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VARIATION OF SOLVENT SCATTERING-LENGTH DENSITY IN SMALL-ANGLE NEUTRON SCATTERING AS A MEANS OF DETERMINING STRUCTURE OF COMPOSITE MATERIALS

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ABSTRACT

As part of our work on the structure of composite materials we have been exploring the use of small-angle neutron scattering using the method of contrast variation to dissect the component form, structure and distribution. This approach has resulted in a new look at very old problem—reinforcement of elastomers by carbon black.

Using this approach we studied an experimental high surface area (HSA) carbon black and a gel of "HSA-bound" rubber in cyclohexane/deuterocyclohexane mixtures. HSA in cyclohexane is found to be short rodlike particle aggregates. The aggregates have a shell-core structure with a high density graphitic outer shell and an inner core of lower density amorphous carbon. The core is continuous throughout the carbon black aggregate, making the aggregate a stiff, integral unit. Contrast variation of swollen composite gels shows that there are two length scales in the gel structure. Above 10 Å, scattering from carbon black predominates, and below 10 Å the scattering is from both carbon black and the elastomer. The HSA in the composite is completely embedded in polyisoprene. An estimate of the carbon black structure factor shows strong exclusion of neighboring aggregates, probably from excluded volume effects. The surface structure of the carbon black is unaltered by the interactions with elastomer and appears smooth over length scales above about 10 Å. These results show that contrast variation can provide information on composite structure that is not available by other means. This information relates to the reinforcement mechanism of elastomers by carbon blacks.

INTRODUCTION

An understanding of molecular arrangements in composite materials and their relationship to mechanical properties is important to an appreciation of the mechanism of composite reinforcement and to the rational design of new materials with greatly enhanced properties. Transmission electron microscopy [1] (TEM) has played an important role in elucidating nanoscale structure. Small-angle scattering techniques, small-angle x-ray scattering and small-angle neutron scattering (SANS) have played a less important role. [2-6] SANS is particularly important in providing unique capabilities that complement other methods. Studies on bulk samples are possible due to the penetrability of the neutron. Further, SANS affords good contrast between light elements and even isotopes of some elements such as hydrogen and deuterium. However, scattering intensity measured by SANS does not have the unambiguous spatial information that can be available from TEM.

The lack of spatial information in the SANS experiment is a result of the loss of phase information in the measured scattering intensity, which in electron microscopy is regained by the use of a lens. There is no such lens for neutrons; thus we must devise other methods of reconstructing phase information if we are to determine the distribution of structural components.

We have outlined one means for recovering spatial information in composite materials by the method of contrast variation. [2,3] This method, which was originally developed for the study of biological macromolecules and assemblies in solution [7-9], 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" rubber [2,3], which remains after extensive high temperature extraction of a carbon black-elastomer composite with good solvents. This material is dried and swelled with deuterated solvents.

We have used this method to determine the form and structure of carbon black suspended in cyclohexane. For a homogeneous solution of non-interacting particles the scattering has a well defined behavior given by

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

where, $\Delta\rho = \bar{\rho} - \rho_s$, is the contrast of the average scattering length density of the particles, $\bar{\rho}$, verses that of the solvent, ρ_s. When $\Delta\rho = 0$ this is the contrast match point. The functions $I_\Omega(Q)$, $I_\xi(Q)$, and $I_{\Omega\xi}(Q)$ 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.[3]

We have discussed the application of equation (1) to solving carbon black aggregate and particle morphology in another publication.[3] One speaks of a hierarchy of structures for carbon blacks where spheroid particles are covalently bound into aggregates, which in turn may be associated by Van der Waal's forces into agglomerates. Our conclusions for the structure of the aggregates of an experimental high surface area carbon black, HSA, given in schematic form in Fig. 1, were:

