

The structure of carbon black-elastomer composites by small-angle neutron scattering and the method of contrast variation

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ABSTRACT

We have been exploring the use of small-angle neutron scattering and the method of contrast variation to give a new look at very old problem—reinforcement of elastomers by carbon black in durable rubber products.

Carbon black has a hierarchy of structures consisting of particles covalently bound into aggregates, which in turn associate by weak interactions into agglomerates. We found that in one carbon black, HSA, the aggregates are rodlike, containing an average of 4-6 particles. The aggregates have an outer graphitic shell and an inner core of lower density carbon. The core is continuous throughout the carbon black aggregate. Contrast variation of swollen HSA-polyisoprene gels shows that the HSA is completely embedded in polyisoprene and that the agglomerates are formed predominantly by end on associations of the rodlike aggregates. The surface structure of the carbon black appears smooth over length scales above about 10 Å. Further studies using production carbon blacks suggest that these structural characteristics are generally present in commercial rubber composites.

1. INTRODUCTION

The manufacture of durable rubber products critically depends on proper formulation of elastomer. Without the reinforcing component rubber tires, for example, would lack sufficient durability to be of practical use. Reinforcement increases other useful properties, such as the storage modulus of rubber. However, reinforcement results in increases in the loss modulus as well, which leads to tire heating, reducing the efficiency of the tire. The most frequently used reinforcement in such durable products is carbon black (CB),¹ the fine powdery "soot" formed by the burning of hydrocarbons under oxygen-depleted conditions. A study by Goodyear predicts that an attainable 5% decrease in the reinforced rubber loss modulus, termed rolling resistance, would result in about a fuel 1% savings. This savings would be of considerable benefit to western economies.

CB-rubber composites are examples of "classical systems" which have heterogeneous microphases of matrix and reinforcement. The carbon black 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. Even so, nearly 90 years after the discovery of the effect of CB on rubber, there is considerable controversy on what the reinforcing mechanism is. Ideas center on particle size and surface structure relating to associations with the rubber, aggregate shape, and the extent and morphology of agglomerates. In the interactions with the rubber, the effects of CB on the strength of the polymer binding and its effect on polymer chain configuration and entanglements are considered highly important. A clearer understanding of the visco-elastic properties of reinforced rubber requires a better picture of the structure of the material and its components *in situ*.

Small-angle neutron scattering, SANS, is particularly important in providing unique capabilities for the study of composite materials that complement other methods. However, scattering intensity measured by

SANS does not have the unambiguous spatial information that can be available from, say, transmission electron microscopy (TEM).

The lack of spatial information in the SANS experiment is a result of the loss of phase information in the measured scattering intensity. We have outlined one means for recovering spatial information in composite materials by the method of contrast variation.²³ This method, which was originally developed for the study of biological macromolecules and assemblies in solution,⁴ uses mixture of protonated and deuterated solvent to produce incremental changes in deuteration. This approach is particularly easy to implement in the study of carbon black-elastomer composites if we limit ourselves to “bound” rubber³, which remains after extensive high temperature extraction of a carbon black-elastomer composite with good solvents. This material is dried and swelled with cyclohexane with different weight fraction of deuterocyclohexane, $f_{C_6D_{12}}$.

2. CONTRAST VARIATION

We have used this method to determine the form and structure of CB and CB-polyisoprene bound rubber in cyclohexane.²³ For a homogeneous solution of non-interacting particles the scattering has a well defined behavior given by

$$I(Q) = \Delta\rho^2 I_{\alpha}(Q) + \Delta\rho I_{\alpha\xi}(Q) + I_{\xi}(Q) \quad (1)$$

where, $\Delta\rho = \bar{\rho} - \rho_s$, is the contrast of the average scattering length density of the particles, $\bar{\rho}$, versus that

