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Characterization of filled rubbers using small-angle X-ray scattering

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It is demonstrated how small-angle X-ray scattering (SAXS) can be used to characterize the structure of fillers such as carbon black and silica both before and after their incorporation into natural rubber. It is found that SAXS has significant advantages over conventional techniques such as gas adsorption or electron microscopy in determining both the size and distribution of sizes of the filler particles. The results are shown to be in good agreement with those obtained using conventional techniques. In addition it is demonstrated that SAXS can be used to characterize the filler particles *in situ* enabling the volume fraction, particle size and particle surface area to be determined for a filled rubber and factors such as aggregation to be examined.

1. Introduction

It is well established that the addition of certain types of filler to rubbers can greatly increase their stiffness, strength, abrasion and tear resistance and other important physical properties [1, 2]. There are several different types of filler that can be employed and they include various grades of carbon black [3] and fine particle silica powder [4] with the best improvements being obtained for fine filler particles in the size range 10 to 100 nm. Filler particles of such dimensions tend to collect together in aggregates containing of the order of several hundred individual particles [5]. Also when the fillers are incorporated in the polymer and the mixing is poor there can be local regions in which there are large agglomerates of the order of 10 to 100 μm in size and made up of many aggregates. Their presence can be detected and monitored using optical techniques such as light microscopy or reflectance methods. The presence of these large agglomerates can significantly reduce the strength of the rubber and it is essential that they are removed by proper mixing.

Hence to fully characterize the distribution of filler it is important to know the structure on three levels; the sizes of the individual particles, the aggregates of particles and the agglomerates. It is the purpose of this present report to show how small-angle X-ray scattering (SAXS) can be used to characterize the size and dispersion of the individual filler particles both before and after incorporation in natural rubber.

The most straightforward method of characterizing the dimensions of fine filler particles is by the use of transmission electron microscopy (TEM) [3–6]. For example, aggregates of carbon black particles have been examined in great detail [5] and good agreement has been found between particle sizes determined by this method and those obtained from gas adsorption measurements [5]. Problems are, however, encountered in the measurement of particle size using electron microscopy because it is often difficult to determine the sizes of several superimposed particles in an aggregate. Also a large number of particle measurements must be made to obtain a reliable idea of the distribution of particle sizes and mean diameters. In addition, it is considerably more difficult to determine the size distribution of particles dispersed in a polymer using electron microscopy since this can only be done with microtomed sections. It will be shown that the SAXS technique is particularly useful because it can be used non-destructively to determine both the size distributions and volume fractions of fillers incorporated into polymers such as natural rubber.

2. Small-angle X-ray scattering

2.1. General principles

Small-angle X-ray scattering (SAXS) is technique that is used widely to characterize multi-phase systems which have structure on the 1 to 100 nm scale. The main requirement is that there is sufficient electron density difference between the different phases that appreciable scattering of X-ray occurs. Systems studied in the past include such widely different materials as amorphous polymers [7], colloidal suspensions [8] and several types of coal [9–11]. There are also reports of SAXS being used to determine the specific surface areas of silica fillers in a silicone rubber [12] and the sizes of voids formed during the deformation of model systems consisting of synthetic rubbers filled with small spheres of glassy polymers [13, 14]. However, it does not appear that the SAXS technique

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had previously been exploited to its full potential in the characterization of filled rubbers.

The most widely-used small-angle X-ray camera is the Kratky camera [15] which employs slit collimation and produces strong scattering using a conventional X-ray generator. There is, however, a disadvantage in slit collimation which is that the data produced normally have to be desmeared, i.e. converted back to the equivalent scattering data from a point source. This procedure is tedious and time-consuming and is normally done using a digital computer. The problem has been greatly eased by several workers developing desmearing programs and making them available for general use. One of the most comprehensive programs is the FFSAXS package written by Vonk [16] since, as well as allowing desmearing to be done, many other useful facilities are also available in the package. This particular program has been employed in this present study.

2.2. Theory

It is a general principle of scattering theory that most of the information about the structure of a sample can be found in measurements over scattering angles (ε) which satisfy the following conditions [10]

$$0.1 \leqslant ha \leqslant 10$$

where

$$h = 4\pi \sin (\varepsilon/2)/\lambda \tag{1}$$

where λ is the wavelength of the radiation used in the scattering experiment and a is a dimension characterizing the size of the scattering entities in the structure. For very small angles $\sin \varepsilon/2$ can be approximated by $\varepsilon/2$ and hence h can be assumed to be directly proportional to the scattering angle. The above relationship means that SAXS measurements using Cu$K\alpha$ X-rays ($\lambda = 0.154\,\text{nm}$) allow structures such as second phase particles or voids with sizes of the order of 1 to 100 nm in a matrix to be characterized.

