V. E. Hanchett
R. H. Geiss

Electron Microscopy of Carbon-Loaded Polymers

It is very difficult to fully characterize the spatial distribution of particles in carbon-loaded polymers using traditional methods. One approach has been to cross-section the polymers, using ultramicrotomy techniques, to a thickness of 80–100 nm. These sections are then examined in a transmission electron microscope (TEM). Unfortunately, the information on particle dispersion obtained from such images is essentially two-dimensional in nature, and therefore does not lend itself easily to a three-dimensional interpretation. By increasing the thickness of the cross sections to 0.5 μm or more, one is able to utilize stereoscopic imaging techniques and obtain a three-dimensional image of the carbon particle dispersion. In this way, the characteristic dispersion of the carbon particles may be fully evaluated along a particular direction in the polymer film. Examples are given of the three-dimensional analyses of polymer films containing different carbon-particle loadings.

Introduction

The morphology of free-standing carbon-black aggregates has been studied using various techniques. Those utilizing electron microscopy techniques include 1) size- and shape-factor calculations, which use aggregate silhouettes seen in the transmission electron microscope (TEM) [1]; 2) stereography (semi-quantitative photogrammetry), which uses the scanning electron microscope (SEM) [2]; and 3) quantitative photogrammetry, which uses the TEM [3]. Photogrammetry, as used here, refers to the science of obtaining analytical information from stereo photographs. Each of these approaches was designed to give information on the three-dimensional morphology of a free-standing carbon-black aggregate. The results of published studies, as well as the principal problems encountered in these experimental studies, are reviewed by Medalia (Ch. 6 of Ref. [4]). Most of the difficulty lies in extrapolating from two-dimensional electron micrographs into the third dimension.

Our interest lies in the much more difficult problem of achieving an understanding of the three-dimensional morphology (i.e., particle and aggregate size and distribution) of a dispersion of these aggregates contained in a polymer matrix. Some results have been reported showing electron micrographs of various types of carbon black in a polymer matrix (for example, see Chs. 1 and 6 of Ref. [4]). However, the same problems persist when one tries to evaluate the three-dimensional nature of dispersions. The reason for this lies both in the method of sample preparation and in the interpretation of the data. The standard method for studying the carbon-polymer composites has been to use ultramicrotomy techniques [5] to obtain very thin cross sections (≈100 nm thick) of the composite specimens and then to examine the sections in a TEM (see Fig. 1). Since the aggregates in the composite have no preferred orientation, this sectioning technique is equivalent to passing a randomly oriented plate, 100 nm thick, through the composite material (see Fig. 2). Because the carbon-black aggregates are usually larger than the thickness of the plate, the plate intersects only portions of the aggregates, cutting some near the middle, while only touching the tips of others close by. It is easy to see why information on the aggregate morphology and dispersion gained in this way can be difficult to interpret, especially if one tries to extrapolate into the third dimension from a two-dimensional electron micrograph.

One solution to this problem is to section the material serially [5]. This technique involves cutting many (e.g., ten to twenty) sequential sections using ultramicrotomy, all sections having the same thickness. These sections must be kept in perfect order so that the three-dimensional structure of the aggregate can be accurately reconstructed after the sections are examined in the TEM. This method is extremely difficult and obviously very tedious. With some materials, because of their cutting characteristics, it is impossible to maintain equal thicknesses of the sections [6].

Another, much easier, solution to this problem is to combine the techniques of ultramicrotomy and stereoscopy of thick sections using the TEM. This technique and our initial investigation of its limitations are discussed in this paper.

Experimental details

The specimens used in this study consisted of polymer films containing dispersions of carbon-black particles. The films were cut into small pieces (2 mm × 4 mm), and the individual pieces were then placed at the ends of flat embedding molds, as shown in Fig. 3. An epoxy-resin mixture was added to encapsulate the film pieces, and the samples were then cured at 60°C for 12 h in order to harden the epoxy. A razor blade was used to manually trim the ends of the hardened blocks to flat-topped pyramids, each top measuring ≈0.5 mm on a side, thus exposing cross sections of the composite films. Each block was mounted in an LKB Ultratome III ultramicrotome and cut into thin cross sections with a diamond knife. (It is important to stress here the need for a high-quality, very sharp knife edge.) After cutting, the sections floated freely on water in a trough attached to the knife. These floating sections were picked up with circular mesh grids (3-mm outside diameter) and examined in a Philips 301 TEM.

