Analyses of hierarchal structures of soft materials by using combined scattering methods

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1. INTRODUCTION

Soft materials, and not least the elastomers in general use, are commonly multicomponent systems of inhomogeneous structure which, as explained below, form hierarchical structures. Elucidation of the successive levels of hierarchical structure and the relation between them is vital for understanding the properties of soft materials. This review looks at how hierarchical structures over a wide scale range are observed and analysed with combinations of elastic scattering methods, primarily X-ray scattering combined with visible light and neutron scattering. The review is structured as follows. Firstly, the observation range of the different techniques is explained along with an account of the optics in small angle scattering, an arena of remarkable progress in recent years. Examples are then presented of the analysis of hierarchical structure by the scattering techniques in filled rubber systems, solvent swollen rubber, and polymer spherulitic structures.

2. SIZE OF STRUCTURE OBSERVABLE BY DIFFERENT SCATTERING TECHNIQUES [1-3]

Figure 1 shows the range of wavenumber q and the length scale observable by the different scattering techniques. The wavenumber q is defined by the following equation:

\[ q = \frac{4\pi}{\lambda}\sin \theta \]  \hspace{1cm} (1)

where \( \lambda \) and \( \theta \) are respectively the wavelength and scattering angle of the incident radiation in the sample.

The wavenumber \( q \) is related to the observation wavelength by the equation \( \Lambda = 2\pi/q \). Scattering with an incident beam of X-rays will first be described.

The wavenumber range observable in wide-angle X-ray scattering (WAXS) or wide-angle diffraction (XRD) is \( 7 \text{ nm}^{-1} < q < 30 \text{ nm}^{-1} \) (the upper limit depends on the optics), allowing observation of the arrangement of atoms in crystals for example. In filled rubber systems, WAXS allows observation of scattering by amorphous phases of the rubber component or of the diffraction patterns of crystals.

Small-angle X-ray scattering (SAXS) enables observation at \( 0.05 \text{ cm}^{-1} < q < 7 \text{ nm}^{-1} \), from the nanometre scale up to a size of around 100 nm. In filled rubber systems it affords information on the structure of the interface between filler and rubber components, and the aggregated structure of fillers.

The \( q \)-range observable in ultra-small angle X-ray scattering (USAXS) extends from the submicron scale up...
to around 10 µm, i.e. to sizes greater than accessible by SAXS; it thus overlaps the light scattering (LS), small-angle neutron scattering (SANS) and ultra-small angle neutron scattering (USANS) ranges. In filled rubber systems it is suited to observing distributed aggregate structures.

Neutrons provide the incident beam in small-angle neutron scattering (SANS) and ultra-small angle neutron scattering (USANS). Although the observation ranges of SANS and USANS allow measurement of neutron scattering at a wider angle, scattering of structural origin is difficult to extract when the material contains a lot of hydrogen, as with filled rubber systems, because the incoherent scattering is stronger than the elastic scattering. The q-range normally employed is therefore \( q < 1 \text{ nm}^{-1} \); however, it has recently become possible to separate incoherent scattering and elastic scattering quantitatively by polarisation analysis using a polarised neutron beam, enabling application to wider angles.

Light scattering offers a way of analysing the inhomogeneous structure of systems by measuring scattering in the visible region due to spatial fluctuation in polarisability or refractive index within the sample. Since polarisability may generally be represented as a tensor, the scattered light intensity varies with the polarisation of incident beam intensity. The observable wavenumber range is roughly the same as the q-range in ultra-small angle scattering. The technique cannot be used in filled rubber systems as they do not normally transmit visible light. Light scattering is used for analysis of network structure, as in crosslinked rubber swollen with solvent.

X-ray scattering would be expected to have wider application than neutron scattering and light scattering for the following reasons. Firstly, the incident beam in light scattering is visible light of wavelength range 1000 nm to 300 nm, which means that only transparent samples are amenable to measurement; coloured samples, and samples like filled rubber that do not transmit light, are accordingly excluded. Moreover, the observable q-range is narrow in light scattering. In contrast, USAXS is applicable to a wider range of samples because it uses an incident beam of X-rays. Again, neutron scattering methods generally require the preparation of a sample in which one or other of the components has been deuterated in order to provide the contrast in scattering, whereas in X-ray scattering methods the electron density itself provides the scattering contrast; structure can hence be observed without the need to prepare special samples. In the case of filled rubber systems, however, neutron scattering measurements can be made without deuteration since scattering contrast arises between the rubber component and carbon black or silica.

