



Rapid internal bubble formation in a microwave heated polymer observed in real-time by X-ray scattering

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ABSTRACT

A combined study of small-angle and wide-angle X-ray scattering (SAXS/WAXS) of the melting of a nylon-6 sample by localized microwave radiation has shown that this method can reveal the presence of bubbles forming and disappearing rapidly in real time in the interior of the sample due to its thermal decomposition.

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1. Introduction

In recent experiments, we have explored the influence of a microwave induced discharge upon the internal structure of materials including metals and polymers [1–3]. In this paper we shall concentrate on the results obtained when a Nylon-6 polymer (Ertalon-6) was heated locally by such a discharge. This work follows on other measurements where we have examined the composition of a discharge plume [1] and of a free floating, dusty plasma [2,3], generated by the concentration of microwaves by means of a metallic electrode initially in contact with the target material. The initial principal motivation for these studies was to understand the physics underlying the operation of a localized microwave heater (e.g. the microwave drill [4]).

The changes in internal structure, caused by the localized microwave heating of the polymer have been followed using real-time Small Angle X-Ray Scattering (SAXS) and Wide Angle X-Ray Scattering (WAXS) measurements, performed at the High Brilliance Beamline ID2 [5] at the European Synchrotron Radiation Facility (ESRF, France).

2. Experimental method

The experimental setup used in this study resembles that used in Ref. [1]. A $1.5 \times 2.0 \text{ cm}^2$ slice, 1-mm in thickness of the target

polymer (Ertalon-6) was mounted in air on a metallic support inside the microwave waveguide, as shown in Fig. 1. This waveguide was fed with $\sim 0.8 \text{ kW}$ of microwave radiation generated by a magnetron. A movable metal rod was lowered into contact with the top edge of the vertical slice. A hotspot was created at the point of contact of the electrode with the polymer due to the microwave concentration and local absorption [4]. A collimated beam of hard X-rays (12.46 keV , $\lambda = 0.995 \text{ \AA}$) entered the waveguide from the side and passed through the polymer sample and onto a two-dimensional SAXS detector (FReLoN), located inside a 10-m long vacuum vessel. A $25\text{-}\mu\text{m}$ thick sheet of mica serves as entrance window for the flight tube. A second CCD detector (MCP-Sensicam), mounted in air on the entrance cone of the SAXS detector allows measurements of wide-angle scattering (WAXS) concurrent with the SAXS measurement [5].

The two detectors measure the angular scattering of the monochromatic X-ray beam. The momentum transfer of the X-rays is parameterized as

$$q = (4\pi/\lambda)\sin(\theta/2),$$

where θ is the angle through which the rays are scattered. The SAXS detector can be displaced with regard to the target from 1.5 m to 10 m in order to vary the range of θ angles that can be detected. In the experiment described here, the target to detector distance was held at 5 m corresponding to a q range of 0.033 nm^{-1} to 2 nm^{-1} . A q range of $3.6\text{--}33.0 \text{ nm}^{-1}$ was covered using the WAXS detector.

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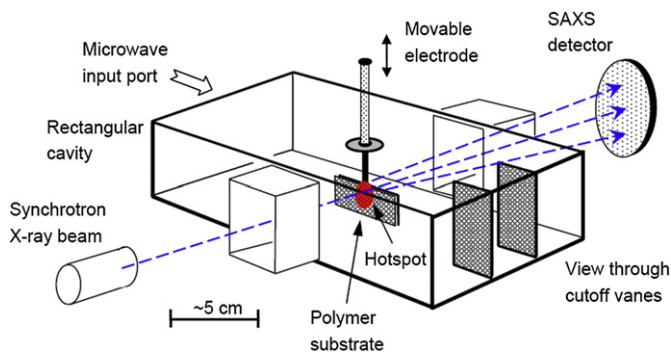


Fig. 1. A schematic of the experimental setup.