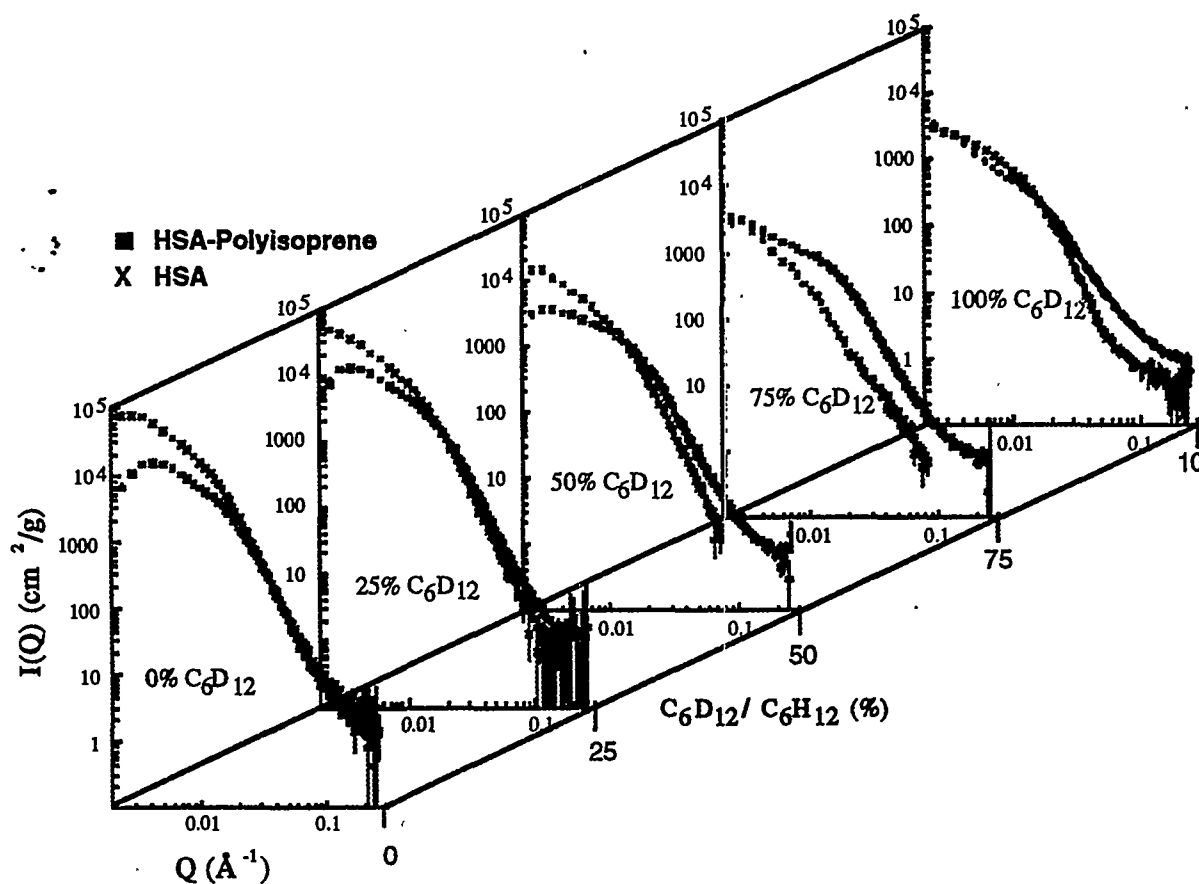


Figure 1: SANS of HSA-polyisoprene Composite Gels and HSA Suspended in different Fractions of Deuterocyclohexane Data: X, HSA; ●, HSA-polyisoprene composite gel.

of the solvent, ρ_s . When $\Delta\rho = 0$, this is the contrast match point. The functions $I_\Omega(Q)$, $I_\zeta(Q)$, and $I_{\Omega\zeta}(Q)$ are the basic scattering functions. The first two arise, respectively, from the solvent-excluding parts of the structure, $\Omega(\mathbf{r})$, the scattering from the internal scattering length density fluctuations, $\zeta(\mathbf{r})$. The last function is the scattering due to 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, $\rho(\mathbf{r}) = \rho_s + \Delta\rho\Omega(\mathbf{r}) + \zeta(\mathbf{r})$. Equation (1) is an approximation for heterogeneous systems, such as studied here, as the different terms are better represented as sums over the different contrasts present in the sample.²

3. CARBON BLACK AND COMPOSITE STRUCTURE

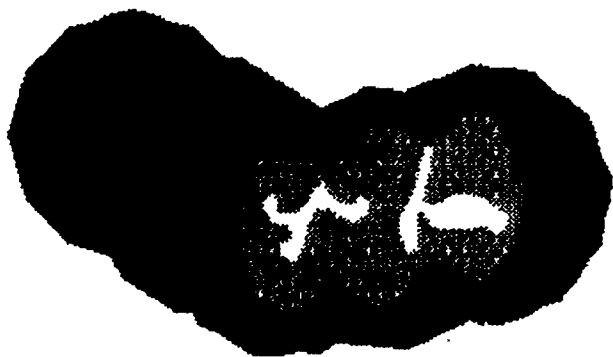


Figure 2: *Schematic of the Carbon Black Aggregate Structure:* The structure consists of a linear array of spheroid particles. The average aggregation number is 4 to 6 with particle sizes being in the range of 240 to 290 Å. The outer shell of the structure (black) consists of graphitic carbon crystallites, with a core (gray) of less dense void-filled (white) carbon.

There are substantial changes in the neutron scattering of HSA and HSA-polyisoprene (HSA-PI) gels when, $f_{C_6D_{12}}$ is changed from 0 to 1.0 (Fig. 1).

