Structure development studies during materials processing

Nuclear Instruments and Methods in Physics Research B 97 (1995) 257–260

ELSEVIER

NIM B
Beam Interactions with Materials & Atoms

Structure development studies during materials processing

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Abstract

In the study of materials processing and structural development it has been necessary to develop sample environments for use with X-ray diffraction experiments. Feasibility study results are shown with examples of real time growth of glass ceramics and the formation of zeolites from silicate precursor gels. A further example is shown where the combination of scattering techniques together with a complicated sample environment could play an important role in the medically important problem of transdermal drug delivery.

1. Introduction

With the development of dedicated synchrotron radiation beam lines and the required instrumentation it has now become possible to study the development of structure in systems subject to perturbations of a thermodynamic, chemical or mechanical nature. With the appropriate sample environments it has become feasible not only to study model systems but also to mimic the conditions of the industrial processing environment. Several of such sample environments have been developed which are suitable for combinations with simultaneous small and wide angle X-ray scattering. Extensive work has gone into polymer research and this will be discussed elsewhere in these proceedings. This paper addresses some of the more exotic systems in which the sample environment is complicated.

2. Small and wide angle X-ray scattering

Recently an instrument enabling SAXS and WAXS experiments to be performed simultaneously has been developed [1]. This instrument has been described elsewhere and will not be discussed in detail here. With this instrument it is possible to study structures with length scales from approximately 1.5 to 900 Å in one single experiment. Several sample environments have been specifically developed so that they can be interfaced to the beam line. Among these are a differential scanning calorimeter [2], a Fourier transform infrared spectrometer [3], reaction injection moulding [4], high temperature cells and high pressure cells [5]. A fast temperature jump instrument, enabling the replication of conditions when polymers are injected into a cold mould, is under development.

3. Zeolite formation

The growth of zeolites, used on a large scale in the chemical industries as carriers for catalysts, is a process which is still relatively poorly understood. This can result in large financial loss if poor processing conditions occur. The study of the growth of zeolites is a good example of the usefulness of the application of two simultaneous scattering techniques [5]. From the WAXS data the development of crystallinity can be monitored while from the slope of the SAXS data a fractal dimension can be obtained which provides information on the density gradients in the sample and on the sizes of the primary particles and aggregates. Due to the high temperatures (180°C) needed in these experiments the hydro thermal pressure rises to approximately 6 bar. It is essential to avoid water loss from the sample since this will otherwise not follow the industrial process conditions. Sample environment window materials must therefore be able to withstand a high pressure, a condition that is contradictory with the requirement of X-ray transparency. A special sample furnace has been designed to enable experiments of this type to be carried out. This furnace can be directly connected to the vacuum chamber which is inserted between the sample position and the two detector systems on the SAXS/WAXS beam

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SSDI 0168-583X(94)00417-X

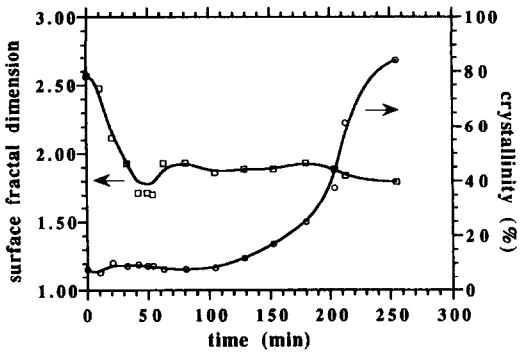

Fig. 1. Surface fractal dimension (derived from the SAXS data) and degree of crystallinity (derived from the WAXS data) during the synthesis of silicalite under hydro thermal pressure as function of time. Sample temperature 140°C. The crystallisation of the zeolite starts only after the surface roughness of the sample has become constant.

line. The only window between the sample furnace and the vacuum chamber is a 250 μm thick Kapton sheet. An electric resistance heater in contact with the sample is used to obtain the required temperature. The sample space can be brought to an overpressure of up to 6 bar with a dry N_2 atmosphere. This counteracts the overpressure generated in the cell due to the vapour pressure of the water released in the manufacturing process. This technique allows the use of thin windows to avoid water loss from the sample whilst retaining high pressure and temperature conditions. In Fig. 1 the results from a typical isothermal zeolite growth experiment, using this sample environment, are shown. The fractal dimension, derived from the SAXS pattern shows a steep decline with time which shows the surface roughness of the aggregates attaining a steady state. When this process is complete the crystallinity, obtained from the WAXS pattern starts a steady increase. This provides information that implies a reorganisation of the amorphous gel phase prior to crystallisation [5].