3. ULTRA-SMALL ANGLE SCATTERING TECHNIQUE IN X-RAY SCATTERING ANALYSIS

It follows from the definition of q that if observations are to be made over a q-range of \( 10^{-3} \text{ nm}^{-1} \) order at the wavelength of X-rays (0.154 nm for Cu-K\(\alpha\)), the scattered beam must be measured at an extremely small angle and with high angular resolution. The methods of measurement may be broadly divided into two according to the USAXS cameras required to attain this small-angle resolution, as follows.

3.1 Bonse-Hart camera

Figure 2 is a sketch of a Bonse-Hart camera USAXS facility [4,5]. The sample is here sandwiched between a first crystal and second crystal. The first crystal accomplishes monochromatisation of the incident X-rays while simultaneously collimating the beam (to obtain a parallel pencil) and the second crystal is rotated so that only scattering that satisfies Bragg reflection conditions in the second crystal is detected; this arrangement provides a small-angle resolution unobtainable by

![Figure 2. Schematic graph of Bonse-Hart camera](image-url)
conventional SAXS and permits measurement across a wide range extending from µm order to several tens of nm. Although the Bonse-Hart camera can utilise a weak source of rotating cathode type, the scattered image has a fuzziness due to the size of the source (a smearing effect), and the effect must be corrected. The samples amenable to examination are therefore restricted to isotropic materials. Another problem is that time resolved measurements are impossible because scans are time-consuming.

3.2 Synchrotron radiation source and long distance camera [5-7]

Scattering measurements in the ultra-small angle range are here achieved using a long camera length (>10 m). Figure 3 shows the set-up for USAXS at the BL20XU beamline of the Spring-8 synchrotron [6-7] where a vacuum path runs from the ring station to the medical applications station sited approximately 160 m away. By arranging the sample in the first hutch and the detector in the second hutch at the medical applications station, it is possible to use the set-up to achieve high angular resolution with a camera length of 160 m. As well as allowing anisotropic scattering patterns to be recorded, the technique permits time-resolved measurements and therefore has a broader scope of application than the Bonse-Hart camera. It is used for measuring anisotropic scattering patterns in the investigation of hierarchical structure in filled rubber system under deformation, and hierarchical structure in crystalline polymers.

4. ULTRA-SMALL ANGLE SCATTERING TECHNIQUE IN NEUTRON SCATTERING

Ultra-small angle scattering analysis with neutron beams is possible with a Bonse-Hart type camera and the focusing SANS technique [8]. As with X-rays, a high resolution is achieved with the Bonse-Hart camera because of the Bragg reflection condition imposed by a crystal. The q-range accessible in USANS with a Bonse-Hart camera is one order smaller than in USAXS, as shown in Figure 1. In the case of filled rubber systems, USANS with a Bonse-Hart camera is capable of identifying structures down to this scale because of the strong contrast from carbon black. The obvious problem is that, just as with the X-ray Bonse-Hart camera, the samples amenable to measurement are limited to isotropic materials because of the smearing effect, and time-resolved measurements are impossible.

The focusing SANS technique adds a condensing arrangement to the conventional SANS spectrometer and focuses the incident neutrons on the detector surface; by using a detector of high positional resolution, this makes it possible to raise the small-angle resolution without loss of intensity, a feature unattainable by collimation with a conventional pinhole (Figure 4). The focusing SANS instrument has been installed at SANS-J-II. Focusing uses a MgF₂ lens, condensing the beam to 1 mm at the detector surface. Enhanced small-angle resolution is sought by combining a two-dimensional photomultiplier with a ZnS scintillator. As a result, small angle measurements are possible down to $q = 3 \times 10^{-3}$ nm⁻¹. Since it uses a two-dimensional detector, the focusing SANS technique also allows anisotropic scattering measurements.
5. EXAMPLES OF HIERARCHICAL STRUCTURE ANALYSIS BY SCATTERING METHODS

5.1 Hierarchical structure of filled rubber systems [9,10]

Examples will be presented of the hierarchical structure analysis of filled rubber systems by different scattering techniques. The filled rubber systems examined were polyisoprene (PI: Nipol IR-2200, Nippon Zeon Co. Ltd.)/carbon black (CB: Shoblack N339, Showa Cabot K.K.) and styrene random butadiene copolymer (SBR: VSL5525-Q, Lanxess AG)/CB. The samples were produced in a Banbury mixer under conditions of temperature 60-80°C, rotor speed 45-60 rpm, and dump temperature 155°C. Figure 5 is a double logarithmic plot of the scattering intensity in USANS, USAXS and SAXS of the PI/CB system versus the wavenumber \( q \).