The theoretical treatment of SAXS is now well-established. For example, it is known [17] that at low scattering angles the intensity of scattering $I(h)$ obeys Guinier's law

$$\begin{aligned} I(h) &= N\Delta\varrho^2 v^2 \exp(-h^2R_g^2/3) \\ &= I(0) \exp(-h^2R_g^2/3) \end{aligned} \tag{2}$$

where N is the number of scatterers per unit volume, $\Delta\varrho$ the electron density difference between the scatterers and the matrix, v is the scatterer volume and R_g is the radius of gyration of the scattering entity. In the case of spherical scatterers R_g is $(3/5)^{1/2}$ times the radius of the spheres. It should be stressed that this equation applies, in the absence of interparticle interference, only to a dilute monodisperse system if the scattering angle is sufficiently small that $hR_g \leqslant 1.0$ [10]. Also if a slit-collimated system is employed such as a Kratky camera the observed smeared intensity is given by [8]

$$I(h) = \frac{3^{1/2}\pi}{R_g} I(0)\, W_i(0) \exp(-h^2R_g^2/3) \tag{3}$$

where $W_i(0)$ is the slit-length weighting function at $h = 0$.

A problem with most real systems is that there is often a range of sizes of scatterers present and so they are not monodisperse. This leads to a curvature in plots of the scattering intensity against h^{-2}, as Equations 2 and 3 are not strictly obeyed. The limiting slopes of such plots lead to weight-averaged values of R_g and it is rather difficult to determine the distribution of scatterer sizes.

At high angles the scattered intensity $I(h)$ depends only upon the the surface area of scatterers and it can be approximated by the Equation [15]

$$I(h) = \frac{2\pi\Delta\varrho^2 S}{h^4} \tag{4}$$

where S is the total surface area separating the two phases in the sample and $\Delta\varrho$ is the difference in electron density between the scatterers. This equation, known as Porod's law, is also modified for slit-smeared data such that

$$\tilde{I}(h) \propto h^{-3} \tag{5}$$

Thus, the surface area of scatterers can in principle be determined from measurements at high angles [15].

The volume fraction of scatterers in a two-phase system, ϕ, can be determined from the total integrated intensity or invariant, Q, which is given by [17]

$$Q = \int_0^\infty h^2 I(h)\,dh = 2\pi^2\Delta\varrho^2\phi(1 - \phi) \tag{6}$$

An equivalent but more complex relationship can be obtained for slit-smeared data [18]. Hence the SAXS measurements are capable of yielding information concerning the size, surface area and volume fraction of scatterers in two-phase systems.

3. Experimental details

3.1. Materials

The polymer used was SMRL natural rubber and the fillers employed were HAF carbon black (Cabot 330, ASTM No. N330) and fine particle silica powder (VN3). The rubber and fillers were mixed in a two-roll mill and vulcanized into sheets with 1 phr (parts by weight per hundred parts of rubber) of dicumyl peroxide. The vulcanization conditions employed were 10 min at 100° C to allow flow in the mould and minimize anisotropy, followed by 50 min at 160° C. Four different loadings of the two types of filler were used which were nominally 10, 20, 30 and 40 phr. However, a certain amount of filler was lost on mixing and so the compositions were checked by both density measurements and thermogravimetric analysis (only for silica fillers).

3.2. Electron microscopy

The structure of the filler particles and the dispersion of the particles in the filled rubbers were examined by transmission electron microscopy. The microscopes employed were a Jeol 100CX and a higher resolution Jeol 200CX ($C_S = 2.0\,\text{mm}$ at 200 kV).

The individual particles of filler were prepared for microscopic examination by dispersing a few milligrams of the powders in about 5 ml of butanone in a glass container using ultrasonic energy. The powders were found to disperse immediately the suspension was placed in the ultrasonic bath in which the container was left for several seconds. A single drop of the suspension was then placed on a standard copper microscope grid covered with a carbon support film and the solvent allowed to evaporate. This method was found to produce a satisfactory distribution of the filler particles on the carbon film which allowed the individual particles to be resolved.

Sections of the filled rubbers were obtained from the two samples containing 10 phr of filler using a glass-knived ultramicrotome operated below the glass transition temperature T_g of the rubber matrix (about -60° C) by cooling with liquid nitrogen. The sections (about 100 nm thick) were collected from the knife blade using standard 200 mesh copper grids. They were viewed directly in the microscope without staining.