4. Ageing of glass

Experiments on the ageing process of glass, during which crystalline regions are precipitated out of the amorphous glass matrix, have to be performed at elevated temperatures (800–1200°C) and generally extend over several hours [6]. The problems posed by this experiment are to achieve a uniform sample temperature and maintain this over an extended period up to 24 h. The solution to this problem has been to built a high temperature furnace based on a Linkam 1500°C hot stage. The furnace has a windowless connection to the vacuum chamber which is inserted between the sample and the two detector systems. However, the Linkam heater element only provides heating from one side of the sample. To reduce the temperature gradients over the sample to an acceptable level a conical shaped polished reflector was mounted at the opposite side of the heater element. A slot was machined into this reflector in order not to obstruct the scattering pattern. In Fig. 2 the results of a typical experiment performed on cordierite glass, heat treated initially at 915°C, followed by further heat treatment at 1010°C, is shown. During heat treatment at 915°C, there was no observable changes in either the SAXS data or WAXS data. This suggests that the sample remains amorphous during this stage of the experiment and that any changes that the sample has undergone is too small to be observed through SAXS. After raising the temperature to 1010°C, the onset of crystallisation, as evidenced by the growth of the crystalline peaks in the WAXS region is preceded by a sharp increase in the intensity at low q-values. An additional peak grows at higher q-values ($q = 0.04$ Å^{-1}), which is thought to be due to inter-crystallite scattering, simultaneously with the growth of the diffraction peaks observed in

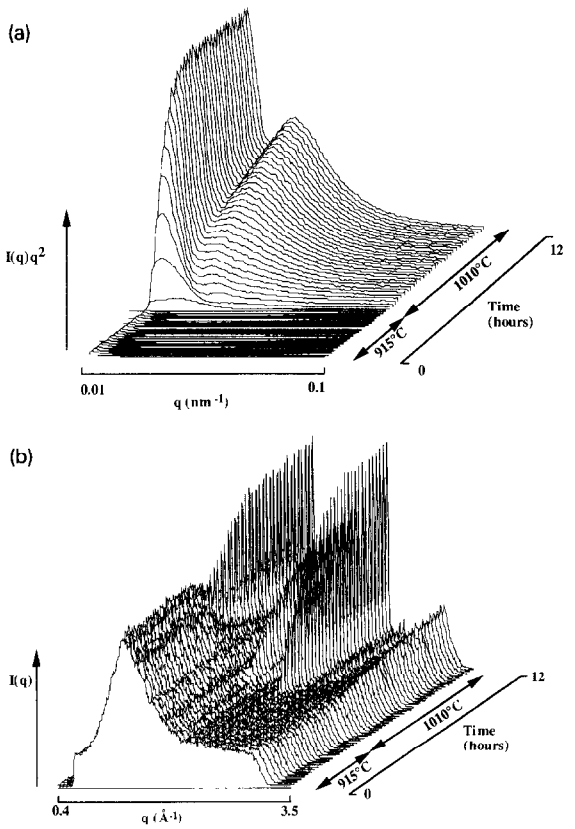

Fig. 2. WAXS and SAXS patterns following the annealing of cordierite glass at 900°C. It can be seen that the onset of crystallisation, as evidenced by the growth of the WAXS peaks, is preceded by an sharp increase in the diffracted intensity at low q-values probably caused by long range density fluctuations in the sample. The peak at $q = 140$ Å^{-1} is thought to be due to inter crystallite interference.

Fig. 2b. The low-q intensity is caused by long range density fluctuations, which are thought to be due to the growth of Cr rich regions at the expense of the depletion of the volume surrounding these regions. In the Cr rich regions, the conditions for crystal growth will ultimately be met. The interesting observation that can be made when comparing these results with previously obtained results is that the transition appears to be taking place at a much faster rate. This is probably due to a smaller temperature gradient over the sample so that the reaction is more uniform over the sample volume. This reflects the industrial bulk processing, in which temperature gradients do occur but over only a small surface region. The transition is being measured with a greater accuracy than in previous experiments [6].

