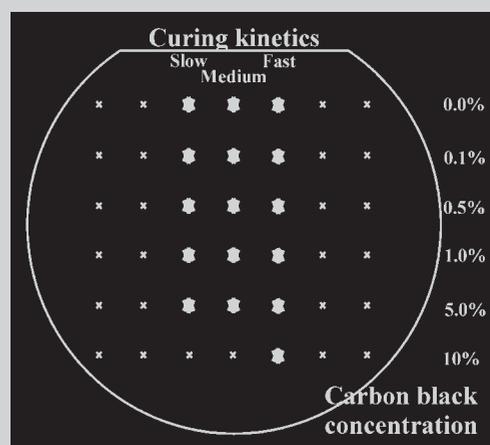


Communication: A systematic investigation into the surface properties of siloxane rubber/carbon black (CB) nanocomposites has been performed, using an automated scanning probe microscope. In this way the influence of CB concentration and curing rate of the siloxane rubber matrix on roughness and conductivity of the composites was studied. Decreasing the curing rate while keeping the CB concentration resulted in a decrease in both roughness and surface conductivity, which can be explained by an additional siloxane-rubber layer formed during curing.



Automated Scanning Probe Microscopy as a New Tool for Combinatorial Polymer Research: Conductive Carbon Black/Poly(dimethylsiloxane) Composites

Riadh Neffati,¹ Alexander Alexeev,² Sergey Saunin,² José C. M. Brokken-Zijp,¹ Daan Wouters,³ Stefan Schmatloch,³ Ulrich S. Schubert,^{*3} Joachim Loos^{*1}

¹Laboratory of Polymer Technology & Dutch Polymer Institute, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands
E-mail: j.loos@tue.nl

²NT-MDT Ltd., 103460 Moscow, Russia

³Laboratory of Macromolecular Chemistry and Nanoscience, Eindhoven University of Technology & Dutch Polymer Institute, P.O. Box 513, 5600 MB Eindhoven, The Netherlands
E-mail: u.s.schubert@tue.nl

Keywords: automated AFM; carbon black nanocomposites; combinatorial materials research; conductivity; high-throughput experimentation; siloxane rubbers

Introduction

Pigments or fillers for elastomers and polymeric coatings have often been utilized, in order to enhance properties or to add functionality. Carbon black (CB) is the filler most frequently used in polymer technology as a reinforcing agent or conductive filler to generate permanent antistatic and electromagnetic interference (EMI) shielding properties.^[1] Siloxane rubber, on the other hand, has nearly constant physical properties over a broad temperature range, good dielectric properties and high resistance against weathering.^[2]

Upon increasing the CB concentration, mechanical properties and volume conductivity of the composite change dramatically at critical volume fractions (ϕ_C) of CB. Certain macroscopic properties scale in a power law fashion when ϕ of the filler is increased. Beyond the percolation threshold an “infinite” cluster of particles spans the sample, inducing a drastic change in, e.g., volume conductivity. Estimations of ϕ_C range from 0.16 to 0.34 (volume fraction), but experimental values of up to 3 orders of magnitude lower (10^{-4}) have been observed.^[3] Both from industrial and fundamental points of view low ϕ_C values are of special interest. In this respect, CB

characteristics (particle size, porosity, specific surface, surface groups, etc.), dispersion, and processing conditions are the key parameters.

When a composite is utilized as a permanent antistatic coating, however, surface properties, such as roughness, surface conductivity, etc., are particularly important. In applications where CB is used mainly to enhance surface conductivity, the presence of CB particles at the surface is essential. A common approach in paints and coatings technology is to adjust the formulation by studying the bulk properties. A volume fraction of CB higher than the percolation threshold should therefore be sufficient to reach reasonable surface conductivity. However, surface and bulk properties are often different, due to the formation of a top layer, a so-called “skin”. Thus, systematic research directed towards better understanding the origin of skin formation and the corresponding factors presents a real challenge.