Analysis of the of the contrast-dependent scattering for the HSA sample, by fitting the data to Eq. (1) and using, in particular, the contrast dependent values for the scattering at $Q = 0$, $I(Q)$ and the radius of gyration, lead to several conclusions for the structure of the aggregates of an experimental high surface area carbon black, HSA, given in schematic form in Fig. 2: The aggregates are approximately 290 Å by 1500 Å and are rodlike, having little branching, with 5 to 6 particles on average. This result is consistent with stereo TEM studies.⁵ The particles have a shell-core structure, consistent with TEM¹ and scanning tunneling microscopy⁶, with an outer shell with density like that of graphite. The core of the particle has density like that of amorphous carbon, but with voids. The particles are fused together by the amorphous cores to form the aggregate. This structure is likely to be very rigid. Finally,

the particles have smooth surfaces on length scales greater than 10 to 20 Å. Studies on the production CB's, N330 and XLH81 suggest that the shell-core structure found in HSA is present in these.

These conclusions have important implications on the mechanism of reinforcement of this carbon black. Ideas about rubber composite properties must take into account the short, rigid rodlike character of the carbon black aggregates. Further, the mechanism of polymer binding must take into account the upper limit of surface roughness determined from the SANS studies.

The SANS of HSA-polyisoprene bound rubber gels is significantly different from that of HSA alone (Fig. 1). These data too can be fit using equation (1). When Q is less than approximately 10 \AA^{-1} , the fits suggests a minimum at a $\Delta\rho$ near the $\bar{\rho}$ value for HSA of about $5.7(3) \times 10^{10} \text{ cm}^{-2}$.² For Q greater than 10 \AA^{-1} there is a shift in the $\Delta\rho$ for the minimum scattering intensity towards the computed $\bar{\rho}$ of $3.2 \times 10^{10} \text{ cm}^{-2}$ of the composite, implying that the contrast of the CB is from the solvent-polyisoprene mixture. Thus, the CB is almost completely coated with elastomer.

The scattering at $f_{C_6D_{12}} = 0.07$, where only CB scattering should be observed, can be calculated from the data in Fig. 1 by interpolation using Eq. (1). The result of this calculation is shown in Fig. 3. For $Q < 0.02 \text{ \AA}^{-1}$ the scattering from HSA is considerably greater than that from the HSA-polyisoprene composite. For Q between 0.02 \AA^{-1} and 0.07 \AA^{-1} the HSA intensity is slightly less than that of the composite. The scattering from the two samples becomes indistinguishable for Q greater than 0.07 \AA^{-1} . We have shown²

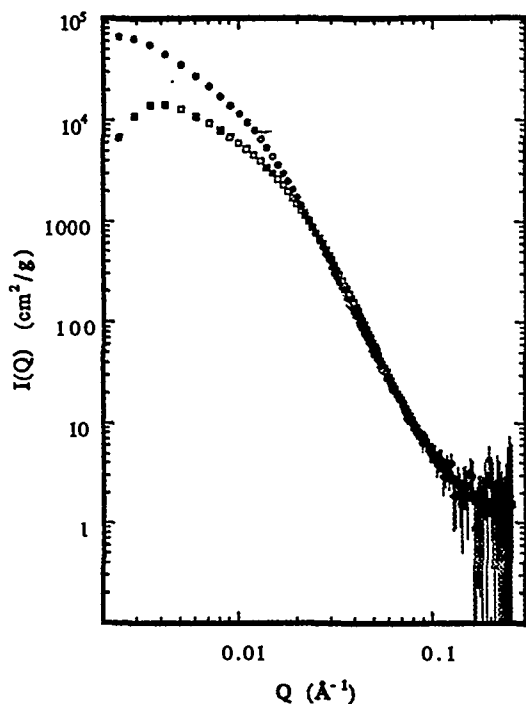


Figure 3: Comparison of Scattering from HSA suspensions and Gels of Bound Rubber Computed for $f_{C_6D_{12}} = 0.07$: Data: \circ , HSA; \square , HSA-polyisoprene.

that the scattering from HSA in suspension (Fig. 1) is very close to that expected from non-interacting particles, and when $f_{C_6D_{12}}$ is between 0 and 0.25 scattering reflects the carbon black aggregate shape. The smaller scattering values from the HSA-polyisoprene composites when ρ_s equals the scattering length density of polyisoprene (Fig. 3) suggests 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 laterally associating. 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, in which case these results show end on association of the rodlike aggregates.

When the incoherent backgrounds are accounted for the scattering in the calculated $f_{C_6D_{12}} = 0.07$ sample falls off as $I \sim Q^{-4}$ at $Q > 0.02 \text{ \AA}^{-1}$, indicating that the smooth surfaces are also present in HSA in the solvent-impregnated polyisoprene. The scattering in this same Q-domain from samples near to the HSA contrast match point fall off with power laws in Q intermediate between -4 and -3. This suggests the strong influence of polyisoprene-solvent scattering, as well as the contrast afforded by the polyisoprene with HSA.

4. ACKNOWLEDGMENTS

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