3. Experimental results

The experiment was performed by raising the microwave power to 0.8 kW and taking 400 combined SAXS and WAXS spectra (typical exposure time per measurement of 20 ms). These were recorded with a minimum dead-time of 300 ms between images, corresponding to the time necessary for readout of the SAXS detector. Visually, it was seen that the initially vertical polymer slice, bent back by an angle of about 10° as it was heated by the microwaves and when the power was turned off, it regained its vertical posture.

Fig. 2 shows the evolution of selected SAXS measurements, taken during the experiment. A curve taken under cold conditions is presented (black curve). The curve labelled Start corresponded to a time 33 s after the start of acquisition when the sample was warm enough so that the scattering data was observed to deviate from that for the cold condition. This change was initially slow but rapidly accelerated after about an additional 19 s, following this so-called Start point.

The broad peak seen in the SAXS spectra shown in Fig. 2 at early times is due to the lamellar structure in the polymer and thus to the density differences between the crystalline and amorphous regions in the material [6,7]. The long period L which represents the periodicity of the sum of the crystalline and non-crystalline thickness is given by $L = 2\pi/q_{\max}$ where q_{\max} is the value of q at the maximum of the broad peak. In this measurement, it is seen that under cold conditions, L has a value of about 9 nm but this value starts to rise

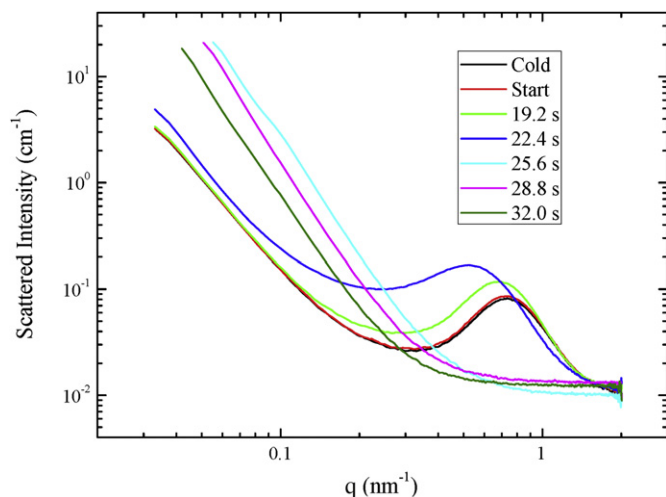


Fig. 2. Measured SAXS curves taken at several times during the microwave heating process.

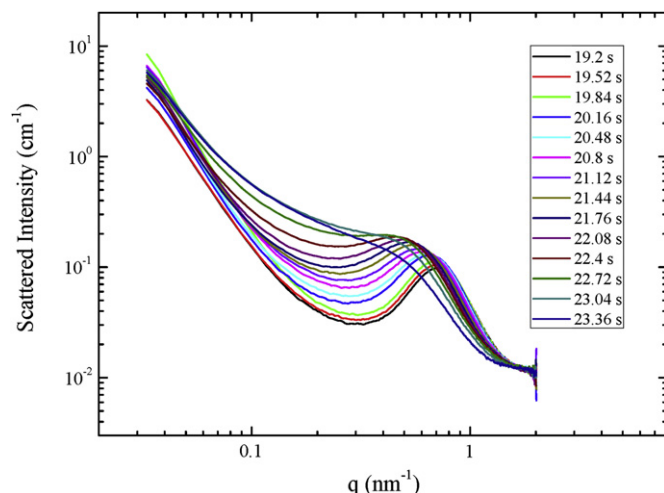


Fig. 3. The black curve shows the peak in the SAXS spectrum which rapidly moves to smaller q indicating that the long period is increasing, finally disappearing about 4 s later.

