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SCATTERING AND CONTRAST VARIATION

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# CARBON BLACK STRUCTURE AND ASSOCIATIONS IN FILLED RUBBER ASSESSED BY SMALL-ANGLE NEUTRON SCATTERING AND CONTRAST VARIATION

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## Introduction

Carbon black (CB)-elastomer composites are examples of heterogeneous microphases of matrix and reinforcement. CB consists of a hierarchy of structures in which spheroid particles are fused into aggregates which associate by van der Waal's forces to form agglomerates. There is a substantial body of work on CB structures and CB-elastomer composites.<sup>1</sup> Even so, over 90 years after the discovery of the effect of CB on rubber, there is controversy on what the reinforcing mechanism is. Ideas center on particle size and surface structure relating to associations with the elastomer, aggregate shape and the extent and morphology of agglomerates. In the interactions with the elastomer, the strength of the CB-polymer binding and polymer chain configuration and entanglements are considered highly important. An understanding of the mechanical properties of reinforced rubber requires a picture of the structure of the material *in situ*.

Our objective is to provide structural information on CB and CB-elastomer composites. This includes the morphology and internal structure of CB particles and aggregates; the association of aggregates in rubber composites; the associations of elastomer and carbon blacks. In this paper, we review our results on the structure of aggregates as probed by neutrons.

## Experimental

**Small-angle Neutron Scattering.** The physical concept behind small-angle neutron scattering (SANS) is the same as for electrons or x-rays, except that neutron scattering is almost entirely from nuclei. These interactions are very small, consequently the neutrons are relatively more penetrable than an electron or an x-ray. Because of this, SANS provides nanoscale and molecular scale structural information in the bulk. Thus, one can study carbon black suspended in fluids or *in situ* with elastomers. In contrast with electrons or x-rays, the neutron scattering length,  $b$ , the measure of scattering amplitude, is not monotonic with atomic number (Table 1). Consequently, neutrons are able to see the distribution of light elements. There are often significant differences in  $b$  from isotopes of the same elements: hydrogen and deuterium (Table 1) is particularly important in this regard.

Table 1. Scattering Lengths of Some Light Elements and Hydrogen Isotopes

Element	Scattering length (fm)
<sup>1</sup> H	-3.7403
<sup>2</sup> D	6.675
C	6.6484
N	9.2600
O	5.8050

Sample structure in the SANS experiment is fluctuations in the scattering length density,  $\rho(\mathbf{r})$ , with position in the sample,  $\mathbf{r}$ , which is sum of the  $b$ 's of the atoms (Table 1) in a volume at  $\mathbf{r}$  divided by that volume. Thus,  $\rho(\mathbf{r})$  reflects density and chemical composition variation in the sample. The scattered intensity,  $I(Q)$ , is the differential cross section per unit mass ( $\text{cm}^2 \text{mg}^{-1}$ ) as a function of the magnitude of the scattering vector,  $Q$ . For elastic scattering,  $Q = (4\pi/\lambda) \sin \theta$ , where  $\lambda$  is the neutron wavelength and  $2\theta$  is the scattering angle. The  $I(Q)$  is related to  $\rho(\mathbf{r})$  by,

$$I(Q) = K \left\langle \left| \int \rho(\mathbf{r}) \exp(-i\mathbf{r} \cdot \mathbf{Q}) d\mathbf{r} \right|^2 \right\rangle. \quad (1)$$

For particles not correlated in position and orientation, the expression in the angle brackets is the spherical averaged form factor,  $\langle P(Q) \rangle$ . The constant,  $K$ , in Eq. (1) is proportional to  $\Delta\rho^2$ ,  $\Delta\rho = \rho_p - \rho_s$ , which is the contrast between the average scattering length density of the particle,  $\rho_p$ , and the background scattering length density,  $\rho_s$ .

LQD at the Manuel Lujan Scattering Center was used for the SANS measurements. The values of  $Q$  accessible to LQD probes length scales from about 10 to several 100 Å (length scales  $\sim Q^{-1}$ ).

**Contrast Variation.** SANS provides a unique capability to change  $\Delta\rho^2$  by suspending the sample in fluids having different weight fractions of deuterated solvent,  $f_{C_6D_{12}}$ . Using this method of contrast variation,<sup>2,5</sup> we studied CB suspensions or CB-elastomer composites (prepared as "bound" rubber<sup>4</sup> remaining after extensive high temperature extraction with good solvents) back-filled with various cyclohexane mixtures, each having different  $f_{C_6D_{12}}$ . An experimental CB, HSA, was used for these studies.