All the electron micrographs presented here were taken at an accelerating voltage of 100 keV. Most of the stereo micrographs were taken by tilting the sample ±6° about the normal, usually at a magnification of 7500× on the original micrographs. To obtain high-resolution images from sections having thicknesses greater than 200 nm, it was necessary to use a very small objective aperture, in this case 10 μm in diameter. This reduces chromatic aberration in the image.

Stereo photography consists of taking two photographs of a three-dimensional object under conditions such that when the images are viewed simultaneously, one by each eye of the observer, the three-dimensionality of the object is perceived. There are three methods for taking pairs of stereo photographs: (a) the camera is moved to view a fixed object from two different angles; (b) the object is translated with respect to a fixed camera, yielding two different views of the object; and (c) the object is tilted about an axis parallel to the image plane of a fixed camera, giving the required two different views of the same object. In the TEM, only method (c) is feasible. It is particularly suitable here, however, since the objective lens of the TEM has a large enough depth of focus

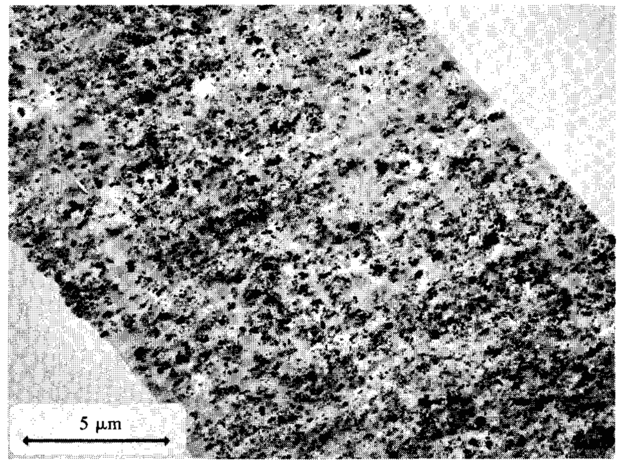

Figure 1 Electron micrograph of an ≈100-nm-thick cross section of Cabot's ®Vulcan XC-72R carbon-polymer composite film. It would be very difficult to understand the three-dimensional morphology of the carbon dispersion from a single image such as this.

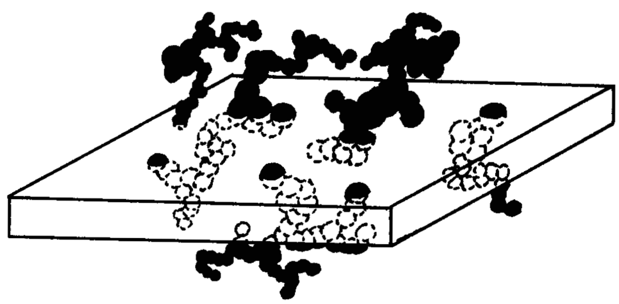

Figure 2 Schematic of a 100-nm plate passing through randomly oriented carbon-black aggregates.

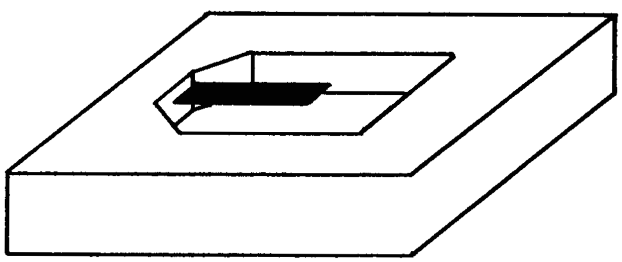

Figure 3 Illustration of carbon-polymer composite film positioned in a flat embedding mold.

that a specimen tilted a small angle relative to the theoretical object plane remains completely in focus. The pair of images photographed in the TEM are often referred to as stereo micrographs or stereo pairs. Stereo micrographs not only give a qualitative three-dimensional impression of the object,