Scanning probe microscopy (SPM) should be a valuable tool to study skin formation, as it covers several technologies to image and investigate surfaces from the micrometer down to the nanometer scale. The principle of SPM techniques is very similar to profilometry; a sharp miniature-size probe scans across the surface to sense different types of interactions, in the near-field region or in contact with the surface. A breakthrough in lateral resolution was achieved by the invention of the scanning tunneling microscope (STM) in 1981,^[4] when for the first time, atomic resolution images were reported under ambient conditions. The limitation of STM of imaging predominantly conducting materials was soon overcome by the development of atomic force microscopy (AFM).^[5] Since then, a large number of polymer samples have been investigated regarding morphology, nanostructure, and molecular order.^[6–12]

Besides the capability of measuring lateral sizes and height features, AFM has the potential to investigate numerous additional materials properties, such as friction forces and adhesion between tip and sample surface, stiffness, hardness and functional properties of the sample, such as conductivity and magnetic properties. Moreover, AFM can be used as an automated characterization method.^[13,14] In the present study an automated AFM was utilized to investigate the properties of a large number of different siloxane rubber/carbon black nanocomposites, prepared in a systematic way. The two main parameters varied in this investigation were carbon black concentration and curing rate. The study moreover demonstrates the potential of automated AFM with respect to combinatorial materials research (CMR).

Experimental Part

Printex XE2, a conductive carbon black grade from Degussa, was dispersed in siloxane melt using a three-roll mill. This premix containing 10 wt.-% of carbon black was diluted in order to obtain samples with lower concentrations.

The siloxane oil used (Gelest Inc.) was a linear vinyl-terminated poly(dimethylsiloxane) with $\bar{M}_n \approx 27$ kg/mol and a polydispersity of about 2.1, as determined by means of gel permeation chromatography (GPC). The siloxane matrix of these dispersions was crosslinked by adding a multifunctional siloxane hydride (Gelest Inc.), generating ethylene linkages between siloxane hydride and the vinyl group. No side products are observed during curing.^[15,16] The kinetics of crosslinking can be affected by several parameters, such as catalyst concentration, temperature and presence of an inhibitor. A platinum catalyst (10 ppm) was added to the mixture before curing.

The curing rate was changed by varying the concentration of the inhibitor. All other parameters affecting the rate (e.g., catalyst concentration, curing temperature) were kept constant. Curing time was 30 min in a vacuum oven at a temperature of 120 °C. Table 1 provides sample nomenclature and sample characteristics. Slow, medium and fast curing are denoted as s, m and f, respectively. This corresponds to a concentration of the inhibitor of 0.3, 0.1 and 0.0 wt.-%. A droplet of the final mixture was deposited on a siloxane wafer (Infineon) before curing.

Optical microscopy (OM) and AFM investigations were performed using an automated Solver P7LS large sample SPM (prototype, NT-MDT Ltd., Moscow, Russia) equipped with a high-resolution OM (Sony Exwave HAD). Non-contact mode was used in order to prevent damages of the sample morphology caused by strong tip/sample interactions during scanning. Silicon cantilevers with spring constants $k \approx 11.5$ N/m and typical resonance frequencies of 255 kHz were utilized. To measure the conductivity of the samples special conductive cantilevers were used in contact mode. For constant voltage the current level was measured at different areas of the surface. The AFM was calibrated with height standards produced by Siloxane-MDT Ltd., Moscow, Russia.

Table 1. Sample characteristics of the siloxane rubber /CB nanocomposites (f, m and s indicate the way of curing, i.e. fast, medium and slow).

| Sample | CB concentration | Inhibitor |
|--------|------------------|-----------|
| | wt.-% | wt.-% |
| 1f | 0 | 0.0 |
| 1m | 0 | 0.1 |
| 1s | 0 | 0.3 |
| 2f | 0.1 | 0.0 |
| 2m | 0.1 | 0.1 |
| 2s | 0.1 | 0.3 |
| 3f | 0.5 | 0.0 |
| 3m | 0.5 | 0.1 |
| 3s | 0.5 | 0.3 |
| 4f | 1.0 | 0.0 |
| 4m | 1.0 | 0.1 |
| 4s | 1.0 | 0.3 |
| 5f | 5.0 | 0.0 |
| 5m | 5.0 | 0.1 |
| 5s | 5.0 | 0.5 |
| 6f | 10.0 | 0.0 |