1) The aggregates have an elongated shape. Thus the aggregates are quasilinear arrays of particles The aggregates can be described as approximately rodlike with little branching.
2) The aggregates consist of 5 to 6 particles on average. The overall aggregate size is about 290 Å by 1500 Å. These results are consistent with stereo TEM studies.[10]
3) The particles have a shell-core structure, consistent with TEM[1] and scanning tunneling microscopy[11], with an outer shell with density like that of graphite. The core of the particle has much lower density, more like that expected for amorphous carbon, but with voids.
4) The particles are fused together by the amorphous cores to form the aggregate. Thus the aggregate is described as a short, quasilinear object with a continuous amorphous carbon core surrounded by a continuous graphitic shell. This structure is likely to be very rigid.
5) The particles have smooth surfaces on length scales greater than 10 to 20 Å. This places an upper limit on the fractal surface roughness determined by gas adsorption studies.[12]
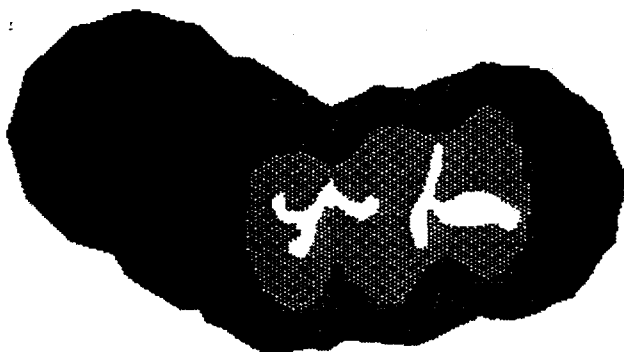

Figure 1: *Schematic of the Carbon Black Aggregate Structure:* A representative structure derived from SANS and high resolution microscopy of a typical HSA carbon black aggregate.[3] The structure consists of a linear array of spheroid particles. The average aggregation number is 4 to 6 with particle 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. The less dense core is contiguous throughout the aggregate.

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.

Here we describe the results of analogous scattering measurements and the initial analysis of bound rubber composites of HSA carbon black with monodispersed polyisoprene swollen in cyclohexane, containing different fractions of deutero-cyclohexane.

METHODS

Bound rubber was prepared from HSA composited with polyisoprene by extensive extraction of composited HSA and polyisoprene with toluene and cyclohexane, as described previously. [2] The polyisoprene, purchased from Scientific Polymer Products, Inc., had a molecular weight of 121 KD and polydispersity index of 1.20. The material was then dried. The disk contained 0.1179 g of material and had 35 % polyisoprene by weight. The disks were swelled with cyclohexane with different weight fraction of deuterocyclohexane, $f_{C_6 D_{12}}$. SANS measurements were done on the low-Q diffractometer at the Los Alamos Neutron Scattering Center, Los Alamos National Laboratory. The instrument, the details of the measurements and the other methods associated with time-of-flight data acquisition and reduction may be found in our earlier work. [2,3]

RESULTS AND DISCUSSION

There are substantial changes in the neutron scattering of HSA-polyisoprene (HSA-PI) gels when, $f_{C_6 D_{12}}$ is changed from 0 to 1.0 (Fig. 2). When $f_{C_6 D_{12}}$ is 0 to 0.5 there is a peak in the intensity at about 0.004 Å^{-1}, which decreases as $f_{C_6 D_{12}}$ increases. In the $f_{C_6 D_{12}}$ = 0.75 and 1.0 samples the peak has disappeared, and a shoulder becomes apparent for Q from 0.015 to 0.02 Å^{-1}. These data can be fit using equation (1). When Q is less than approximately 10 Å^{-1}, the fits suggests a minimum at a $\Delta\rho$ near the $\overline{\rho}$ value for HSA of about 5.7(3)x10^{10} cm^{-2}, or $f_{C_6 D_{12}}$ = 0.86. [3] For Q greater than 10 Å^{-1} there is a shift in the $\Delta\rho$ for the minimum scattering intensity towards the computed $\overline{\rho}$ (determined from the composite composition [2,3]) of 3.2x10^{10} cm^{-2} ($f_{C_6 D_{12}}$ ≈ 0.5) of the composite. These observations imply that at length scales larger than 10 Å the scattering fluctuations from the carbon black dominate the scattering. At length scales smaller than 10 Å the scattering arises from fluctuation in both the carbon black and elastomer components. This finding
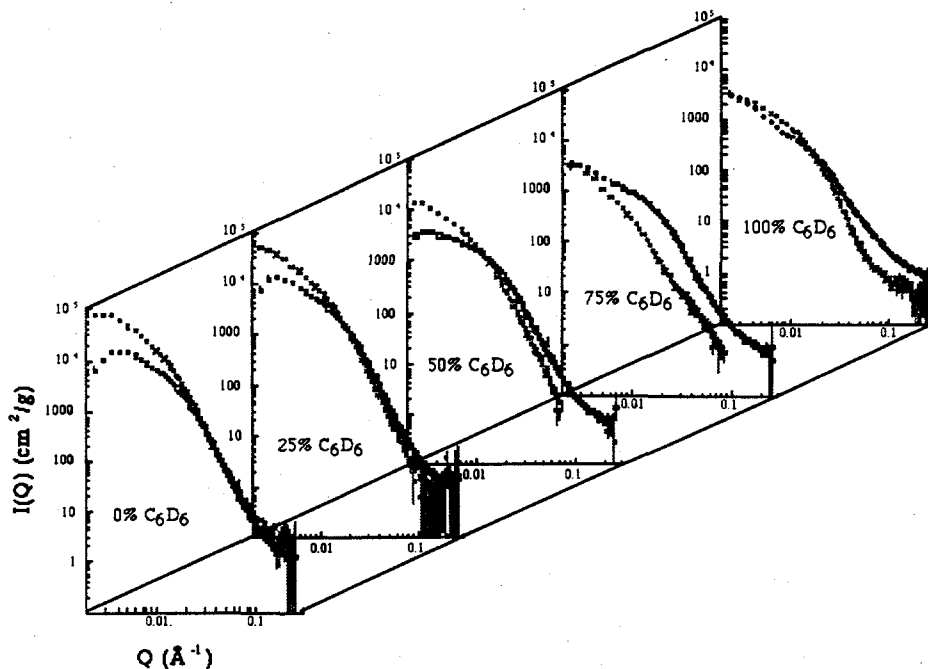