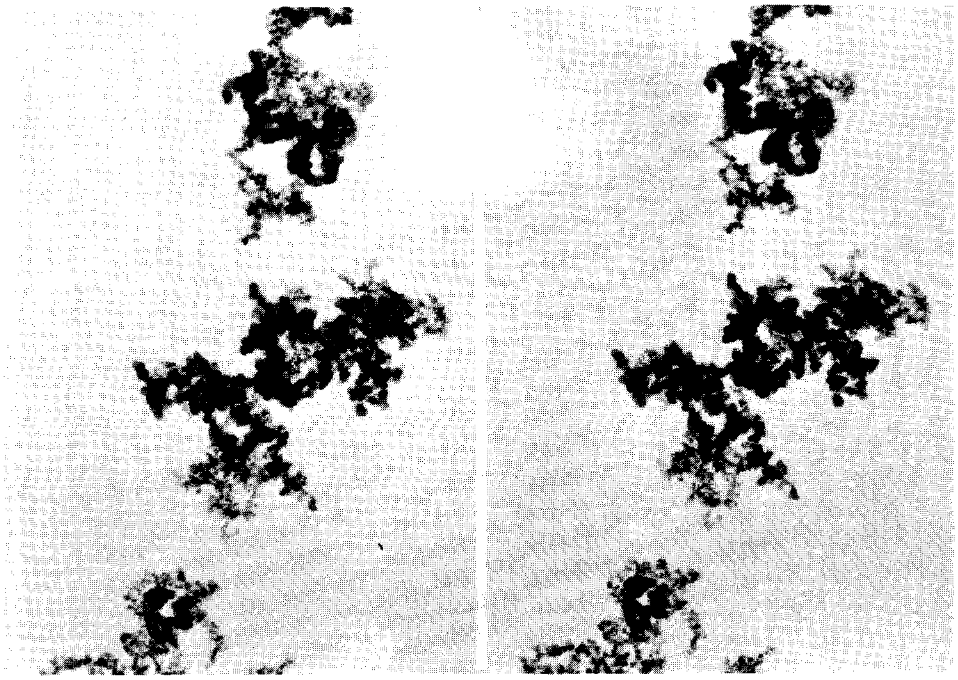

Figure 4 Stereo micrographs of free-standing XC-72R carbon-black aggregates. The measured height of the aggregates is ≈450 nm and the image magnification is 20 000× (2 cm = 1 μm).

but can also provide quantitative information about the thickness of the object or about the vertical distance between objects contained in the same micrograph. Quantitative information is obtained by measuring the parallax, or difference in the positions, between two corresponding points on the two micrographs. The difference in height Δh between the two points is determined from the measured parallax Δy according to the expression

$$\Delta h = \frac{\Delta y}{2M \sin(\theta/2)},$$

where M is the magnification of the image and θ is the angle that the specimen was tilted between the two micrographs. Parallax measurements were used to determine the thicknesses of the polymer-composite cross sections.

Results

In order to gain some familiarity with the three-dimensional morphology of the carbon-black aggregates, the first sample studied was a free-standing carbon-black aggregate. Figure 4 shows a stereo pair of this sample taken in the TEM. The height of the structure is ≈450 nm, as determined from measurements of the parallax between two carbon particles at the extremes of the structure. There are three distinct sizes of carbon particles in the dispersion, having approximate diameters of 20, 30, and 60 nm. It can be seen that particles having the same dimensions tend to form fused aggregates during the manufacture of the carbon black, and that these aggregates are randomly distributed. This specimen was prepared by ultrasonically dispersing in alcohol a small amount of ®Vulcan XC-72R powder (Vulcan is a trademark of Cabot Corporation, Billerica, MA) and by drying a drop of this dispersion on a TEM grid that had a supporting carbon film. Vulcan XC-72R is a somewhat porous conductive furnace black with a high *level of structure*. The terminology "level of structure" refers to the tendency for the carbon particles to form strings or chains in the primary aggregates. That is, the higher the level of structure, the greater the tendency for the individual carbon particles to fuse into chains, and for these chains to form complex branching aggregates. A recognized measure of the level of structure may be obtained by measuring the volume of a liquid, such as dibutylphthalate (DBP), needed to completely fill the void spaces in a known amount of carbon black [7]. This is referred to as the DBP number (ml of DBP per 100 g of carbon black). More meaningfully, the level of structure may also be defined by the weight average number of particles per aggregate [8].