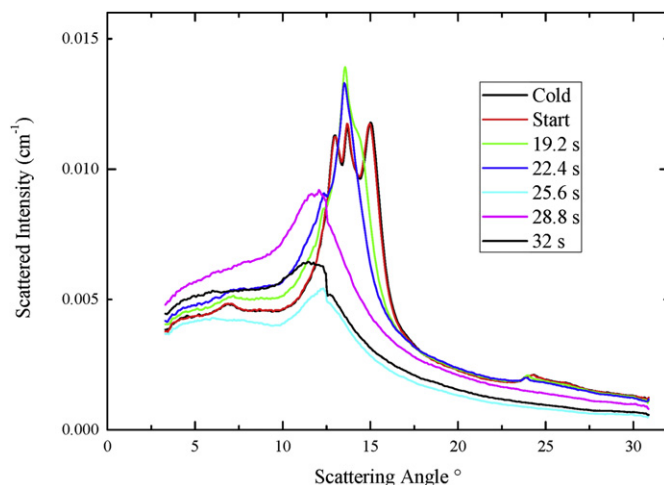


Fig. 4. Measured WAXS curves taken at several times during the microwave heating process. The q values have been converted to scattering angle for ease of comparison with other work with the wavelength being 0.995 Å.

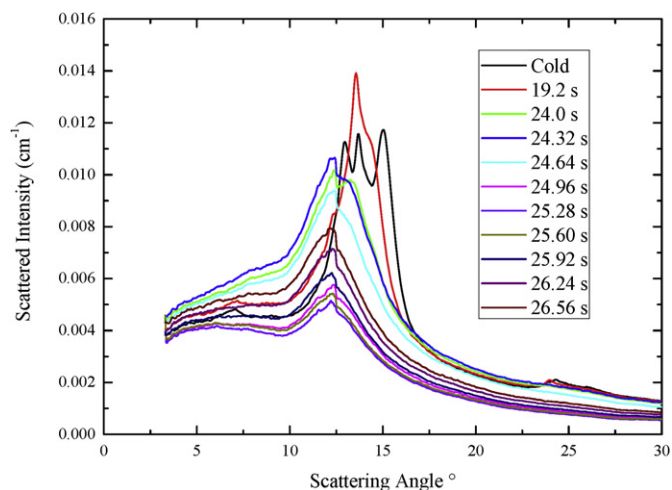


Fig. 5. Detailed view of the changes in the WAXS spectrum from the 19.2 s point on as in Fig. 3. Note the oscillation of the intensity between 24.64 s and 26.56 s.