**Particle Structure Characterization.** The size,  $R$ , and mass,  $M$ , of the particles can be determined by Guinier approximation,

$$I(Q) = \frac{\phi V_p^2 \Delta\rho^2}{M} \exp\left(-\frac{Q^2 R_g^2}{3}\right), \quad (2)$$

which applies over the domain  $Q < R^{-1}$ . In Eq. (2),  $\phi$  is the volume fraction of particles,  $V_p$  is the particle volume, and  $R_g$  is the radius of gyration. The models can be refined by fitting the scattering to  $\langle P(Q) \rangle$  using Eq. (1).

Particle areas per unit mass,  $S$ , are measured over length scales,  $QR \gg 1$ , where the scattering can be described as a Porod-law,

$$I(Q) = 2\pi S \Delta\rho^2 Q^{-4}. \quad (3)$$

When there are particle interactions, so that the positions and or orientations are correlated in some way, it is necessary to reinterpret Eq. (1) as

$$I(Q) = S'(\mathbf{Q}) \langle P(\mathbf{Q}) \rangle. \quad (4)$$

Here,  $S'(\mathbf{Q})$  is the structure factor, which arises from particle correlations.

Scattering is a quadratic function of contrast:

$$I(Q) = \Delta\rho^2 I_\Omega(Q) + \Delta\rho I_{\Omega\zeta}(Q) + I_\zeta(Q). \quad (5)$$

The basic scattering functions,  $I_\Omega(Q)$  and  $I_\zeta(Q)$ , arise, respectively, from the solvent-excluding parts of the structure,  $\Omega(\mathbf{r})$ , and from the internal fluctuations,  $\zeta(\mathbf{r})$ . The function,  $I_{\Omega\zeta}(Q)$ , is the scattering from correlations between  $\Omega(\mathbf{r})$  and  $\zeta(\mathbf{r})$ . In this representation, the structure is defined as the sum of the shape and internal structure terms; thus,  $\rho(\mathbf{r}) = \rho_s + \Delta\rho\Omega(\mathbf{r}) + \zeta(\mathbf{r})$ . Eq. (5) is an approximation for heterogeneous systems, such as studied here.<sup>2,3</sup>

The Guinier analysis of Eq. (5) yields the contrast dependence at  $Q = 0$

$$(I(0))^{1/2} = \sqrt{\frac{\phi}{M}} V_p \Delta\rho, \quad (6)$$

and the contrast dependence of  $R_g$ ,

$$R_g^2 = R_c^2 + \frac{\alpha}{\Delta\rho} - \frac{\beta}{\Delta\rho^2}. \quad (7)$$

In Eq. (7),  $R_c$  is the  $R_g$  of  $\Omega(\mathbf{r})$ ,  $\alpha$  is proportional to the second moment of  $\zeta(\mathbf{r})$  and  $\beta$  is proportional to the first moment-squared of  $\zeta(\mathbf{r})$ .

## Results and Discussion

**Carbon Black Structure.** The Guinier analysis (Eqs. (2), (6) and (7)) for HSA is summarized in Table 2 ( $\beta \approx 0$ ). Three conclusions are drawn from

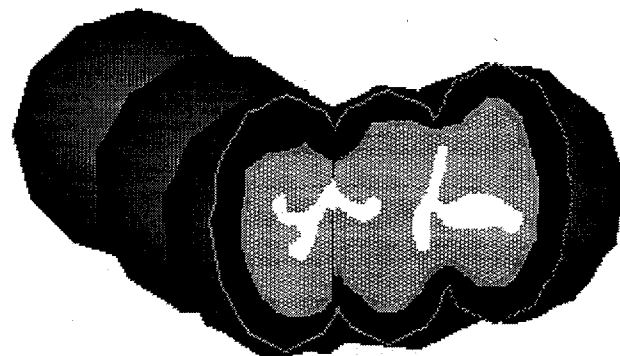


Figure 1. Schematic of the Carbon Black Aggregate Structure. The structure consists of a quasi-linear array of fused, spheroid particles. The outer shell of the structure (black) consists of graphitic carbon crystallites, with a core (gray) of less dense void-filled (white) carbon.

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the large positive value of  $\alpha$ . First, it shows that the aggregates have a shell-core structure, consistent with TEM<sup>1</sup> and STM<sup>2</sup>, with a graphitic outer shell of density (Fig. 1). Second: the core of the particle has an amorphous carbon-like density, but with voids. Third: the amorphous core is continuous through the aggregate.  $I_a(Q)$  for the aggregates, determined using Eq. (5), was fitted to a prolate ellipsoid of revolution 290 Å by 1500 Å, showing that the aggregates on average are rodlike, having little branching, with 5 to 6 particles. This is consistent with stereo-TEM studies.<sup>6</sup>  $I_a(Q)$  obeys Porod's Law (Eq. (3)); thus, the aggregates have smooth surfaces on length scales greater than 10 Å.  $S$  can be measured (Table 2). Production CB's, N299, N330 and XLH81 show the same shell-core structure found in HSA.<sup>8</sup>