When the pair of micrographs in Fig. 4 is viewed in stereo, it is apparent that the aggregate structure is as large in the z direction as it is in the x and y directions. Therefore, it is important to realize that although carbon-black aggregates are often smaller than those shown here, cross sections of a

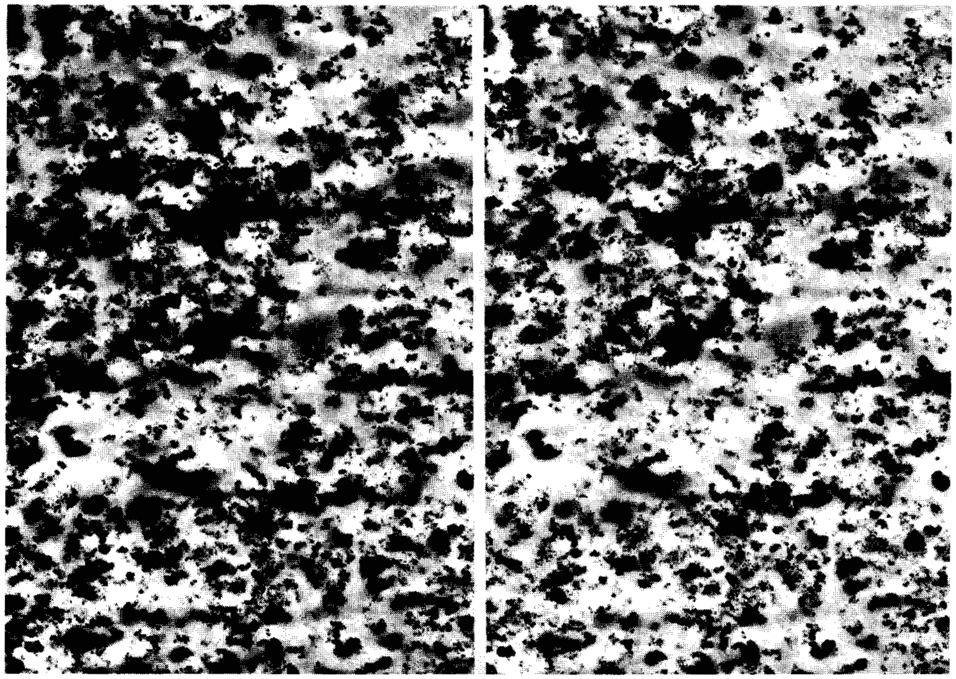

Figure 5 Stereo micrographs of a 150-nm-thick cross section of the XC-72R composite. The three-dimensional morphology of the aggregate dispersion is not completely defined; image magnification is 10 000× (1 cm = 1 μm).