3.3. Small-angle X-ray scattering

The SAXS experiments were performed on a Kratky small-angle X-ray scattering camera used in the step-scan mode with a proportional counter. The X-ray source employed was a Philips generator operated at 40 kV and 20 mA with a standard-focus copper-target tube. The radiation was monochromatized using a Ni $K\beta$ filter and a pulse-height discriminator. The scattering was placed on an absolute level using a calibrated polyethylene (Lupolen) sample supplied by Kratky [19]. Entrance and exit slits of 80 and 200 μm, respectively, were used. The diffraction angle was varied between 0.0015 and 0.05 rad in steps of 0.000 25 rad. Most diffraction curves were measured three times in succession over a period of about 17 h.

The SAXS experiments were carried out on filler powders by sandwiching samples of the powder between two pieces of thin adhesive tape across a slit in a sheet of aluminium. The scattering was also measured from the tape in the absence of powder to ensure that the tape did not contribute to the scattering. The SAXS data were obtained from the moulded sheets of filled rubber by placing single sheets of the order of 1 mm thick directly in the X-ray beam.

The SAXS data were processed with the aid of the computer program FFSAXS5 described previously by Vonk [17]. The program, written in Fortran, was modified where necessary to run on the Queen Mary College ICL 2988 main-frame computer. In the program the data from a number of runs are averaged, corrected for drift in the main-beam intensity and then corrected for background scattering [16]. Volume distribution functions $D_V(d)$ were determined as a function of the particle diameter, d, by the two independent methods available in FFSAXS5 and described by Vonk [20]. The first method (I) uses the subroutine DIST which calculates the particle size distribution function is calculated using the method of least squares [20]. The second method (II) employs the subroutine CORL which calculates the correlation function. The particle size distribution was determined by a method which essentially uses the approach of Schmidt *et al.* [21]. In both cases slit-smeared data were used and it was assumed that the slit was effectively infinite and the scattering entities were spherical. The two methods were found in all cases to give essentially the same results. However, since Method II requires that the raw data are smoothed and produces particle size distribution curves which are prone to spurious oscillations [20] all the results presented here are for $D_V(d)$ determined using Method I and subroutine DIST.

4. Results and discussion

4.1. Characterization of fillers

There is considerable literature concerned with the characterization of fillers, especially in relation to carbon black [3, 5, 6]. The particle size in such materials is generally determined using either electron microcopy or gas adsorption methods where good agreement between the different techniques is generally obtained [3]. In this present study the SAXS particle size distribution function $D_V(d)$ has been determined and compared with the size distribution measured using electron microscopy.

4.1.1. Electron microscopy

Fig. 1 shows micrographs of aggregates of the particles of carbon black and silica. This aggregation is typical of such filler particles and has been studied extensively by other workers [3–5]. It can be seen that the carbon black (Fig. 1a) has of the order of 100 particles in the aggregates whereas the silica aggregates appear to contain somewhat fewer particles (Fig. 1b). However, to obtain a complete idea of the state of aggregation it is necessary to examine a large number of aggregates [5]. The aggregation of particles makes the determination of the size distribution of the individual particles rather difficult and prone to error. Nevertheless, an attempt has been made to determine the size of the particles by measuring manually the diameters of a large number of individual particles and the results are presented in the form of histograms in Fig. 2. The data have been normalized such that the peak of the histogram has a value of unity.

4.1.2. Small-angle X-ray scattering

The scattering of X-rays at small angles was found to be very intense for the carbon black and silica filler powders and typical measurements in the form of plots of log I against log ε after correction for background scattering are given in Fig. 3. Both curves have a slope of -3 at high scattering angles although the slopes tend to decrease at lower angles. Since the plots are of smeared intensity $\tilde{I}$ against ε a slope of -3 would be expected at high angles when Porod's law (Equation 4) is obeyed. The normalized particle-size distribution functions determined from these data are plotted as curves in Fig. 2 along with the histograms derived from direct particle size measurement. It can be seen that there is quite good agreement between the SAXS-determined distribution functions and the directly measured particle sizes. There appears to be a slight horizontal shift between the two types of determination with the histograms peaking at particle