The USANS scattering curve has been shifted to overlap the SAXS and USAXS curves in the range \( q = 0.004-0.01 \) nm\(^{-1}\). The SAXS and USAXS scattering curves have each been reduced to absolute intensity and are unshifted. Examining first the scattering curves from SAXS and USAXS in the wider angle region, it will be seen that \( q^{-3.7} \) scattering behaviour obtains in the wide angle range 0.3-1 nm\(^{-1}\). The exponent of \( q \) is thus not as severe as the \( q^{-4} \) in Porod’s law. The explanation could be that 1) the CB itself has a fractal surface rather than a smooth surface, or 2) the bound rubber phase adhering to the CB particle surface is of fractal form. A shoulder appears at \( q = 0.03 \) nm\(^{-1}\) on the small angle side of the -3.7 exponent range; this originates from the aggregate structure of the CB particles. It is clear from the position of the shoulder that the average size of the aggregates is 40 nm. The appearance of a linear region of slope -2.2 is characteristic of behaviour at still smaller angles and occurs in the USANS and USAXS ranges at \( q = 0.0002-0.008 \) nm\(^{-1}\). The scattering intensity thus obeys a \( q^{-2.2} \) power law, indicating that the primary aggregates adopt a self-similar structure of fractal form.

Figure 6 shows the structure of the PI/CB system as established from the scattering curves. The system evidently forms a hierarchy of fractal structure built with CB particles \( \circ \) primary aggregates \( \circ \) secondary aggregates.

5.2 Analysis of crosslinked structure in rubber

The crosslinked structure in rubber is elucidated by swelling the rubber with solvent, thereby creating contrast between network and solvent, and recording the scattering pattern. Ikeda et al. [11] discovered that the scattering function of the swollen rubber may be expressed as the sum of an Ornstein-Zernike-Debye (OZD) function and Debye-Buech (DB) function as follows:

\[
I(q) = \frac{I_{DB}(0)}{1 + q^2 \Xi^2} + \frac{I_{OZD}(0)}{1 + q^2 \xi^2}
\]

and showed that two characteristic lengths exist in the network structure, the network mesh size \( \xi \) and the magnitude \( \Xi \) of the inhomogeneity, which is dependent on the sparseness or richness of crosslinks; in other words crosslinked rubber has a hierarchical structure. Ikeda et al also examined in detail how the lengths \( \xi \) and \( \Xi \) depended on the fraction of sulphur or zinc oxide. To examine whether an even larger nonuniform structure existed, we used focusing-SANS to elucidate the inhomogeneity of swelled rubber on the submicron scale. SANS measurements were also made, and the hierarchical structure of the swollen network from submicron scale to nanoscale was studied. The sample used was made by mixing at the ratio SBR/sulphur/ZnO/stearic acid/accelerator (TBB) = 100/1.5/3/1/1.5. The product was

Figure 5. USANS, USAXS and SAXS profiles of PI/CB

Figure 6. Hierarchical structur of PI/CB
brought to equilibrium swelling by immersion for 12 hours in a deuterated hexane (d-hex)/hexane (h-hex) = 79/21 (vol/vol) solvent, then loaded to a quartz cell along with solvent for SANS and focusing-SANS measurements. The results are shown in Figure 7. It will be seen that the plot continues to rise in the $q < 0.03$ nm$^{-1}$ region observed by focusing-SANS, revealing the existence of structural inhomogeneity even at the submicron scale. Taking into account the submicron scale inhomogeneity, curve fitting was carried out with the following equation:

$$I(q) = \frac{l_{DB1}(|0|)}{1 + q^2l^2} + \frac{l_{DB2}(|0|)}{1 + q^2\xi^2}$$

(3)

A DB function (the first right-hand term) has here been added to equation (1) to describe the submicron scale inhomogeneity. The quantity $l$ is the characteristic length of the submicron scale inhomogeneity. The solid line in Figure 7 shows the results of fitting and closely describes the scattering function. As shown in Figure 8, three characteristic lengths can be identified in the rubber network: the network mesh size $\xi$, the magnitude $\Xi$ of the inhomogeneity dependent on sparseness or richness of crosslinks, and the size $l$ of even larger inhomogeneity. The question of how these inhomogeneities arise, and how they are expressed in the rubber properties, is a matter for future research.

