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Distribution of Carbon Black in SBR

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Synopsis

The distribution of HAF carbon black in SBR was studied with the electron microscope and Fraunhofer diffraction. The interparticle distance between black aggregates is 8000 Å at 20 phr and 7000 Å at 40 phr, but above 60 phr it spreads broadly in the vicinity of 4000 Å. The size of black aggregates at 20 phr extends from 300 Å to 3000 Å, and the average diameter is 1200 Å. At 40 phr and 60 phr, black trends to aggregate more than at 20 phr and the average diameter is about 1500–1600 Å; the maximum diameter exceeds 5000 Å. In a black aggregate, there are about 40 spherical particles independently of filler concentration. From the relation between the size and interparticle distance, the connection of black aggregates initiates at 40 phr level and affects the physical properties of filled rubber.

INTRODUCTION

The physical properties of filled rubber are affected mainly by the distribution and structure of carbon black. Many authors have reported the properties of carbon black, e.g., specific surface area, particle diameter, and structure;[1–7] however, carbon black in rubber has so far only been observed qualitatively by electron microscopy,[8–10] and there are no reports of the interparticle distance of black or of the dimensions. An x-ray technique is useful for the analysis of the microstructure of polymeric materials, but in this case the wavelength of x-rays is very short and Fraunhofer diffraction[11] is more suitable for the distribution of black in rubber.

EXPERIMENTAL

The sample was SBR-1500, a butadiene–styrene random copolymer of 23.5 wt % styrene content. The filled carbon was HAF black made by Tokai Carbon Co. Ltd. The average particle diameter was 280 Å; the DBP absorption value, 115 cc/100 g; iodine number, 90 mg/g. This HAF black consists of aggregates of several particles fused together. The recipes and molding conditions were described elsewhere.[12]

Electron microscopy was carried out by a direct transmission method with ultrathin films of filled rubber. The electron microscope was a Nippon Denshi JE7A type.

Since the diameter of the mass of black in rubber is larger than several hundred

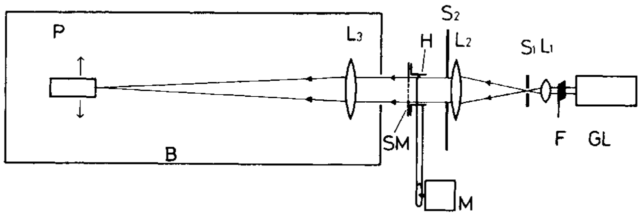

Fig. 1. Apparatus for Fraunhofer diffraction.

angstroms and interparticle distance is more than 1000 Å, small-angle x-ray scattering is not applicable for filled rubber.[11] Furthermore, a laser beam cannot get through the thin film of filled rubber. Because of these reasons, the electron micrograph was used for a sample mask of Fraunhofer diffraction.

The apparatus in Figure 1 is used for Fraunhofer diffraction. The light source (GL) is a He–Ne gas laser made by Nakamura Rika, type KNL-801, power 1.4 mW, wavelength 6328 Å. A flag (F) chops the laser beam with a frequency of 28 c/s, since the intensity of scattered light was detected by a photoelectric cell with an alternating-current amplifier. The laser beam passing through the lens (L_2) is parallel and reduced to the size of a sample mask. The beam passes the sample mask (SM) on a sample holder (H) which is spun by a motor (M). The rotation of the mask makes the diffraction intensity average in all azimuthal angles. The beam next goes through a black box (B) and is gathered by another lens (L_3). The focal length of L_3 is 100 cm. The diffraction intensity was counted by a photometer (P) on the focal plane of L_3 at a speed of 1°/16 min. The receiving slit is a circle 0.7 mm in diameter.

The sample mask was made as follows. Figure 2 is a sectional photograph of SBR filled with 40 phr. Carbon black and the white traces of black were painted by India ink. The area of this microphotograph is about $10^5 \times 10^5$ Å^2, and there are 1000 masses of black at 20 phr, 2500 at 60 phr. This photograph painted in India ink was overexposed, so that black only was left over. Next, four positive films were collected and photographed again. Therefore, the number of black masses is four times as large (see Fig. 3). The negative film of this photograph is the sample mask. On a sample mask, 10^4 Å corresponds to 0.3945 mm. The error of hand writing is small and can be neglected, since the interparticle distance of the black mass is not affected by the inaccuracy of the outlines of black.