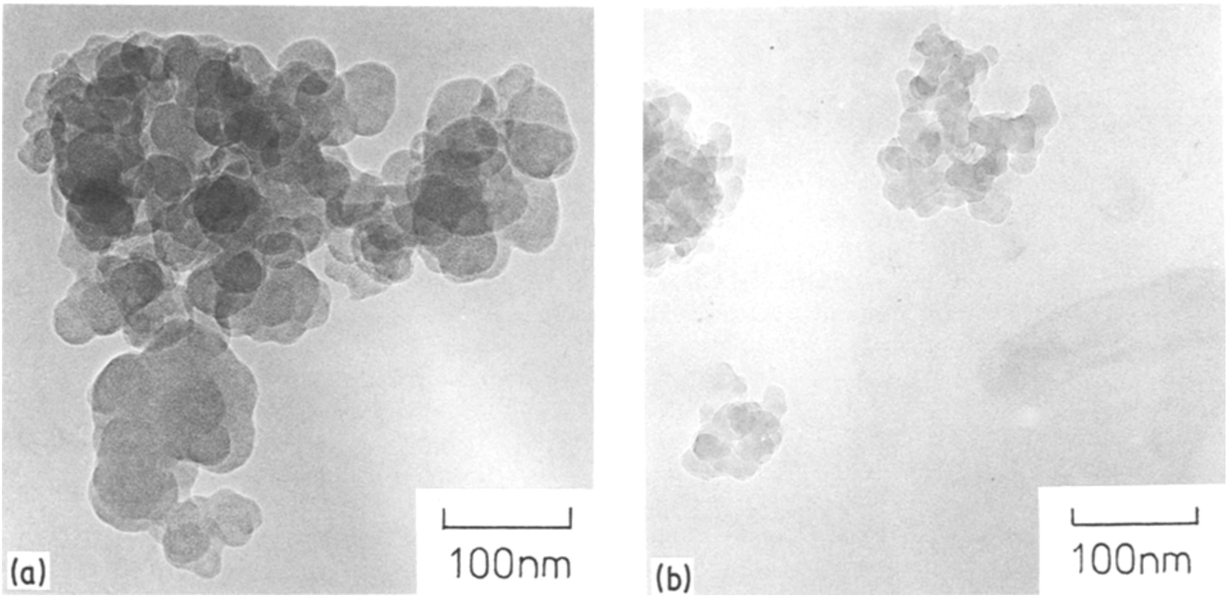

Figure 1 Transmission electron micrographs of aggregates of filler particles deposited on a carbon film. (a) HAF carbon black (N330). (b) Fine particle silica powder (VN3).

diameters slightly higher than the peaks in the SAXS distribution curve. However, as the data in Fig. 2 have been calculated using completely different and independent techniques, neither of which require prior calibration, the agreement gives considerable confidence in the use of SAXS to determine the dimensions of filler particles.

The average particle size can also be determined for both methods and the results are summarized in Table I. The number average diameter, $\bar{d}_n$ can be readily calculated from the histograms as

$$\bar{d}_n = \Sigma N_i d_i / \Sigma N_i \qquad (7)$$

where N_i is the number of particles of diameter d_i. The results of such a calculation yield a value of $\bar{d}_n = 33.5$ nm for the carbon black and $\bar{d}_n = 19.7$ nm for the silica. The value for the carbon black is close to the 31.7 nm value quoted [3] for a similar black with the same ASTM number (N330). Similarly the value of $\bar{d}_n$ for the VN3 silica is within the quoted range of 15 to 20 nm [4]. These quoted values for carbon black and silica were both determined from enlarged electron micrographs and so the good agreement with values measured in this present study using the same technique is not unexpected. The program FFSAXS5 also generated average particle sizes directly from the particle size distribution functions. Values of 24.6 nm for the carbon black and 21.5 nm for the silica are produced from $D_V(d)$ determined using DIST [20]. The value of average particle diameter for the silica is similar to that determined from the histogram whereas the value for the carbon black is somewhat less.

It is possible also to calculate the specific surface area, s, of the filler particles if it is assumed that they are in the form of non-porous spheres. It can be shown that

$$s = 6/d\varrho \qquad (8)$$

where d is the particle diameter and ϱ is the density of the particles. The values of s determined using this equation are also given in Table I taking the specific gravities of carbon black and silica to be 1.80 and 1.95, respectively. The values of specific surface area are in general agreement with values of s determined from adsorption methods [3, 4].

4.2. Characterization of filled rubbers

The main purpose of this present investigation was to determine the extent to which SAXS could be used to

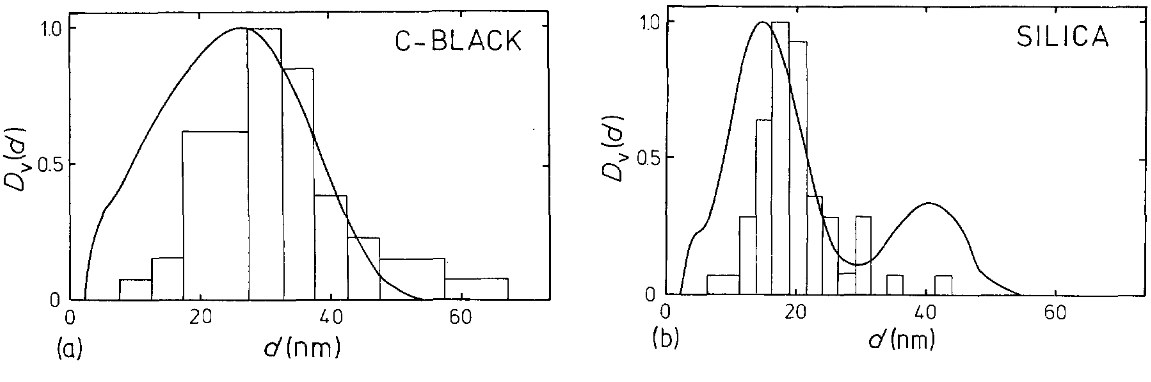

Figure 2 Particle size distributions measured from micrographs (histograms) and using SAXS (curves) for the filler powders. (a) HAF carbon black (N330). (b) Fine particle silica powder (VN3).