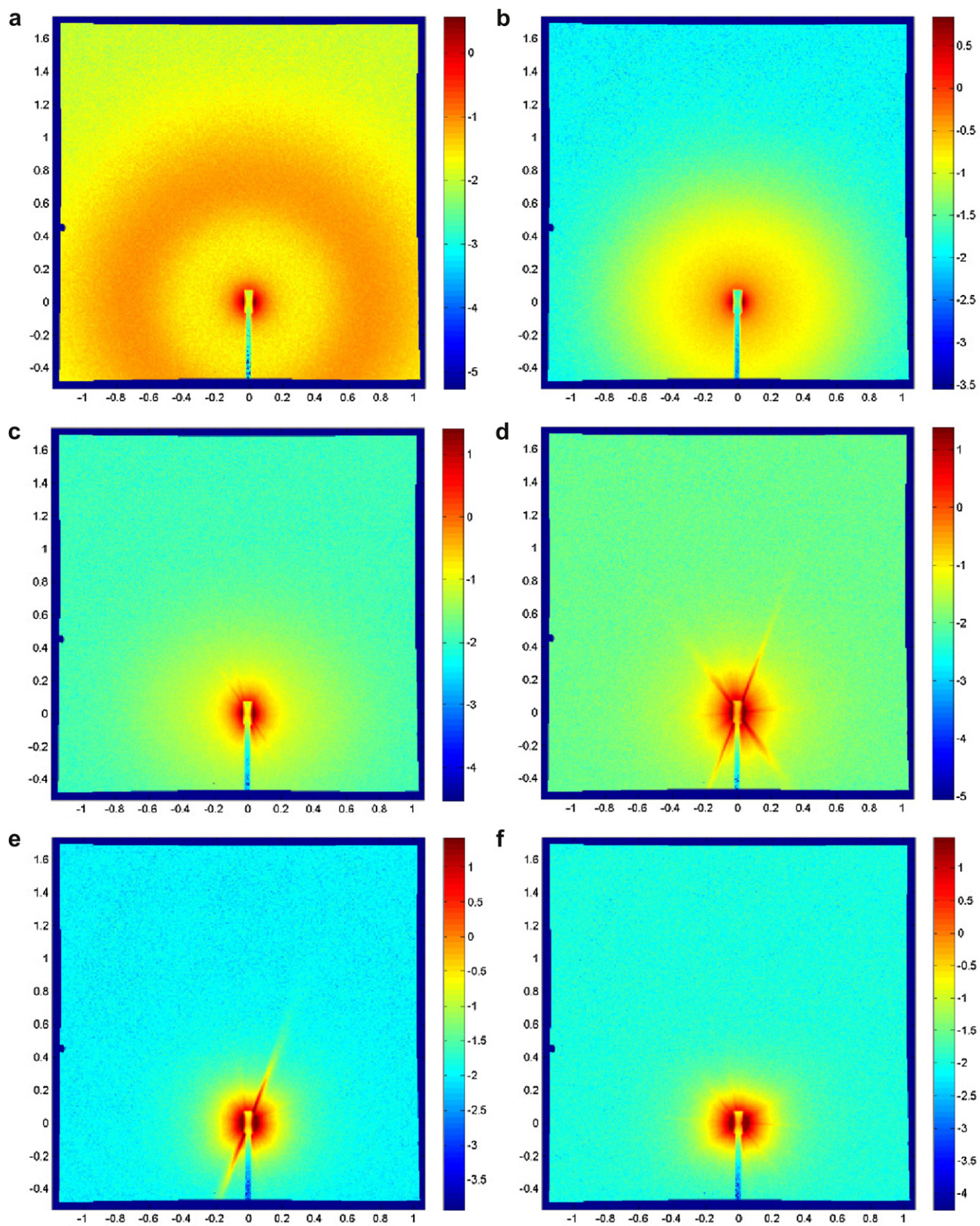


Fig. 6. SAXS detector images taken at consecutive times as described in the text. (a) Start point; (b) 23.68 s after start; (c) 24.32 s; (d) 24.64 s; (e) 25.28 s; and (f) 25.5 s. The axes are presented as q (nm⁻¹) and the intensity scale is logarithmic.

very steeply at the 19.2 s point, almost doubling in size within a further 3 s. Between 22 and 25 s after the defined start point, the peak due to the crystalline structure in the polymer completely collapses, leaving behind an amorphous structure. This rapid change is illustrated in more detail in Fig. 3.

Fig. 4 shows the evolution of selected WAXS measurements, taken during the experiment concurrently with the SAXS measurements and plotted as a function of scattering angle θ to allow for ease of comparison with other work. Again a curve taken under cold conditions is presented (dark blue triangles) with the same start point taken as in Fig. 2.

The collapse of the crystalline structure and its conversion is reflected in the WAXS data, where the sharp peaks are seen to rapidly blur out, with the multiple peaks merging to form a single peak at lower q . At the start of the measurement, there are two peaks corresponding to the (200) and (002) crystalline planes of the α form of Nylon-6 (at 13.0° and 15.0°) with a central peak (at 13.7°) and a small peak at 7.0° corresponding to (020) and (200) planes of the γ form of the polymer. As the heating progresses, the α peaks are seen to decrease and disappear with the γ form becoming dominant (at about 19 s). This peak then collapses and a broad amorphous peak centered at about 11.6° is left.