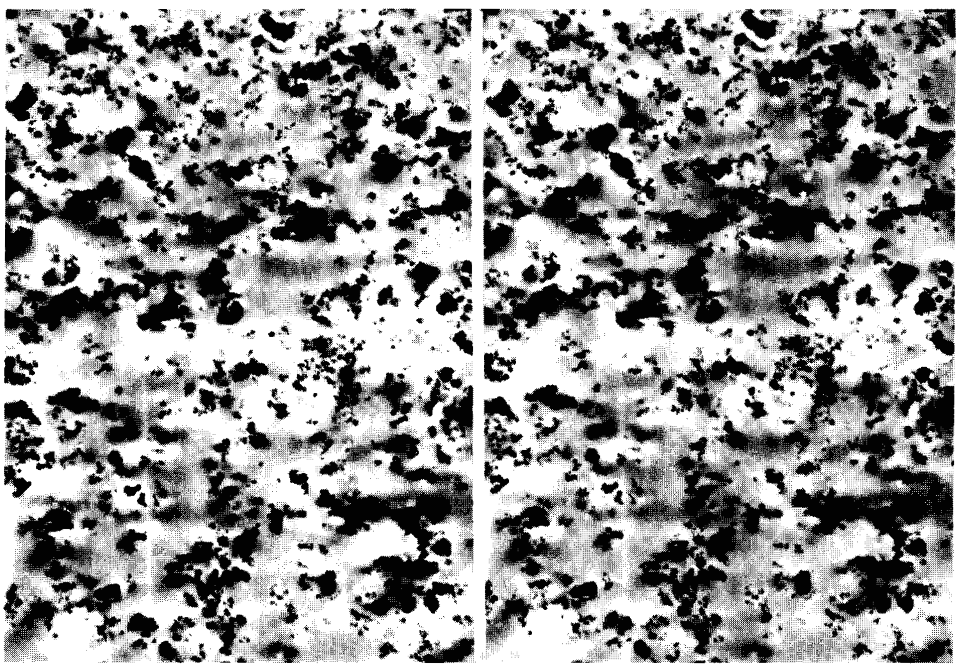

Figure 6 Stereo micrographs of a 150-nm-thick cross section of the Knapsack composite. As in the XC-72R composite shown in Fig. 5, the three-dimensional morphological features are not fully represented. The lower loading of the Knapsack composite is also evident; image magnification is 10 000×.

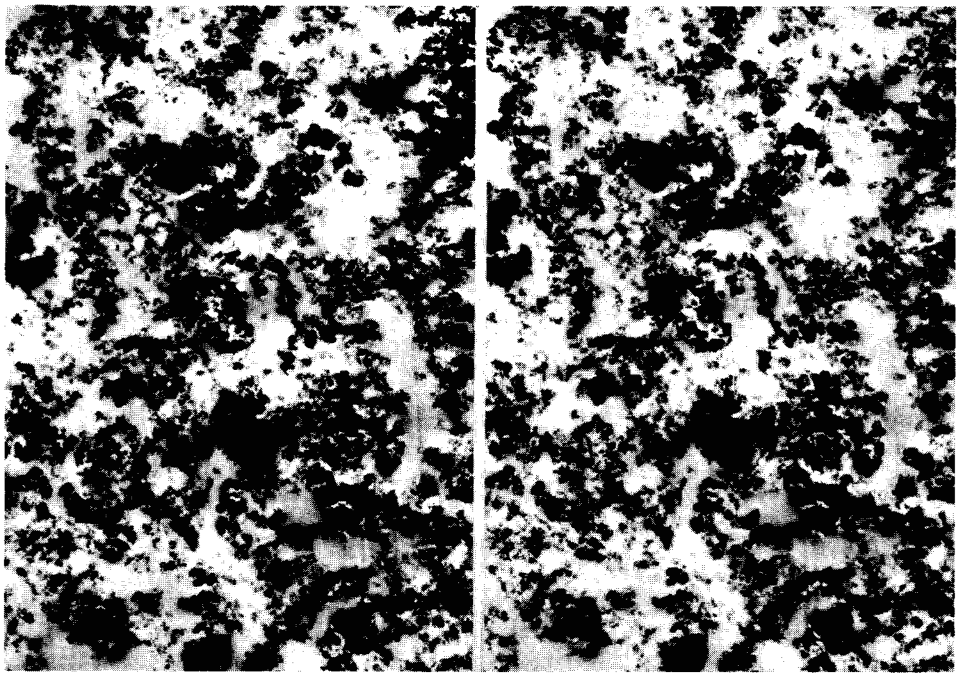

Figure 7 Stereo micrographs of a 300-nm-thick cross section of the Knapsack composite. The three-dimensionality of the aggregate dispersion morphology is more evident in this thicker section. Note especially the formation of strings or chains by the smaller particles; image magnification is 10 000×.

Table 1 Comparison of aggregate characteristics in Knapsack and Vulcan XC-72R carbon blacks.

	Average aggregate area (μm^2)	*Weight average no. particles per aggregate*
Vulcan XC-72R	0.136	500
Knapsack	0.52	1000

carbon-polymer composite should be at least 0.5 μm thick to ensure that the entire aggregate structure is included. This is crucial if one hopes to measure inter-aggregate distances and to trace possible paths of electrical conduction through the composite film. A review of the theoretical and experimental aspects of the electrical properties of carbon-polymer composites may be found in Ref. [9].