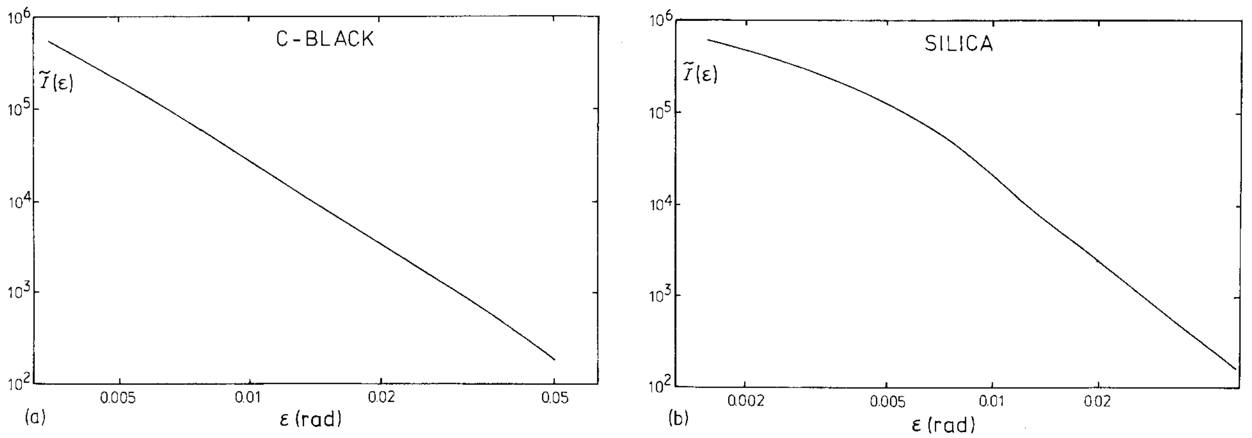

Figure 3 Variation of smeared scattering intensity, $\tilde{I}(\varepsilon)$, with scattering angle, ε, for the filler powders (after correction for background scattering).

characterize the structure of filled rubbers. In particular, it has been employed in the determination of both the size and distribution of fillers in the rubber. It has also been used to measure the volume fraction of fillers and the specific surface area of the fillers within the rubbers.

4.2.1. Electron microscopy

Sections of the samples of rubber containing a nominal 10 phr of the two types of filler were examined using transmission electron microscopy. Fig. 4 shows sections of the carbon black filled natural rubber obtained at two magnifications. The low magnification micrograph (Fig. 4a) shows the general distribution of particles. There are certain areas in which some agglomeration occurs but the distribution is fairly uniform. The micrograph obtained at higher magnification (Fig. 4b) shows the individual particles. It can be seen that they are in the form of aggregates containing from a few to several hundred particles. However, the resolution of the structure is considerably more difficult than for the filler alone (Fig. 1a).

Fig. 5 gives sections of the silica-filled natural rubber (10 phr). It can be seen from the low magnification section (Fig. 5a) that the distribution of particles is not very uniform and there is considerable