Fig. 5 shows this restructuration in more detail with 20-ms duration measurements taken every 300 ms over a 7 s period. It can be seen that the effect is very rapid and that there is a sharp decrease in the intensity of the amorphous scattering peak from 0 s to 25.28 s followed by an increase in intensity up to 26.56 s. This is an indication of the rapid change of structure within the material following the collapse of the crystallinity. Further oscillations in the height of this peak are observed at later times though with smaller amplitudes. These observations illustrate how the crystalline structure within the polymer matrix, unravels as the polymer melts. The decay of the crystalline peaks has been studied in previous X-ray experiments that have systematically followed the melting process in polymers [6,8].

The purpose of this paper, however, is to highlight an additional phenomenon that was observed during the experiments, namely the internal boiling of the material due to microwave absorption. This was seen by examining the 2-D images taken by the SAXS detector. A homogeneous target gives rise to an isotropic scattering pattern as presented in Fig. 6a and b, which show the disappearing of the lamellar structure upon melting. The SAXS curves shown in Figs. 2 and 3 are simply the integral through 360° of these images, plotted as a function of scattering angle, expressed as the q value. Thus, the initial peak in the *Intensity vs q* distribution is due to the annular structure seen in Fig. 6a which is subsequently seen to disappear in Fig. 6b.

The sudden appearance of spikes in the scattering pattern is noted in this series of images. These spikes appeared (Fig. 6c, d), changed orientation (Fig. 6e) and disappeared (Fig. 6f) within a timescale of about 1 s. As the heating continued, more spikes with different orientations appeared and disappeared in a random fashion.

In previous X-ray scattering studies of Nylon fibres [9], SAXS patterns displaying an equatorial streak have been seen and this has been attributed to elongated voids or regions of differing density within the structure, but it can also be attributed to the refraction of X-rays at the surface of the fibres.

Spikes such as are seen in the present study have been seen in neutron and X-ray scattering experiments on foams [10,11], where they are due to specular reflections off bubble surfaces, and during crystallization, where they are due to the formation of micro-crystals on the surface of a capillary containing a supersaturated liquid leading to a sharp change in the electron density [12].

Thus what is being seen in the images in Fig. 4 is the reflection of bubbles produced by the thermal decomposition of the polymer



Fig. 7. Enlarged photo of the Ertalon-6 sample ($2.0 \times 1.75 \text{ cm}^2$) following the experiment. Note that the charred material and the visible bubbles are within the sample. The external surface of the sample is clear and smooth.

leading to the vaporization of the material. The fact that the spikes come and go is due to the boiling action of the polymer that gives rise to random incidences where the reflections occur. Etrillard et al. [10] have discussed the phenomenon of X-ray reflection and have demonstrated that if the reflection is from a flat surface, there are intensity oscillations along the spikes whilst this does not occur with reflections from Plateau boundaries where bubbles meet solid surfaces or at the junctions with other bubbles. The latter seems to be the origin of the spikes seen in our work where there are no apparent oscillations. This series of measurements was repeated three times with the same effect seen each time.

Fig. 7 shows a photo of the polymer sample taken after the measurements. It is noted that while the outer surface of the sample is smooth and clear, the inside of the sample has clearly undergone thermal processing and there are indications of bubbles having been formed. The notch at the top is where the microwave concentrating electrode was in contact with the sample.

4. Discussion

The high intensity X-ray beams produced by a 3rd generation synchrotron light source such as the ESRF allows in-situ measurements of dynamic phenomena to be studied rapidly in real-time. In this experiment, we have shown that it is possible to follow the rapid melting and boiling inside an initially rigid polymer. This type of measurement could have applications in the study of the action of fire retarding agents, of the ignition of electrical cables due to inter-conductor arcing, and of the dynamics of the piercing of materials using the microwave drill technique [4], as well as microwave heating processes of polymers.

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