Figures 5 and 6 show thin sections of two different carbon-black dispersions: a 27%-by-weight loading of XC-72R in a polymer matrix (Fig. 5) and a 24%-by-weight loading of ®Knapsack carbon black (Knapsack is a trademark of Hoechst, Frankfurt, W. Germany) in the same matrix (Fig. 6). These sections, measured to be 150 nm thick, show little added detail when viewed in stereo. Only small portions of individual aggregates are seen, and possible conduction paths between aggregates are impossible to trace. The Knapsack carbon has essentially two sizes of particles, 40 and 80 nm in diameter, with the smaller-diameter particles typically tending to aggregate in groups of five to ten particles. The XC-72R carbon shows three different-sized particles, as before, with all three in about equal abundance.

Knapsack is an acetylene black, and has a higher level of structure than XC-72R (see Table 1). Electrical conductivities of composites made with Knapsack at the 24% loading level are similar to those of composites made with XC-72R at the 27% loading. Since it has a higher level of structure, the Knapsack carbon forms larger and more complex aggregates than XC-72R carbon. Thus, the inter-aggregate distances in the Knapsack composites are smaller at the same loading level. However, the cross sections shown in Figs. 5 and 6 are too thin to enable one to see these differences in structure.

By increasing the thickness of the cross sections, more of the three-dimensional character of the aggregate structures can be seen, as shown in Figs. 7 and 8. Here, the complex structure of the Knapsack (Fig. 7) begins to emerge in a 300-nm-thick cross section of the composite. Note especially the long chains of small-diameter (≈40 nm) particles weav-

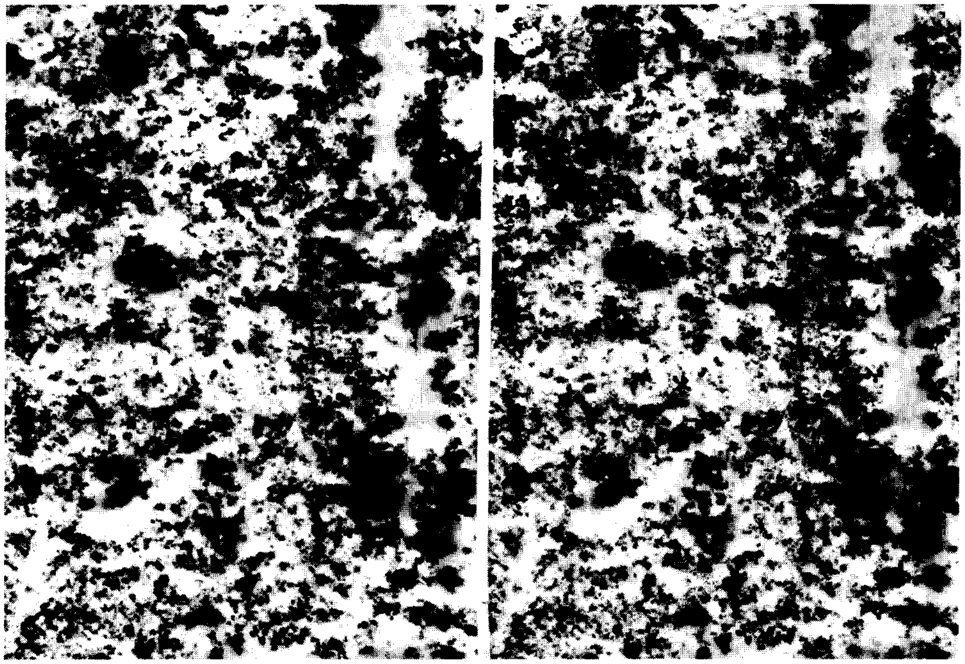

Figure 8 Stereo micrographs of a 230-nm-thick cross section of the XC-72R composite. The three-dimensionality is more pronounced than in Fig. 5. Due to the higher loading of this composite, these micrographs show a higher density of carbon particles than is seen in Fig. 7. Because of the lower structure of the XC-72R carbon, less chain formation by the particles is seen when compared to the Knapsack composite; image magnification is 10 000×.