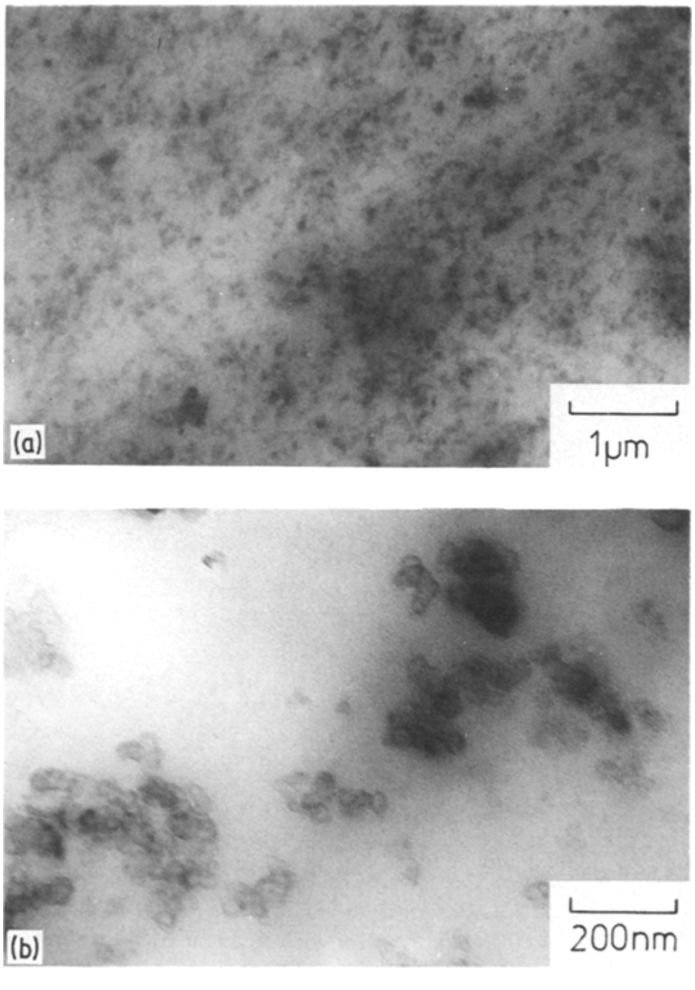

Figure 4 (a) Transmission electron micrograph of a microtomed section of carbon black filled (10 phr) natural rubber (SMRL). (b) Higher magnification micrograph of (a).

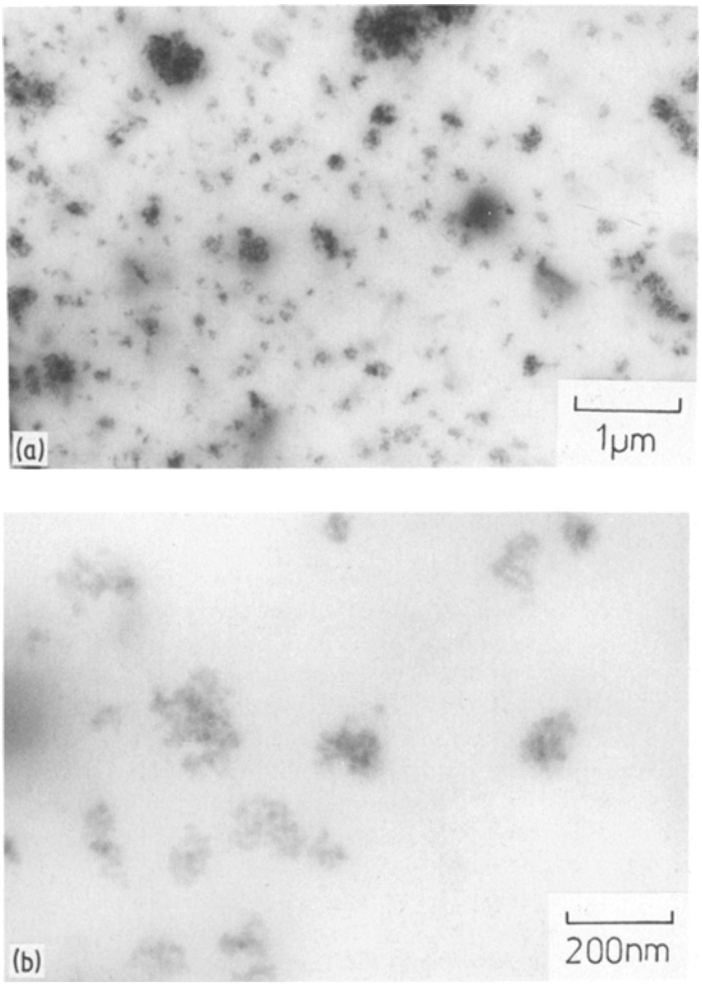

Figure 5 (a) Transmission electron micrograph of a microtomed section of silica filled (10 phr) natural rubber (SMRL). (b) Higher magnification micrograph of (a).

agglomeration. Fig. 5b shows a section observed at higher magnification where the aggregates of individual particles can be seen. Again, the resolution of the technique is rather poor and it is difficult to measure the individual particles in any detail.

4.2.2. Small-angle X-ray scattering

The intensity of the small-angle X-ray scattering as a function of scattering angle was determined for the samples of rubber reinforced with four different amounts of the two types of filler particles. The scattering curves were put on an absolute scale and corrected for background scattering. The particle size distribution curves and average particle sizes were determined using FFSAXS5. The volume distribution functions $D_V(d)$ are plotted in Fig. 6 for the carbon black filler and the two samples of black-filled rubber. It can be seen that the distribution curves for the filled rubbers are similar to each other but differ significantly from that of the isolated carbon black. The filled rubbers have two major peaks, one at about 5 nm and another at about 60 nm. In contrast the isolated carbon black powder has a single peak at around 30 nm. The average particle diameters determined using X-rays are given in Table I and it can be seen that the value of $\bar{d}$ remain approximately constant as the amount of filler in the rubber increases. The value for silica appears unaffected by incorporation in the rubber whereas $\bar{d}$ for the carbon black is considerably higher when it is in the rubber. It appears, therefore, that the structure of the carbon black has been significantly affected by incorporation in the rubber.