Figure 2: *SANS of HSA-polyisoprene Composite Gels and HSA Suspended in different Fractions of Deuterocyclohexane* Data: X, HSA; O, HSA-polyisoprene composite gel.

is in agreement with the results of our previous studies on the composites of N121 and N762 with polyisoprene and styrene-butadiene rubber. [2]

Comparison of the contrast-dependent scattering from the HSA-polyisoprene composite with those from HSA alone at the same $f_{C_6D_{12}}$ (Fig. 2) provides insight into the composite structure, particularly when $\rho_s = \overline{\rho}$ for polyisoprene (calculated to be 0.24×10^{10} cm^{-2}, or $f_{C_6D_{12}} = 0.07$). The scattering at $f_{C_6D_{12}} = 0.07$ was not measured, but can be calculated from the data in Fig. 2 by interpolation using equation (1). The result of this calculation is shown in Fig. 3. For $Q < 0.02$ Å^{-1} the scattering from HSA is considerably greater than that from the HSA-polyisoprene composite. For Q between 0.02 Å^{-1} and 0.07 Å^{-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 Å^{-1}. We have shown previously [3] that the scattering from HSA in suspension (Fig. 2) is very close to that expected fror non-interacting particles, and when $f_{C_6D_{12}}$ is between 0 and 0.25 scattering relfects 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 are strong correlations among the HSA aggregates in the composite.

On the assumption that the computed scattering for the composite at $f_{C_6D_{12}} = 0.07$ has negligible contributions from the polyisoprene we model the scattering as