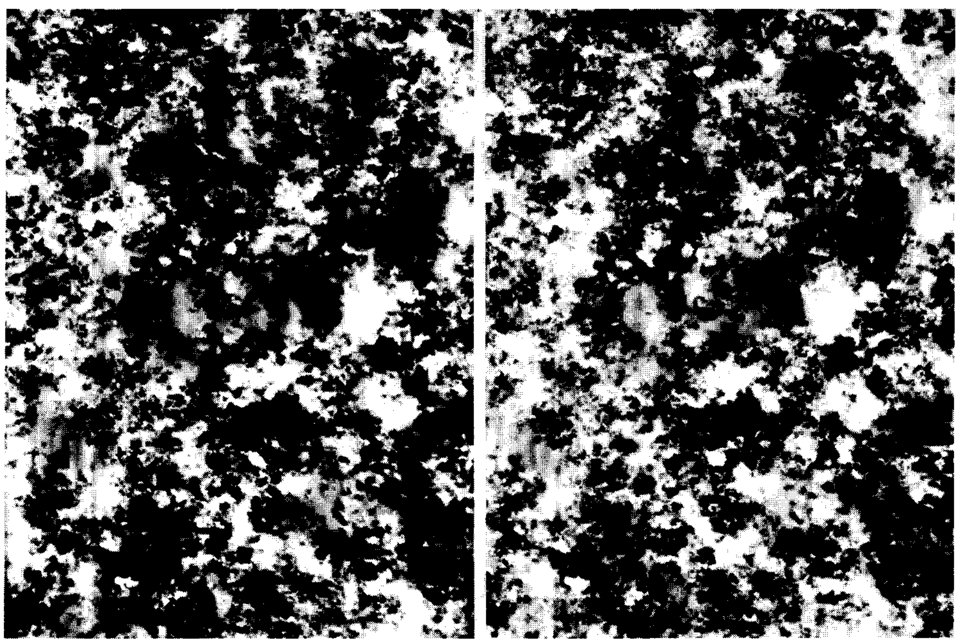

Figure 9 Stereo micrographs of a 600-nm-thick cross section of the Knapsack composite. Image quality is degraded because of the section thickness; nevertheless, a fuller understanding of the aggregate dispersion morphology is possible. The image magnification is 10 000×.

ing from the top to the bottom of the section. The larger particles do not appear to form such chains; they only form clumps which do not go through the entire cross section. Figure 8 is a cross section of the XC-72R composite which is 230 nm thick. Three particle sizes again can be seen, but little of the chain structure seen in the Knapsack is observed. The particles tend to form space-filling clusters containing only similar-sized particles. Because of the higher loading, the greater density of the XC-72R is apparent, even though the cross section of the XC-72R composite is thinner than that of the Knapsack composite.

When the section thickness was increased still further, the density of the XC-72R composite sample became too great to permit clear micrographs at the 100-keV accelerating voltage available on the Philips 301 TEM. However, as shown in Fig. 9, satisfactory images could still be obtained from a 600-nm section of the Knapsack composite. Two particle sizes still dominate, and chain formation is quite evident. Because of the thickness of the polymer matrix, chromatic aberration begins to limit the image quality of such thick sections at 100 keV; still, an increase in the three-dimensional information is apparent.

To study thicker sections, one needs to increase the accelerating voltage of the TEM. To ensure the complete characterization of the carbon aggregate dispersions, the composite cross sections should be ideally at least 0.5 μm thick, and preferably from 1 to 2 μm thick. The application of high-voltage microscopy (>200 keV) to the study of thick sections is currently being pursued [10].