The volume distribution functions $D_V(d)$ are

TABLE I

Sample	C-black	A1	A2	A3	A4	Silica	B1	B2	B3	B4
$\bar{d}_n$ (nm)–TEM	33.5	–	–	–	–	19.7	–	–	–	–
$\bar{d}$ (nm)–SAXS	24.6	40.7	40.1	41.2	39.4	21.5	20.3	23.5	18.9	19.0
s ($m^2 g^{-1}$)–TEM	99.5	–	–	–	–	156.2	–	–	–	–
phr–measured*	–	10	20	30	40	–	9.74	15.35	28.65	35.49
Specific gravity	1.80	0.961	0.998	1.035	1.058	1.95	0.958	1.009	1.078	1.099
ϕ(%)–from phr	–	4.8	9.2	13.2	16.7	–	4.4	6.7	11.8	14.2
ϕ(%)–from density	–	4.7	8.9	13.1	15.7	–	3.7	8.6	15.3	17.4
ϕ(%)–from SAXS	–	4.3	8.2	9.8	13.9	–	3.5	7.6	8.5	10.3
s ($m^2 g^{-1}$ (sample))	–	18.5	29.2	24.7	40.2	–	19.3	31.5	42.5	52.0
s ($m^2 g^{-1}$ (filler))	–	185	146	82.3	100	–	198	205	148	146

*Only for silica.

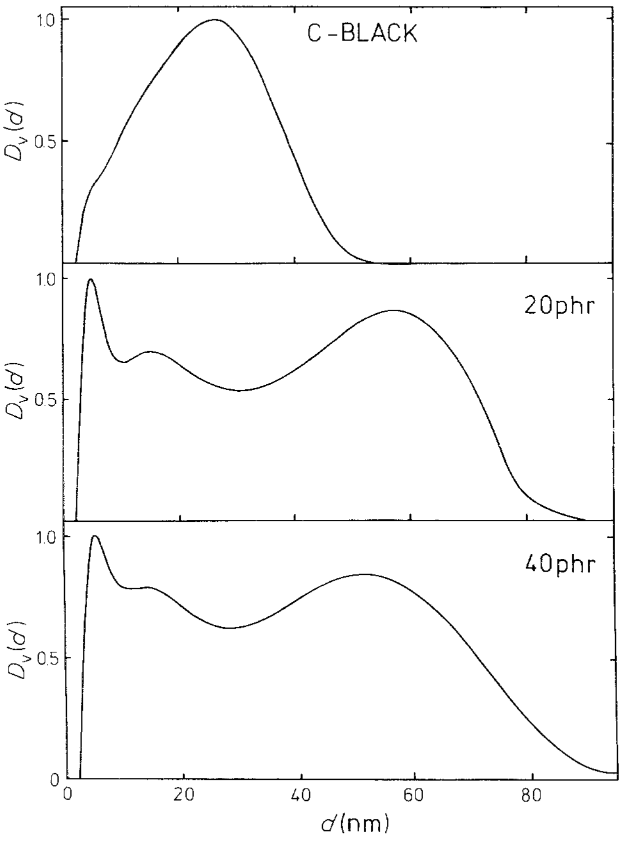

Figure 6 Particle size distribution curves for the carbon black powder and two samples (20 and 40 phr) of filled rubber.

plotted in Fig. 7 for the silica filler and the two samples of silica-filled rubber. The shape of all three curves is very similar with a major peak at 10 to 15 nm and a small one at 40 to 50 nm showing that the particle size distributions are very similar for both the filler and filled rubbers. This is also evident from examination of the average filler diameters listed in Table I which do not change significantly with the amount of silica in the rubber. It seems that unlike the carbon black, mixing and incorporation of the silica in the rubber does not significantly affect the particle size distribution.

The increase in the average particle diameter by nearly a factor of two following its incorporation into the rubber implies that the carbon black aggregates into entities which contain several particles. It is possible that this may be related to the fact that blacks such as the HAF type are generally termed as being "active" as they produce high levels of reinforcement [1–3]. This does not happen for the silica used in this present study which tends to produce more modest levels of reinforcement. It appears therefore that it may be possible to use the SAXS technique to follow the aggregation of the fillers in rubbers which may then be related to the mechanical properties of the material. This is currently undergoing further investigation.