Results and Discussion

The automated AFM prototype (Figure 1a) offers several features not common for conventional AFMs: (i) large sample holder and moving system for exact positioning of samples having diameters up to 20 cm, (ii) high-resolution optical microscope and integrated frame grabber for optical imaging of the sample, (iii) advanced control software allowing automated sample positioning and sample measurement using up to 16 different interaction/contrast modes simultaneously, and (iv) advanced data acquisition and database software allowing almost unlimited storage and data handling ability. The AFM is thus capable of measuring an infinite number of sample positions, limited only by the amount of data-storage capacity.

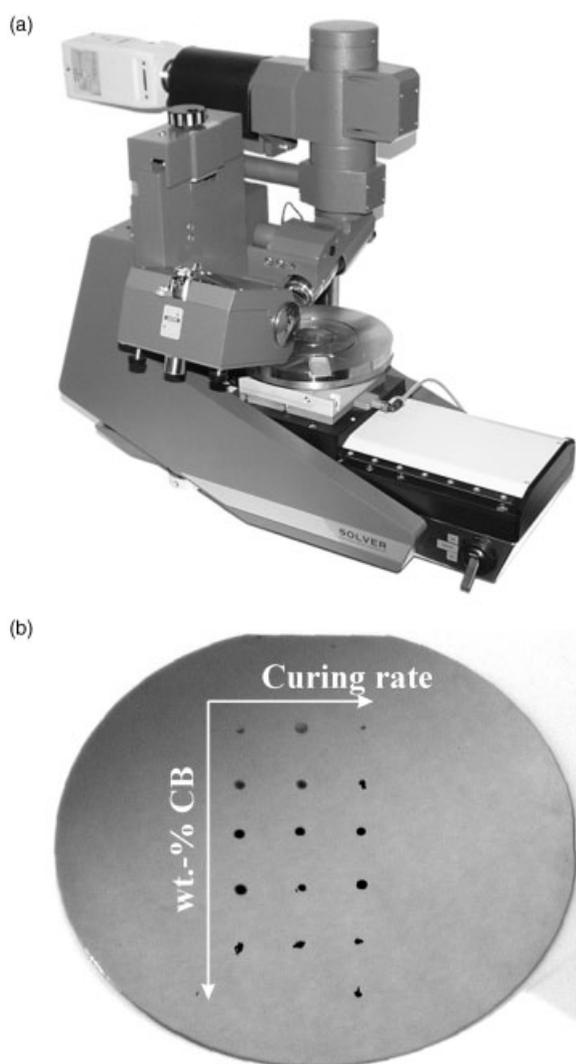


Figure 1. (a) Side view of the automated AFM prototype equipped with high-resolution optical microscope and large sample stage (20 cm in diameter), (b) 16 siloxane rubber/carbon black samples deposited on a standard siloxane wafer at particular coordinates. The directions of increased carbon black concentration and curing rate are indicated.

For a fast screening of the influence of preparation parameters on the performance of siloxane rubber/carbon black nanocomposites, the AFM was used for automated imaging of the optical appearance, measurement of the surface roughness, and determination of the surface conductivity. Figure 1b shows the 16 nanocomposite samples investigated with increasing CB concentrations (top to bottom) and increasing curing rates (left to right), deposited on a standard siloxane substrate at defined coordinates. In a CMR environment, the same substrate/nanocomposite specimen may be used for further automated characterization techniques, such as FT-IR spectroscopy, X-ray photoelectron spectroscopy and scanning electron microscopy.