RESULTS AND DISCUSSION

Figure 4 is the Fraunhofer diffraction pattern of SBR filled with 40 phr. Figure 5 shows the equatorial scattering intensity curves of filled rubber. In this figure, the standard lines of intensity were raised for 60, 80 phr.

Up to a loading of 40 phr, there is only one peak at a low angle on each curve. One peak indicates that black masses distribute at comparatively equal distances from each other. Above 60 phr, there are several shoulders, and the distance between particle centers spreads over a wide range. Table I shows the interparticle distance calculated from the peaks or shoulders by the following equation:

$$d \sin \theta = n\lambda \tag{1}$$

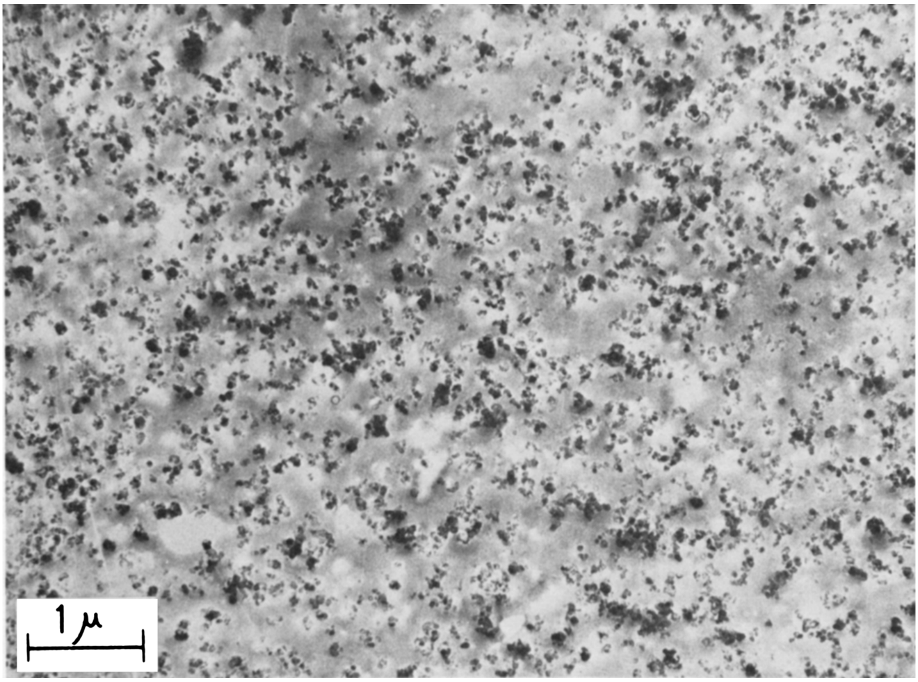

Fig. 2. Electron micrograph of a section of SBR filled with 40 phr.

where d is the interparticle distance, θ is the diffraction angle, n is an integer, and λ is the wavelength of the laser. The maximum distance at each loading decreases linearly, as shown in Figure 6. On the intensity curves, there are multiple peaks or shoulders, but these are not the higher-order reflections of a low-angle reflection. At 20 phr, there is no second-order reflection, although the first-order reflection is a very strong peak. Furthermore, there is no regularity between the position of a peak or a shoulder.

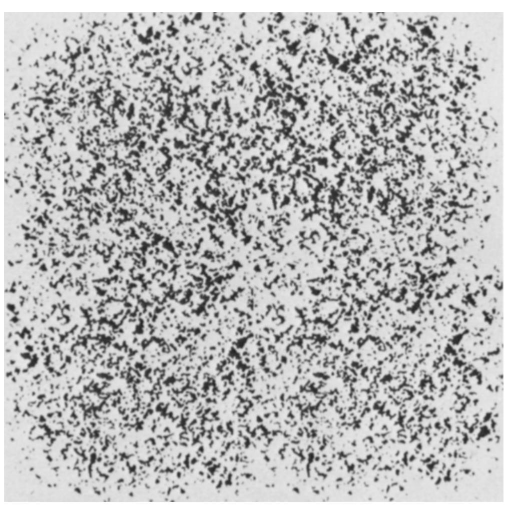

Fig. 3. Magnified positive film of a sample mask (40 phr).