It was demonstrated in Section 2.2 that the volume fraction of scatterers, ϕ, in the filled rubbers can be readily determined from the total integrated intensity of the radiation scattered at small angles and the results of such calculations are listed in Table I. Since the scattering data were determined over a limited range of scattering angles it was necessary to extrapolate both ends of the measured scattering curves to $h = 0$ and $h = \infty$ [15]. This facility is available in FFSAXS5 [16]. The volume fractions determined from the density measurements and thermogravimetric analysis are also given in Table I. It can be seen that there is reasonably good agreement between the volume fraction determined from density and thermogravimetric measurements. The volume fractions determined by SAXS agree quite well with the other two techniques up to volume fractions of the order of 10% but at higher volume fractions they tend to fall below values determined using these techniques. This discrepancy may be because rubbers with high volume fractions of fillers may no longer be considered dilute solutions. The consequent interparticle interference [15] will lead to a decrease in the total scattered intensity and a lower X-ray determined volume fraction.

The specific surface areas, s, of the filler particles in the rubbers can be calculated using Equation 4 and this facility is available in FFSAXS5. The values of s determined by this method are also listed in Table I using electron densities of 0.514, 0.899 and 0.975 mol cm^{-3} for the rubber, carbon black and silica respectively. The values of s are determined initially in terms of m^{2}g^{-1} of sample but they can be converted into m^{2}g^{-1} of filler using the known sample composition. Both values are given in Table I. It can be seen that although there is considerable spread in the data the specific surface areas of the carbon black particles in the rubber are generally higher than the accepted value [3] and the values of s determined from TEM using Equation 8 assuming particles to be spherical. On the other hand the values of s for the silica-filled rubbers are in the range 150 to 200 m^{2}g^{-1}

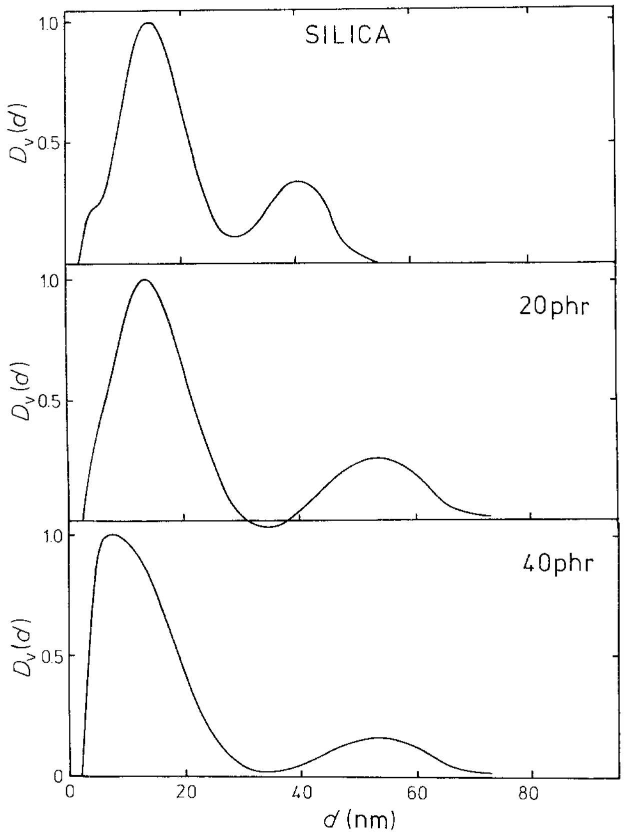

Figure 7 Particle size distribution curves for the silica powder and two samples (20 and 40 phr) of filled rubber.

and so very similar to the value of $156\,m^2\,g^{-1}$ determined from TEM. It seems therefore that silica particles behave as if they are spherical and their specific surface area is not affected by mixing in the rubber. The behaviour of the carbon black is not so simple and its structure does seem to be affected by the incorporation in the rubber.

5. Conclusions and implications

The results described above show that SAXS is a powerful technique for the study of the structure of fillers in rubbers. In particular it can be used to determine the size distributions of the filler particles, the volume fractions of fillers and the specific surface areas of the filler particles. The potential for further development of the technique is considerable and the following possibilities arise.

1. It should be possible to use a sample of rubber incorporating a well-dispersed filler as an absolute intensity standard for SAXS. The scattering from such a system can be very intense and it is more practical than aqueous suspensions of silica particles which have been suggested by previous workers as such standards [8].
2. The ability to perform SAXS measurements *in situ* in rubbers means that it is possible to study the change in filler and/or matrix structure during deformation of bulk samples. It should be possible to monitor the occurrence of voiding and/or strain-crystallization during deformation by measuring changes in the total scattered intensity of X-rays.

This development is currently under investigation.

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