Nano-structural observation of carbon black dispersion in natural rubber matrix by three-dimensional transmission electron microscopy

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Generally, commercial rubber products are produced as composites with inorganic fillers of nanometer size (nano-fillers), and form a group of typical soft materials. For example, pneumatic tires for passenger cars and for heavy-duty usages (such as aircrafts and heavy-weight trucks), and rubber bearings for a seismic isolation system, are made from natural rubber (NR) with or without blending a synthetic rubber in conjunction with a suitable reinforcing nano-filler and a sulfur/accelerator cure system for crosslinking [1]. So far, carbon black has been most widely used as a reinforcer for rubbers [1, 2]. This is the reason for black color of many rubber products as typically recognizable from automobile tires.

In material design of rubbery nano-composites, dispersion of the nano-filler in amorphous rubbery matrix has been known to be most important to specify the structure and properties of the product [2]. On this line, rubber technologists have paid much attention on the dispersion of carbon black, and various analytical methods have been used for elucidating its dispersion in the rubbery matrix, among which transmission electron microscopy (TEM) has been assumed to be the most powerful and direct technique [3]. However, not only TEM but also most of the optical microscopies have projected a three-dimensional (3D) structural body onto a two-dimensional (2D) plane. The structural informations on the thickness direction (z-direction) of the sample are difficult to acquire by these microscopic methods.

For 3D structural observation, a series of TEM images at various angles should be obtained by a single-axis or, in a few cases, a conical tilting of the sample, and 3D images are reconstructed by the backprojection of 2D-TEM images [4]. With a recent development of computerized tomography, 3D-TEM is developed into electron tomography, which is establishing as a powerful tool for the elucidation of morphology in 3D space first in bioscience [4, 5], and more recently in materials science [5–8]. The present authors have reported 3D nano-structure of particulate silicas in NR matrix for the first time [8].

In this study, carbon black-filled NR vulcanizates are subjected to 3D-TEM observation in order to elucidate the characteristics of carbon black mixed in NR using an electron tomography technique. Several techniques are currently used or are under development for electron tomography applications. Here, rubbery samples are the object, which are basically amorphous, thus a bright-field electron tomography is used for 3D-TEM imaging [4, 8]. This is the most established technique in terms of both hardware and software, while the others, e.g. high-angle annular dark-field (HAADF) imaging is still actively under development [9, 10], and may be applicable to crystalline samples. In addition, this technique uses only a part of irradiated electron for imaging, which is not favorable for measuring number of (2D) TEM images for a 3D image reconstruction. This holds especially on organic polymeric materials, which are not much resistant to electron beams [11].

This communication is reporting on 3D-TEM/electron tomography observation of a carbon black dispersion mixed in NR. Vulcanizates were prepared as follows: NR (RSS No. 1) was masticated and mixed with carbon black (HAF grade, N330) and the other reagents for curing on a two-roll mill. The total mixing time was between 20 and 30 min, depending on the loading amount of carbon black. The compounds (mixes ready for curing) are subject to press-curing in a mold at 150 °C for 20 min. The recipe for preparation of NR vulcanizates was as follows: in parts per one hundred rubber by weight (phr), 1 phr of stearic acid, 5 phr of ZnO, 2 phr of sulfur, 1 phr of cyclohexylbenzothiazyl sulfenamide and 10, 20, 30, 40, 50, 60 or 80 phr of carbon black. All ingredients were commercially available ones, and used after a drying procedure. In case of carbon black, it was at 120 °C for 2 hr. In the sample code, NR represents an NR vulcanizate, and the following figures represent phr of mixed carbon black, e.g. NR-80 is an NR vulcanizate with 80 phr HAF black.