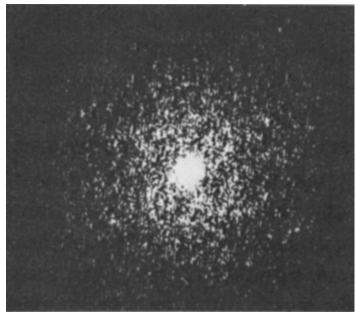

Fig. 4. Fraunhofer diffraction pattern of SBR filled with 40 phr.

8000 Å at low loading of black corresponds to the distance between large masses of black on an electron micrograph. The distance between large masses decreases with the loading of black, and an interaction between close distances, in the vicinity of 4000 Å, develops. The shoulders corresponding to about 4000 Å are weak and have changeable positions and numbers. Above 60 phr, there are only weak shoulders, and the particle distance spreads widely in the vicinity of 4000 Å.

Next, the dimension of the black mass must be investigated. Figure 7 shows the frequency distribution of an apparent diameter measured on an electron micrograph (×25000). The apparent particle diameter D is defined with eq. (2):

$$D = (a + b)/2 \tag{2}$$

where a is the length of the long axis of black aggregates and b is the short axis. A spherical particle of black in this experiment has a diameter of about 280 Å

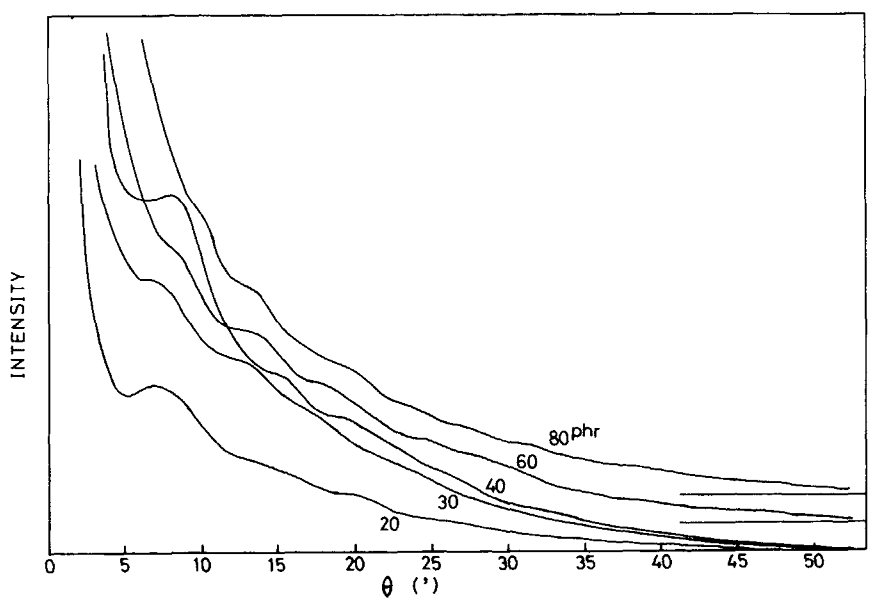

Fig. 5. Scattering intensity curves of filled rubber.

TABLE I

Black loading, phr	Particle distance, Å		
20	8180	2730	
30	8440	4400	
40	7035	3645	2885
60	6570	4220	3100
80	5380	4155	2800

and HAF black has the structure. In this case, D is about 700–800 Å. The distribution peaks at small D values attribute their effect to the structure of HAF black. At 20 phr, the diameter spreads from 300 Å (one particle) to 3000 Å. The frequency decreases quickly with increase in D value. At 40 phr, the diameter D shifts slightly to a larger value than at 20 phr, with a maximum diameter of 5000 Å. At 60 phr, the distribution of D is the same as at 40 phr. The average diameter $\overline{D}$ is 1200 Å at 20 phr, 1600 Å at 40 phr, and 1500 Å at 60 phr.

The number of spherical particles in a black aggregate may be estimated as follows. In an electron micrograph, there are about 1000 black aggregates in a volume of $10^5 \times 10^5 \times 500$ Å^3 at 20 phr, i.e., 2×10^{14}, in unit volumes. At 20 phr, black occupies 8.73 vol % of filled rubber,[12] so that there are 7.6×10^{15} spherical particles (280 Å diameter) in a unit volume. The number of the spherical particles in a black aggregate is calculated as follows:

$$7.6 \times 10^{15}/2 \times 10^{14} = 38$$

Another method to investigate is the calculation with the average diameter $\overline{D}$. At 20 phr, $\overline{D}$ is 1200 Å; accordingly, there are about 4.3 particles in one side, namely, about 80 particles in one cube. Table II shows the number of particles in a black aggregate calculated similarly to 20 phr. But the particle number from $\overline{D}$ varies broadly, depending on $\overline{D}$, and is overestimated. A reliable number of particles will be about 40.