5. Transdermal drug delivery

Delivery of certain drugs in accurate doses through the skin is an attractive alternative to oral or intravenous intake. However, the outermost layer of the skin, the epidermis, is generally an effective barrier [7]. Some penetration enhancers are known but the action of these enhancers is relatively poorly understood. The main problem is that the structure of the lipids in the skin, which are thought to be the actual pathway through the skin, is not known. The main constituents of these lipids are cholesterol, ceramides and free fatty acids. The structure of this mixture can be studied by a combination of SAXS and WAXS whereby the SAXS pattern provides information on the distance between the lipid lamellae and WAXS can be used to determine the crystallographic register in which the tails of the lipids are placed with respect to each other. Generally several lipid phases are in coexistence. This can be shown when the sample is subjected to a heat treatment. In a real time SAXS/WAXS experiment it can be seen that several peak sets are related due to the fact that they show the same behaviour as function of temperature. An example of this is given in Fig. 3 in which the scattering patterns of a mixture of cholesterol and ceramides, obtained from real skin, are shown as a function of temperature. From the SAXS data it can be seen that there are at least two lamellar phases present, which have different melting temperatures. The WAXS data provides an indication that a combination of two hexagonal systems which become disordered above 70°C. The amount of material used in these experiments is less than 1 mg and the sample thickness is far from the optimum thickness. This indicates that it is indeed possible to perform real time experiments on skin samples on a time scale which is relevant to transdermal drug delivery (for instance electro ionophorese). Presently a system is being developed which will allow the effect of electro iontophorese to be studied. From the study of samples before and after treatment it is known that the structure of the lipid systems changes substantially. It would be of clear interest to be able to study this, and similar systems, in real time in order to obtain a better understanding of these processes.

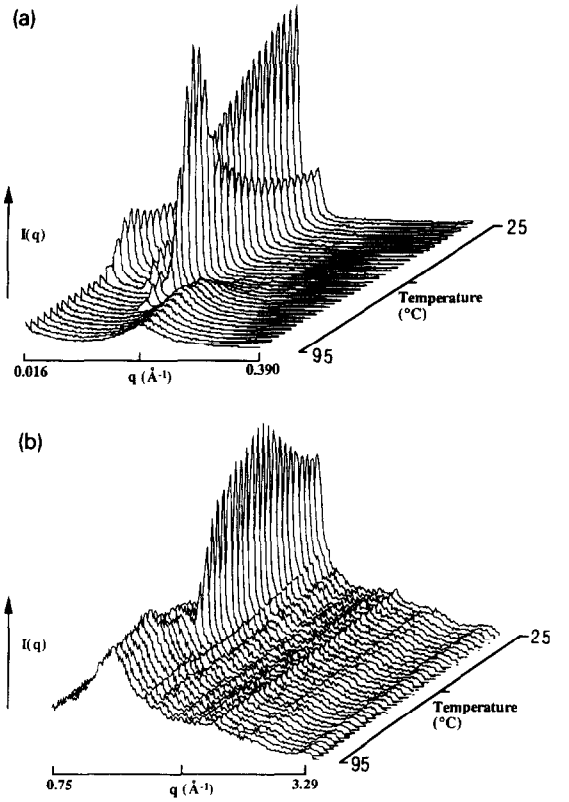

Fig. 3. WAXS and SAXS patterns of showing the results of an heating experiment on a 1:1 cholesterol:ceramides mixture extracted from human skin.

6. Conclusion

At present the research tool of time resolved combined small and wide angle X-ray scattering is predominantly used by polymer scientists. However, there is a large potential of other uses for this technique. Besides the examples given here several other systems have been studied. Among these are the phase behaviour of medicinal creams, the structure of ice grown from super cooled water and the effect of freezing on artificial cell membranes. With careful sample environment instrumentation a wealth of other material science subjects can be studied successfully and provide more insights in both fundamental and applied research subjects.

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