Electrical volume resistivity of NR vulcanizates was measured in accordance with JIS K6911. 3D-TEM measurements were performed on a TECNAI G2 F20

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(FEI Co.). TEM images were taken by the bright field method. It is noted that the NR vulcanizates were subjected in advance to the extraction by organic solvents for removing Zn compounds. The remaining Zn compounds, which were derived from ZnO (one of the additives for sulfur curing), scattered electron beam to result in a smeared TEM image. The details of this effect will be published separately [12]. After this treatment, thin vulcanizate samples of ca. 200 nm thickness were prepared using an ultra-microtome FC-S (REICHERT Co.) equipped with a cryo-system in liquid nitrogen. For 3D-TEM observation, 2D-projection images with tilt angles ranging from -65° to $+65^\circ$ with 2° increment (total 66 TEM images) were automatically acquired at 200 kV by a CCD camera using the attached software in the TECNAI G2 F20. The 2D-projections were aligned by using "IMOD" [13–15]. Using a quick automatic observation system combined with a Fourier reconstruction method based on the electron tomographic technique [4, 16, 17], 3D mass density distributions of the samples were calculated by the backprojection of the 2D images, and visualized by using "Amira" of TGS Inc. [18, 19]. The data were further binarized based on reference [20], after which the carbon black inclusions were presented as volume renderings of the reconstructed mass density distribution.

The 3D nano-scale morphology of carbon black in NR matrix is observed as shown in Fig. 1 a–c, where the contrast was reversed in order to make the 3D images clearer and the white parts in the space were identified as carbon black particles. These images are one set of perspective views from one direction. The carbon black is composed of many aggregates of various sizes. It is noted that most carbon black particles are aggregated even in NR-10 where the volume fraction of carbon black is quite low. For easy recognition of the dispersion of carbon black particles, neighboring particles (aggregates) were painted in color as shown in Fig. 2 a–c. It must be noted that each colored block represents either an isolated primary carbon particle or an aggregate, and various sizes of aggregates were observed. In the 3D-TEM images from various directions, many aggregates of carbon black in NR matrix were clearly detected. This observation is achieved by using 3D-TEM/electron tomography for the first time. Much more aggregates were found in NR-80 than in NR-10 or NR-20, of course, but it should be noted that 10 phr or 20 phr of carbon black (in terms of volume fraction only 0.050 or 0.095) in NR is strongly aggregated like the one in NR-80 (volume fraction, 0.296).

In Fig. 3 is shown the volume resistivity (ρ_v) of NR vulcanizates against carbon black loading at room temperature. The resistivity decreased much with the increase of carbon black, and it seemed to be approached a saturated value at 50 phr loading (volume fraction, 0.208). This is an example of well-known percolation-like behavior, and the value 0.208 in terms of carbon black volume fraction is near to the reported ones, i.e. between 0.13 and 0.17 in NR [21]. This should be related with structural factors of carbon black dispersions. From three-dimensional nano-structural images as shown in Fig. 1 or Fig. 2, average distance between two nearest neighboring aggregates (D_n) was calculated and displayed in Fig. 4. The distance D_n shows a

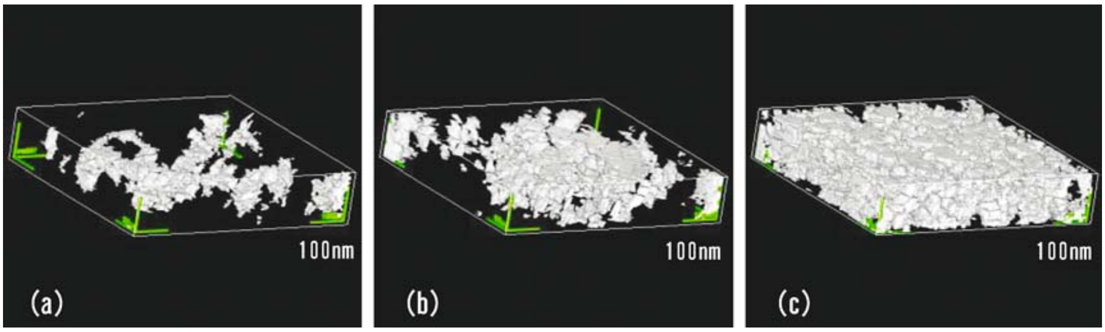

Figure 1 Volume rendered views of the reconstructed mass density distribution of the carbon black inclusion in NR vulcanizates. Frame is shown in reconstructed perspective geometry (length and width: 614 nm, thickness: 181 nm). Bar for each direction shows the distance of 100 nm. (a) NR-10, (b) NR-20 and (c) NR-80.