Conclusions

The use of stereographic techniques with transmission electron microscopy to study the morphology of carbon-black aggregates dispersed in a polymer matrix has been evaluated. Although the results presented here have not been completely quantified, a few important observations should be noted. First, specimens obtained by standard ultramicrotomy techniques (100–200 nm) are too thin to give an accurate assessment of the characteristics of the carbon dispersions. Second, doubling the thickness of the cross sections to 250 to 400 nm provides specimens giving a more reliable picture of the three-dimensional morphology of the carbon dispersion. It is still possible to obtain high-resolution micrographs of such sections at 100 keV by using a small objective aperture (i.e., 10 μm) to reduce chromatic aberration. Morphological differences can be distinguished between two composites containing carbon blacks having different levels of structure, where the loading is less than 30 weight percent carbon. Third, the sample thickness ideally should be greater than 500 nm in order to contain whole aggregates in the cross section. However, at 100 keV, image quality suffers, even for a composite with less than 25 weight percent carbon loading. To study composites with higher loadings or greater cross-sectional thicknesses, it is necessary to use electron microscopes with higher accelerating voltages.

References and note

1. A. I. Medalia and F. A. Heckman, "Morphology of Aggregates: 2. Size and Shape Factors of Carbon Black Aggregates from Electron Microscopy," *Carbon* **7**, 567–582 (1969).
2. H. N. Mercer, A. H. Boyer, P. L. Brusky, and M. L. Deviney, "The Third Dimension of Carbon Black Structure," *Rubber Chem. Technol.* **49**, 1068–1075 (1976).
3. H. N. Mercer, A. H. Boyer, and M. L. Deviney, "3-D Carbon Black Primary Structure Characterization Via a New Electron Microscopy-Photogrammetry Technique," *Rubber Chem. Technol.* **52**, 377–386 (1979).
4. E. K. Sichel, *Carbon Black-Polymer Composites*, Marcel Dekker, New York, 1982.
5. N. Reid, *Practical Methods in Electron Microscopy—Ultramicrotomy*, A. Glauert, Ed., American Elsevier Publishing Co., Inc., New York, 1975, Vol. 3, Part II.
6. A. I. Medalia, Cabot Corporation, Concord Road, Billerica, MA 01821; private communication.
7. "ASTM Test D2414-76," in *1982 Annual Book of ASTM Standards, Part 37: Rubber, Natural and Synthetic—General Test Methods, Carbon*, published by ASTM, 1916 Race Street, Philadelphia, PA 19103.
8. A. I. Medalia, E. M. Dannenberg, F. A. Heckman, and G. R. Cotten, "Characterization of New Technology Carbon Blacks," *Rubber Chem. Technol.* **46**, 1239–1255 (1973).
9. E. K. Sichel and J. I. Gittleman, "Electrical Properties of Carbon-Polymer Composites," *J. Electron. Mater.* **11**, 699–747 (1982).
10. *Note added in proof.* Since this paper was written, we have had the opportunity to evaluate the use of high-voltage electron microscopy up to 1.2 MeV for sections up to 4 μm thick. Image contrast is definitely reduced as the accelerating voltage is increased, but not to the point of being a limitation, however. The major limitation is related more to the maximum thickness of the cross section in which the carbon dispersion can be visualized and understood. At the loadings discussed in this paper we have found that a reasonable upper limit to usable cross-section thickness is 1 μm. Since such thickness cross sections can usually be imaged well at 120–200 keV, depending on the optical parameters of the objective lens of the electron microscope, we have not found any advantage in using very high accelerating voltages.

Received January 14, 1983

Roy H. Geiss *IBM Research Division, 5600 Cottle Road, San Jose, California 95193.* Dr. Geiss is a member of the magnetics research project in the Physical Sciences Department in the San Jose Research Laboratory. He joined IBM in 1973. He received a B.S. in physics from Lafayette College in 1959 and a Ph.D. in applied physics from Cornell University in 1967. He had previously worked at the Carpenter Steel Company, Reading, Pennsylvania, and at the University of Virginia. He is a member of the American Crystallographic Association and the Microbeam Analysis Society.

Virginia E. Hanchett *IBM Research Division, 5600 Cottle Road, San Jose, California 95193.* Ms. Hanchett is a member of the conducting polymers project in the Physical Sciences Department at the San Jose Research Laboratory. She joined IBM in 1977 after completing a certificate in electron microscopy at San Joaquin Delta College. She previously attended the University of California at Davis. She is a member of the Microbeam Analysis Society and Electron Microscopy Society of America.