From SEM and transmission electron microscopy (TEM) studies it has been concluded that Printex CB has a particle diameter of approximately 40 nm, aggregated in primary agglomerates with a typical size in the range of 100 nm.^[17] In siloxane oil, these primary CB agglomerates aggregate in clusters with a size of about 1 to 100 μm , which can easily be visualized with an OM. Figure 2 shows bright-field OM images of two siloxane rubber/CB nanocomposite samples

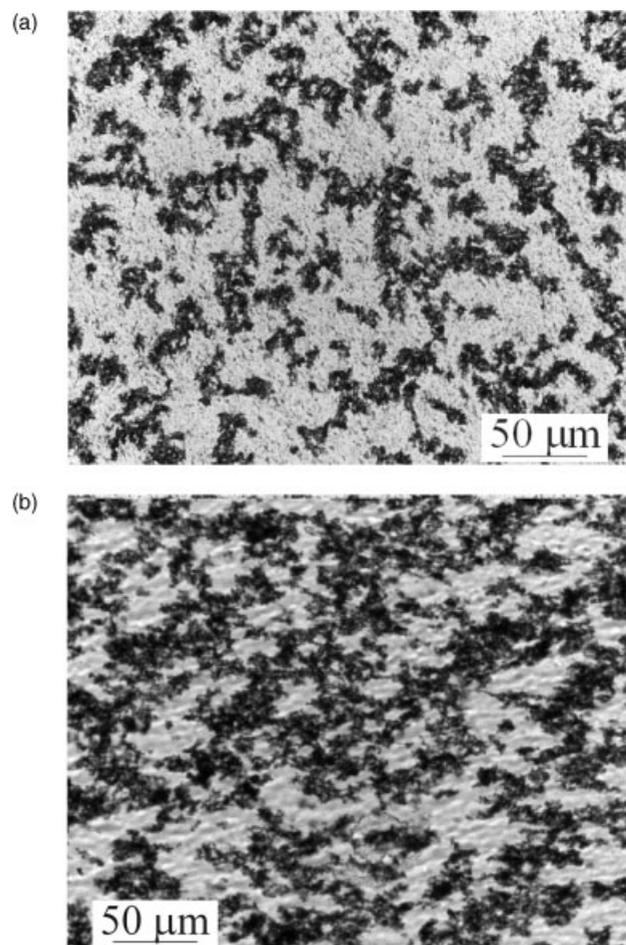


Figure 2. Optical images of two siloxane rubber/carbon black samples containing 0.1 wt.-% (a) and 1.0 wt.-% (b) of carbon black.

containing 0.1 wt.-% and 1 wt.-% of CB. At CB concentrations above a given threshold ϕ_C CB forms a network within the matrix, which is not affected by the final curing of the siloxane rubber matrix. Additional numerical treatment of such images provides information on the fractal dimension of a percolation aggregate of the CB network for both non-cured and cured systems. Such calculated fractal dimensions contain information about the volume conductivity of the nanocomposites, i.e. whether the CB concentration is higher than ϕ_C , resulting in the formation of a network or not. In the present case, ϕ_C is in the order of 0.03 wt.-% CB.

In addition to conventional optical imaging of the siloxane rubber/CB nanocomposites, AFM measurements offer more insight in surface morphology and other specific surface properties of the samples.^[18] Figure 3 presents a series of topographic images of siloxane rubber/CB nanocomposite samples. The effect of CB content (increasing from top to bottom) and applied curing rate (increasing from left to right) on the roughness of the samples can be studied by AFM in height-contrast mode. At high curing rate (no inhibitor), CB concentration seems to be the pertinent parameter in determining the roughness. In this case roughness increases with raising the CB concentration. However, for lower curing rates and the same CB concentration sample roughness is reduced drastically. In the latter case, the amount of CB present at the surface no longer represents the bulk concentration of CB, thus disfavoring the formation of a conductive CB network at the surface as compared to the bulk of the same sample. This is particularly valid for low CB concentrations near the percolation threshold.