5.3 Analysis of hierarchical structure in PE

As shown in Figure 9, the spherulitic structure of polyethylene (PE) is hierarchical, comprising crystalline domains of regularly folded-back polymer chains, lamellar structure made up of these crystalline domains and amorphous domains, dendritic structure of aggregated lamellae extending helically from the centre, and spherulites several µm in size through which the dendritic structure of the lamellar phase has spread. We used two-dimensional USAXS (2D-USAXS) at the BL20XU facility to observe the changes in internal structure at the submicron scale in spherulites of linear low density polyethylene (LLDPE) during stretching and studied the effect of differences in molecular weight on structural change. We also examined the stretching-related changes in crystal lattice structure and crystal lamellar phase by SAXS and WAXS and investigated the effects on hierarchical structure. Three different LLDPE samples were used: LLD-a (density 0.918 g/ml [25°C], melt index 1.0 g/10 min [190°C/2.16 kg]); LLD-b (density 0.926 g/ml [25°C], melt index 50.0 g/10 min [190°C/2.16 kg]); and LLD-c (density 0.931 g/ml [25°C], melt index 26.0 g/10 min [190°C/2.16 kg]).

Figure 10 plots the stress versus extension for the three kinds of LLDPE. The elongation ratio $e$ was defined...
as (sample length after stretching/sample length before stretching). At relatively low extension a difference in stretching behaviour was evident in the maximum stress in the samples, and the existence of a yield point only in LLD-b and c. To explore the reasons for such differences in stretching behaviour, X-ray scattering was used to examine the changes in structure at each level in the hierarchical structure under elongation.

The changes due to stretching of the small-scale structure were studied by SAXS and WAXS. The scattering patterns from the three kinds of LLDPE in the unstretched state are shown in Figure 11; the 2D-WAXS scattering in the stretched state is shown in Figure 12. While all three samples give an isotropic scattering pattern in the unstretched state, the stretched samples show increased intensity of reflection from the (200) crystal plane at right angles to the stretching direction. This indicates that stretching orients the a-axis of the crystal lattice perpendicular to the stretching direction. Moreover, the angle of reflection is unchanged after stretching, showing that the size of the unit cell is unaffected by stretching. Figure 13 shows the 2D-SAXS scattering from unstretched samples of the three kinds of LLDPE. All the samples produce an isotropic scattering pattern, indicating that the crystal lamellae lack any specific orientation. Figure 14 shows the 2D-SAXS scattering of the three samples after stretching. All exhibit anisotropic scattering patterns, longer in the direction perpendicular to the stretching direction. Clearly, therefore, the crystal lamellae orient parallel to the stretching axis under elongation. It follows also from the change in long period of the crystal lamellar structure in the course of stretching that the deformation in all three kinds of LLDPE is consistent with affine deformation. Thus, no great difference was evident in the crystal lattice structure or crystal lamellar structure of samples under elongation.

The changes in submicron scale structure due to stretching were examined by 2D-USAXS. Figure 15 shows the 2D-USAXS scattering pattern of the respective samples in the unstretched state. All the unstretched samples exhibit isotropic scattering, with a rise in scattering intensity at the small angle end of the range. This shows that in all the materials there is an isotropic submicron scale density fluctuation in the unstretched state. The scattering intensity I in this region obeys the power law $I \sim q^{-2.6}$, which means that the inhomogeneity in density of the dendritic structure comprising crystal lamellae as shown in Figure 9 has a mass fractal structure of fractal dimension 2.6. The scattering pattern after stretching, on the other hand, differs greatly among the different LLDPE samples. As shown in Figure 16, the scattering pattern of LLD-a in the stretched state is elliptical, extending at right angles to the stretching direction. This indicates that the dendritic structure of the spherulite interior has been uniformly elongated parallel to the stretching direction.
direction. In contrast, the scattering in LLD-b and c after stretching exhibits a butterfly pattern extending parallel to the stretching direction. Structures producing butterfly scattering may be illustrated by an unevenly deformed gel. It is known that since deformation behaviour under elongation is different in strongly and weakly crosslinked regions, greater inhomogeneity develops in the stretching direction and the scattering intensity in the low q region increases, resulting in the appearance of a butterfly pattern. The scattering pattern in this case presumably developed because the phases of high and low crystal density within the dendritic structure undergo nonuniform deformation under stretching. Furthermore, the scattering intensity of stretched LLD-b and c increased both perpendicular to the stretching direction and parallel to the stretching direction, showing that density fluctuation has increased. It is clear from the results that change in submicron scale structure in LLDPE due to stretching differs greatly with molecular structure.

6. CONCLUSIONS

Scattering methods for the analysis of hierarchical structure in soft materials provide an effective tool for examining structure at different levels in the hierarchy and for constructing an overall picture of the correlation between levels. In particular, combinations of X-ray diffraction technique using strong beams from synchrotron emission allow in situ observation of change in hierarchical structure and their inter-level correlation over a wide scale range under the influence of an external field such as shear or elongation, and should hence be able to shed greater light on property-structure relations. Moreover, by combining the observations with X-ray CT analysis of larger structures it should be possible to provide a seamless observation scale and at the same time allow seamless elucidation of the relation between basic properties and products.

REFERENCES