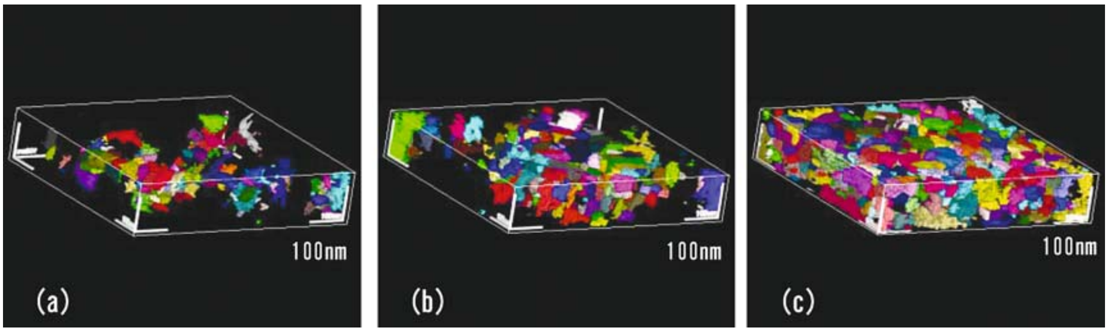

Figure 2 Colored volume rendered views of the reconstructed mass density distribution of the carbon black inclusion in NR vulcanizates. The individual carbon black particles and aggregates were isolated from the neighbors by coloring. Frame is shown in reconstructed perspective geometry (length and width: 614 nm, thickness: 181 nm). Bar for each direction shows the distance of 100 nm. (a) NR-10, (b) NR-20 and (c) NR-80.

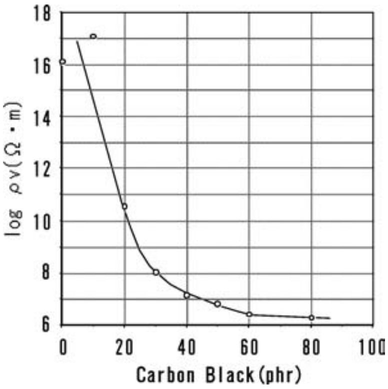

Figure 3 ρ_v of NR vulcanizates against carbon black loading at room temperature.

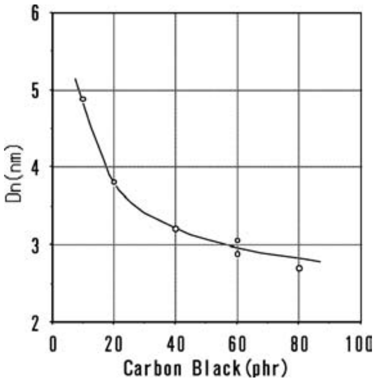

Figure 4 D_n of NR vulcanizates against carbon black loading at room temperature.

very similar behavior to that of the resistivity (Fig. 3). Again, 50 phr seems to be a threshold value. D_n at 50 phr is ca. 3 nm, which is assumed to be the distance that electron, may possibly hop in NR matrix at room temperature. Similar results on carbon black (N234) in polyisobutylene were reported using atomic force microscopy (AFM, dynamic mode) giving threshold value of 0.09 [22]. However, the results were on distance of center-to-center and based on only pseudo three dimensional data.

The concept of 3D-TEM is not new, rather in bioscience area it has already become more or less a conventional technique. It has recently been focused as a powerful analytical method in material science area with the development of electron tomography. Present study on the soft natural rubber-based nanocomposites would be useful for the development of nano-technology, especially of soft nano-composites. Further details will be reported in our following papers, especially on the more detailed three-dimensional nano-structure of carbon black aggregates in NR matrix and the relationship between the nano-structure and electrical and mechanical behaviors.

Acknowledgments

Authors are grateful to Dr. J. Ye, Messrs H. Sawabe, N. Kojima, T. Suda, Ms. M. Gonda, and M. Nishioka (Nissan Arc, Ltd.) for their experimental assistance and stimulating discussions. Thanks are also due to the financial supports for S. K. and Y. I. by a Grant-in-Aid for Science Research (B) (2) No. 15404011 from JSPS and the Research Grant from President of KIT (2004), respectively.

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Received 24 August 2004
and accepted 6 January 2005