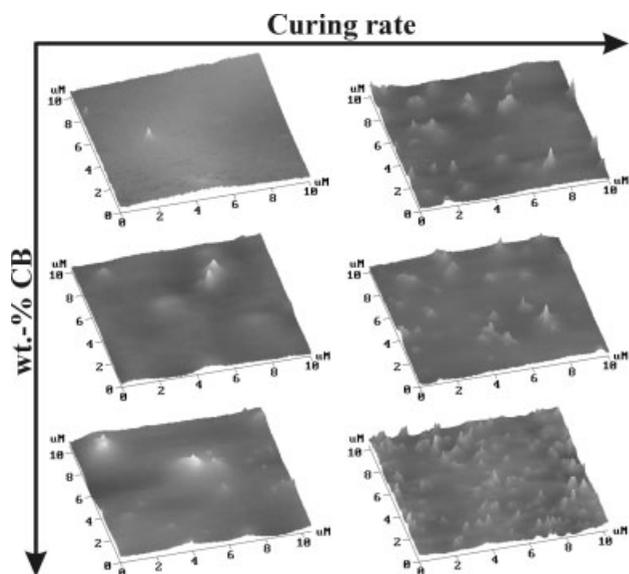


Figure 3. Series of AFM topography images. Sample roughness, equivalent to the number of CB particles at the surface, decreases with decreased carbon black concentration (bottom to top) and decreased curing rate of the siloxane rubber matrix (right to left).

Further information on the CB distribution within the siloxane rubber matrix could be derived from surface conductivity measurements. At the present development stage of the automated AFM, the standard silicon nitride tip had to be exchanged manually by a special conductive tip. (This procedure is supposed to be automated in the future.) Figure 4 shows a 3-dimensional representation of the conductivity distribution at the surface of a medium-cured nanocomposite containing 5 wt.-% of CB. Higher features in the image indicate higher surface conductivity; the rather flat background of the image represents the non-conductive siloxane rubber matrix. Even though the values are qualitative, it is obvious that the sample is conductive only where CB particles are present at the surface. Most of the sample surface is not involved in active charge transport. This means that, besides the bulk CB concentration, also the actual CB concentration on the surface, which in turn is influenced by the curing rate of the siloxane rubber matrix, determines the conductivity level. Consequently, the performance of the nanocomposites is strongly affected by the formation of a non-conductive skin at the sample surface. Therefore, even for CB bulk concentrations above the percolation threshold the conductivity of the nanocomposite might be insufficient if an isolating skin is formed. A detailed discussion of possible reasons inducing skin formation will be provided elsewhere.^[17] Briefly, two basic physical forces might cause the settling of CB aggregates and thus skin formation: The characteristic convex-shaped appearance of the siloxane rubber around CB particles at the samples' surfaces imaged by means of AFM (Figure 3) indicates the presence of capillary forces. In addition, simple gravity could play a role.

Optimization of the performance of siloxane rubber/CB nanocomposites and, especially, achieving a high conductivity level includes controlling and avoiding the skin formation process. Sedimentation can be prevented using a curing recipe that solidifies or crosslinks the siloxane rubber matrix as fast as possible. Furthermore, sedimentation can

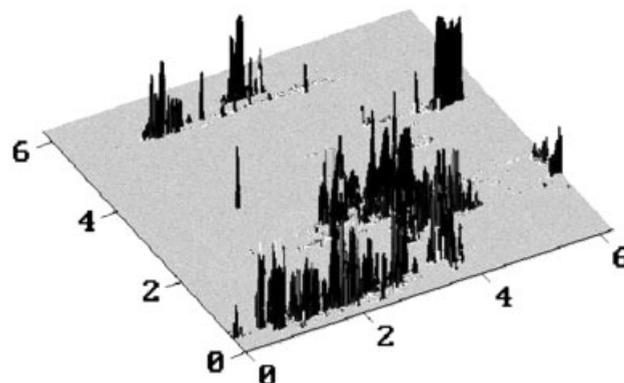


Figure 4. 3D image representing the local surface conductivity as measured by means of AFM using a conductive cantilever. Scale bar in micrometer.

be stopped simply if the sample surface is parallel to the direction of gravity. However, minimizing the present capillary forces around the CB particles is virtually impossible due to the fact that mixing and processing of the nanocomposites require high capillary forces for sufficient wetting.