Let us examine the relation between the size of a black aggregate and the interparticle distance. At 20 phr, the frequency of the contact between black aggregates is very small, since the maximum diameter is much smaller than the interparticle distance, i.e., 3000 Å and 8000 Å, respectively. In an electron mi-

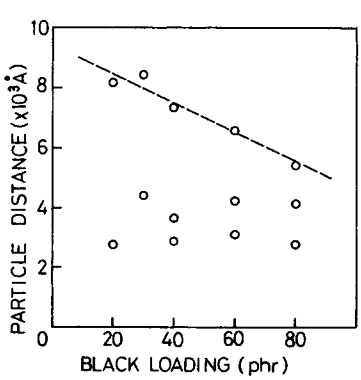

Fig. 6. Interparticle distances.

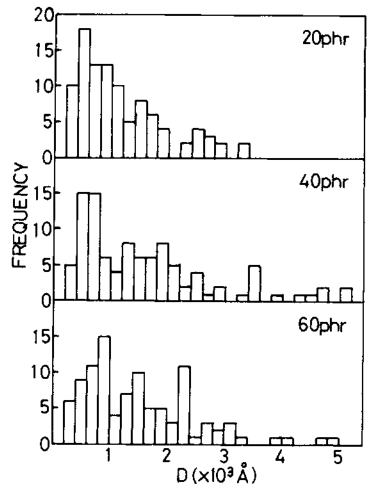

Fig. 7. Frequency distribution of an apparent diameter.

crograph, black aggregates separate from each other completely. At 40 phr, the maximum D is about 5000 Å, and the interparticle distance is 7000 Å. Black aggregates assume a stretched, ragged shape rather than a sphere, so that the long axis of the aggregates easily reaches twice the maximum D. At 40 phr, it initiates contact between black aggregates. At 60 phr, the maximum D is about 5000 Å and the interparticle distance is mainly in the vicinity of 4000 Å. Reflecting upon the stretched form, carbon black particles connect with each other everywhere.

The connection between black aggregates affects the physical properties of filled rubber. The electrical resistance of this rubber decreases abruptly at 40 phr,[13] and this indicates that the sequence of black aggregates is completed in part. In the case of silver particles in the matrix of bakelite, electrical resistance decreases at 35 vol % of silver.[14] Filled rubber with HAF black changes its property of conductor effectively at about 13 vol % (40 phr level) because of the stretched form of the aggregates. The energy component of the total stress of filled rubber increases also suddenly at 50 phr.[15] The rubber elasticity is the entropic elasticity, but the sequence of black, directly or through bound rubber, contributes to the energetic component of the stress. The black loading which changes the physical properties of filled rubber corresponds to the beginning of the sequence of black aggregates, i.e., 40 phr level.

TABLE II

Black loading, phr	Number of particles in an electron micrograph ($10^5 \times 10^5 \times 500$ Å^3)	Volume % of filler	Number of particles
20	1000	8.73	38 (80)[a]
40	1500	16.0	46 (190)
60	2500	22.24	39 (145)

[a] Number of particles from $\overline{D}$.

CONCLUSIONS

The interparticle distance between black aggregates in rubber was estimated by Fraunhofer diffraction with the mask of an electron micrograph of filled rubber. Up to 40 phr, the distribution of interparticle distance has a sharp peak centered at 8000 Å with 20 phr and at 7000 Å with 40 phr. Above 60 phr, the interparticle distance distributes broadly in the vicinity of 4000 Å. The size of black aggregates at 20 phr extends from 300 Å (one particle) to 3000 Å, and the average diameter is 1200 Å. Above 40 phr, black trends to aggregate more than at 20 phr, and the average diameter is about 1500–1600 Å, the maximum diameter being 5000 Å. In one black aggregate, there are about 40 spherical particles. The relation between the size and interparticle distance shows that isolated black aggregates are distributed in rubber under 40 phr and that at 40 phr they begin to connect partly with each other. Above 60 phr, a network of chains of black develops everywhere. The connection of black aggregates at 40 phr level corresponds to the abrupt change of physical properties of filled rubber.

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