Table 2. Structural Parameters for HSA

$V_p$ (nm <sup>3</sup> )	$\bar{\rho}_p$ (cm <sup>-2</sup> )	$R_c$ (nm)	$\alpha$	$S$ (m <sup>2</sup> g <sup>-1</sup> )
5.4 (3) 10 <sup>4</sup>	5.7 (0.3) 10 <sup>10</sup>	29.3 (4)	2.0 (3) × 10 <sup>-2</sup>	170 (4)

**Carbon Black Associations in Elastomer.** The SANS of HSA-polyisoprene bound rubber gels is significantly different from that of HSA alone.<sup>4</sup> The contrast match point of polyisoprene at  $f_{C_6D_{12}} = 0.07$ , where only CB scattering should be observed (Fig. 2) was calculated from the data by interpolation using Eq. (5). For  $Q < 0.02$  Å<sup>-1</sup> the scattering from HSA is considerably greater than that from the HSA-polyisoprene composite. For  $Q$  between 0.02 Å<sup>-1</sup> and 0.07 Å<sup>-1</sup> the HSA intensity is slightly less than that of the composite (Fig. 2). The scattering from the two samples becomes indistinguishable for  $Q$  greater than 0.07 Å<sup>-1</sup>. We have shown<sup>2</sup> that the scattering from HSA alone in suspension (Fig. 2) is very close to that expected from non-interacting particles. Further, when  $f_{C_6D_{12}}$  is between 0 and 0.25, scattering reflects the carbon black aggregate shape with little contribution from the internal structure. Thus, we could use Eq. (4) to calculate  $S'(Q)$  (Fig. 3).

We have not interpreted  $S'(Q)$  quantitatively as yet. However, some guidelines to the interpretation are apparent. Some features of  $S'(Q)$  probably arise from the fact that the CB aggregates are elongated. That  $S'(Q)$  is significantly smaller than unity at low  $Q$  implies that there is strong exclusion of CB particle neighbors in the HSA-PI composite. It is likely then that on average each CB aggregate is separated by a considerable amount of polymer that prevents the aggregate from making lateral associations. On the other hand, the amount of CB in this sample, 65% by weight in the dried material, is above the percolation limit. Thus, the CB aggregates must be touching, or at least have only small amounts of polymer in between, in which case these results must reflect end on association of the rodlike aggregates.

## Conclusions

These results have important implications on the mechanism of reinforcement of rubber by HSA. Ideas about rubber composite properties must take into account the short, rigid quasi-rodlike character of the carbon black aggregates. Further, the mechanism of polymer binding must take into account the upper limit of the length scale for CB surface roughness<sup>9</sup> at 10 Å from the SANS studies. Information on the association of the CB in HSA-polyisoprene composites when  $S'(Q)$  is interpreted should give an understanding of the morphology of the CB network in the composite.

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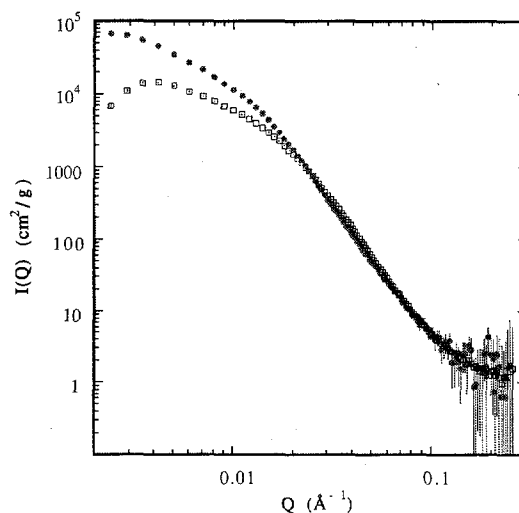


Figure 2. Comparison of Scattering from HSA suspensions and Gels of Bound Rubber Computed for  $f_{C_6D_{12}} = 0.07$ . Data: ●, HSA; □ HSA- polyisoprene.

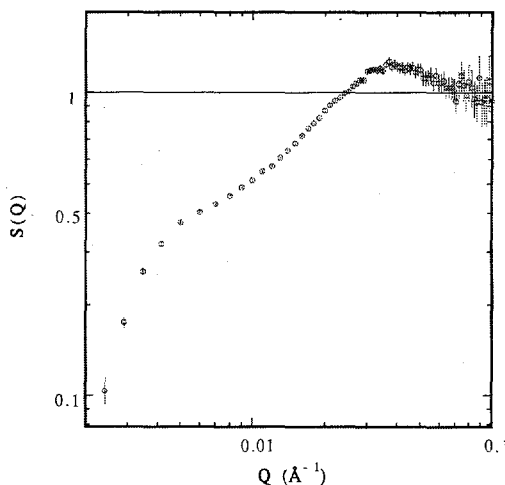


Figure 3. Structure factor from the scattering of HSA in the Composite Gel of Bound Rubber. Calculated values: ○.