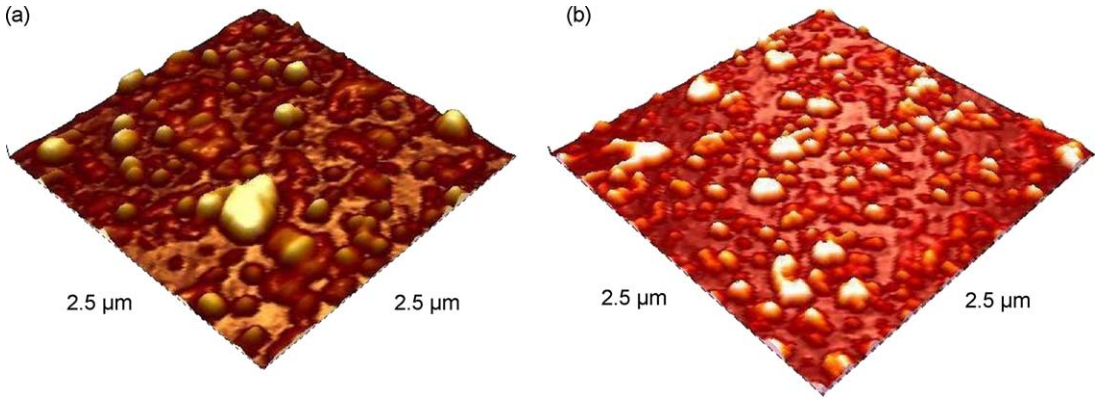

Fig. 2. 3D EFM topographic images of NBR/CB composites: (a) 30 phr of HP130 and (b) 60 phr of N220.

the morphology of the composite. To examine the topography of the sample with better clarity, the EFM images were analyzed by image analysis software. Fig. 2 compares 3D topography of NBR/CB composites containing HP130 (30 phr) and N220 (60 phr). The images were taken at the same tip voltage of 5 V. It shows more detailed morphological features of the composites. The bright parts representing carbon black particles were located in an elevated position relative to the NBR matrix. The height of these bright parts varied from place to place depending on the connectivity between the CB particles forming the structure, applied voltage and CB location. Comparison of these images clearly demonstrated the difference in the structure of CB aggregates. While the former image showed the presence of large amount of interconnected CB particles, the latter showed the presence of many individual CB particles. The variation in the height features of the images is attributed to the difference in the conductivity. The flat background of the image represents the non-conducting NBR matrix. Furthermore, some of the CB particles, which are embedded in the rubber matrix, were also raised to some height depending on the coverage of rubber over the CB particles. Additionally, an increase in CB content increased the surface roughness and formation of an interconnected structure responsible for higher electrical conductivity (Fig. 2b).

Since the CNT is also electro-conductive, we expanded the EFM study to NBR/CNT composites with 11 phr ($\phi_{CNT}=0.041$) of CNT, which has never been reported so far in the literature. Fig. 3a shows the AFM image under tapping mode with zero tip voltage and the CNT dispersion could not be seen clearly. However, the EFM images with 7 V tip voltage clearly showed the even distribution of CNT. The observed CNT were in the form of bundles placed about 20 nm apart rather than an individual CNT, possibly due to the lack of lateral resolution less than the order of 20 nm in the lift mode EFM (Fig. 3b). Greater details of distribution of CNT in the NBR matrix were obtained from the 3D image (Fig. 3c). The average diameter of the nanotube bundles was found to be around 50 nm.

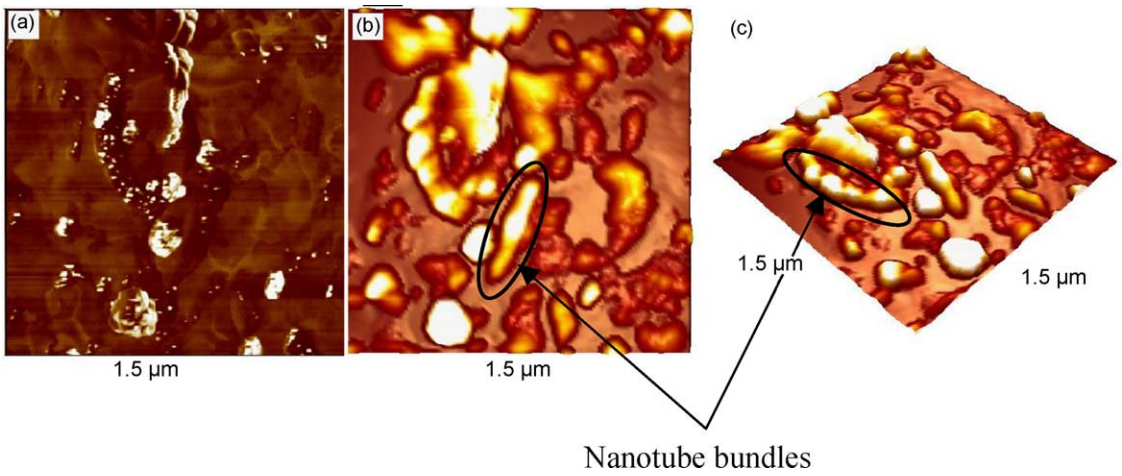

Fig. 3. Effect of tip voltage on EFM phase images of a NBR/CNT composite (11 phr): (a) 0 V; (b) 2D image at 7 V; and (c) 3D image at 7 V.

4. Conclusions

The electrostatic force microscopy (EFM) technique was successfully applied for the characterization of the morphology of NBR/CNT composites together with NBR/CB composites. The images became clearer with increasing the voltage of the probing tip. The filler distribution and interconnectivity could be distinguished based on the type, shape, structure and loading. The CNT was found to be distributed evenly in the NBR matrix in the form of bundles of about 50 nm in diameter.

Acknowledgements

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