$$I(Q) = S(Q)|F(Q)|^2 \qquad (2)$$

where $|F(Q)|^2$ is the aggregate form factor or the scattering intensity resulting from a single randomly oriented particle and S(Q) is the scattering structure factor due to interaggregate correlations. We can compute S(Q), by dividing the intensity by $|F(Q)|^2$, which according to our previous analysis [3] is just the scattering computed for HSA at $f_{C_6D_{12}} = 0.07$ (Fig. 3). The results of this is shown in Fig. 4. Equation (2) is an approximation for HSA, the aggregates of which have an elongated form. We see from Fig. 4 that there is strong exclusion of carbon black particle neigh-
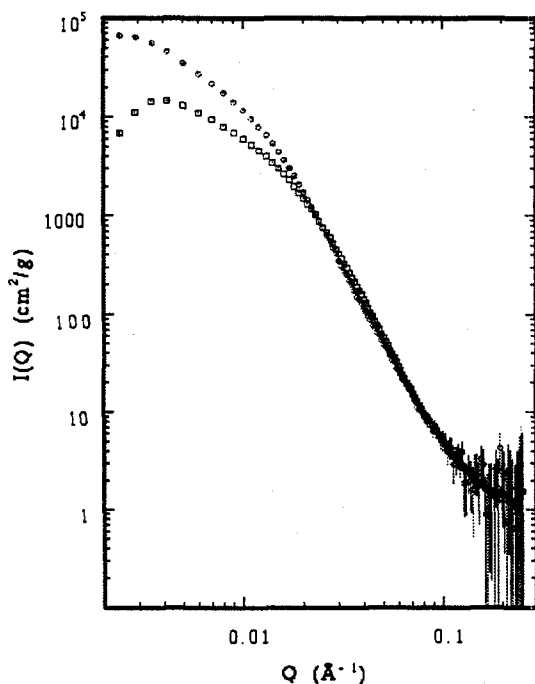

Figure 3: *Comparison of Scattering from HSA suspensions and Gels of Bound Rubber Computed for* $f_{C_6D_{12}} = 0.07$: Data: O, HSA; □, HSA-polyisoprene.
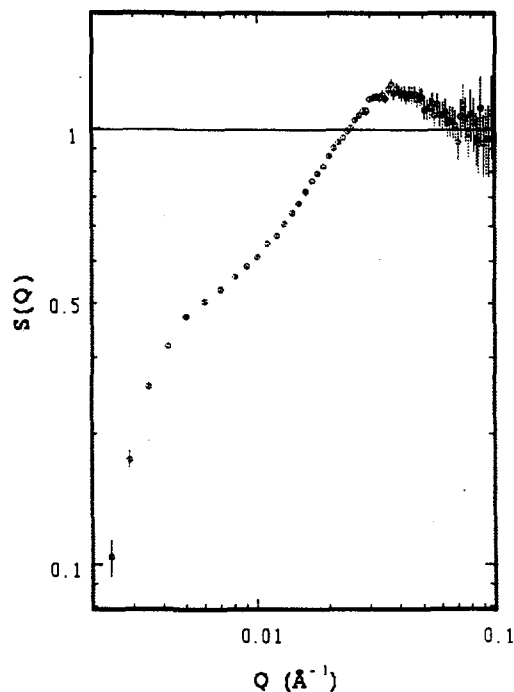
Figure 4: *Structure factor from the scattering of HSA in the Composite Gel of Bound Rubber:* Calculated values: O.

bors in the HSA-polyisoprene composite. Much of this is undoubtedly due to excluded volume effects. However, features of S(Q), such as the peak at about 0.04 $Å^{-1}$ (Fig. 4), which corresponds to a spacing smaller than the dimensions of the carbon black particles [3], are not explained by these effects. Thus, further analysis is required to fully exploit the information contained in S(Q) on the distribution of carbon black in the composite.

Some aspects of the data (Fig. 2) are understandable in terms of HSA carbon black completely embedded in material consisting of polyisoprene plus solvent. Thus the HSA shape function, $I_\Omega(Q)$, of equation (1) dominates the scattering, even when ρ_s is near $\bar{\rho}$ for HSA as is the case for $f_{C_6D_{12}} = 0.75$ (Fig. 2) where the scattering from the HSA at Q-values greater than 0.02 $Å^{-1}$ are due to the shell-like structure of the aggregate. [3] When the incoherent backgrounds are accounted for the scattering in the calulated $f_{C_6D_{12}} = 0.07$ sample falls off as $I \sim Q^{-4}$ at $Q > 0.02$ $Å^{-1}$, indicating that the smooth surfaces observed in the HSA aggregate are also present in HSA embedded in the solvent-impregnated polyisoprene. The scattering in this same Q-domain from samples near to the HSA contrast match point fall of with power laws in Q intermediate between -4 and -3. This suggests the strong influence of polyisoprene-solvent scattering, as well at the contrast afforded by the polyisoprene with HSA.

Other aspects of the scattering are open to further analysis, as we have not yet completed the interpretation of these data. However, the results to date give strong evidence of the utility of contrast variation techniques as probes of composite structure. The results of this analysis will have substantial bearing on understanding the structural basis of reinforcement in these systems.

ACKNOWLEDGMENTS

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