Conclusions

Combinatorial methods and high-throughput experimentation in polymer science require fast screening methods in order to investigate important parameters that determine the structural and functional properties and the overall performance of the materials. Such approaches are promising with respect to establishing structure/property relationships in more detail and to a fast and lower-cost decision-making in R&D. In the present study, an AFM prototype equipped with a high-resolution optical microscope has been utilized for automated investigation into the surface properties of siloxane rubber/carbon black nanocomposite samples with different CB concentrations and being cured at different rates. From optical microscopy (and other investigations not presented in this study), it has been concluded that CB forms a network above a distinct percolation threshold, which determines the conductive (surface) behavior of the samples. Furthermore, AFM measurements demonstrated that the roughness of the samples is equivalent to the number of CB particles present at the surface. The number of CB particles present at the surface decreases with bulk CB concentration, but also with decreased curing rates for the same bulk CB concentration. The latter effect can be explained by the formation of a skin layer that is caused by capillary forces and gravity. Local conductivity measurements of the sample surfaces by means of AFM revealed clearly the influence of the CB particles on the conductivity at the surface over a larger surface area; the siloxane rubber matrix acts as a local isolator. Thus only high amounts of CB particles present at the surface in combination with a conductive CB network in bulk guarantee the functional performance of the investigated nanocomposites. Finally, automated AFM could be shown to represent an extremely powerful tool in combinatorial materials research.

Acknowledgement: The authors thank *Océ-Technologies B.V.* for supplying materials and fruitful assistance. We thank the *DPI* for financial support. U.S.S. thanks the *Fonds der Chemischen Industrie* for continuous support.

Received: September 29, 2002

Revised: October 22, 2002

Accepted: October 22, 2002

- [1] J. B. Donnet, R. C. Bansal, M.-J. Wang, *Carbon Black*, 2nd ed., Marcel Dekker Inc., New York 1993.
- [2] S. J. Clarson, J. A. Semlyen, *Siloxane Polymers*, PTR Prentice Hall Inc., Englewood Cliffs, NJ 1993.
- [3] D. van der Putten, J. T. Moonen, H. B. Brom, J. C. M. Brokken-Zijp, H. A. J. Michels, *Phys. Rev. Lett.* **1992**, *69*, 494.
- [4] G. Binning, H. Rohrer, Ch. Gerber, E. Weibel, *Phys. Rev. Lett.* **1982**, *49*, 57.
- [5] G. Binning, C. F. Quate, Ch. Gerber, *Phys. Rev. Lett.* **1986**, *56*, 930.
- [6] Y. Nakagawa, *Denshi Kenbikyō* **1997**, *32*, 5.
- [7] H. Schonherr, D. Snetivy, G. Vancso, *Polym. Bull.* **1993**, *30*, 567.
- [8] H. Zhou, G. J. Wilkes, *Polymer* **1997**, *38*, 5735.
- [9] S. N. Magonov, M. H. Whangbo, "Surface Analysis with *STM and AFM*", VCH, Weinheim 1996.
- [10] S. J. Sutton, K. Izumi, Y. Miyaji, K. Fukao, Y. Miyamoto, *Polymer* **1996**, *37*, 5529.
- [11] W. Han, S. M. Lindsay, M. Dlaki, R. E. Harrington, *Nature* **1997**, *386*, 563.
- [12] W. Han, S. M. Lindsay, T. Jing, *Appl. Phys. Lett.* **1996**, *69*, 4111.
- [13] A. P. Smith, J. F. Douglas, J. C. Meredith, E. J. Amis, A. Karim, *J. Polym. Sci., Part B: Polym. Phys.* **2001**, *39*, 2141.
- [14] J.-B. D. Green, *Langmuir* **2000**, *16*, 4009.
- [15] I. Ojima, in: *The Chemistry of Organic Siloxane Compounds*, S. Patai, Z. Rappoport, Eds., John Wiley & Sons, New York 1989.
- [16] B. Marciniec, *Comprehensive Handbook on Hydrosilylation*, Pergamon Press, U.K. 1992.
- [17] R. Neffati, A. Alexeev, J. C. M. Brokken-Zijp, J. Loos, in preparation.
- [18] V. Ferreira, J. F. Douglas, E. J. Amis, A. Karim, *Macromol. Symp.* **2001**, *167*, 73.