Advances in Physics Theories and Applications
ISSN 2224-719X (Paper) ISSN 2225-0638 (Online)
Vol.41, 2015

In-Situ Studies of Polymer Processing for Optimised Structure and Properties

Khalid Hassan Bader
University of Babylon, College of Education for Pure Sciences

Abstract
The transformation from a molten polymer to a crystalline solid product is a complex process. We show how special x-ray/rheology tools can be used to follow the development of structure during flow and the subsequent crystallization process and to identify the critical steps in this transformation. We have found that time-resolving x-ray scattering studies are a valuable approach, especially when coupled with other in-situ techniques such as neutron scattering and ex-situ methods such as electron microscopy. We illustrate the use of these tools with a study of the crystallization of polyethylene blends after being subject to shear flow in the melt. The resultant crystal textures and hence properties are strongly dependent on the shear strain imposed in the melt. High shear strain in the melt leads to a high density of row nuclei which serve to template the subsequent crystal growth. The microscopy on the final samples provides a complementary technique which offers valuable information on the spatial distribution of the morphology.

1. Introduction

The transformation from a polymer melt to a semi-crystalline polymer product is a complex process. It is widely known that a degree of molecular variability is required to ensure processability and appropriate final properties. However, the precise role of each molecular fraction in technologically relevant materials is not well understood. We have set out to develop tools which allow us to follow the development of structure during flow and the subsequent crystallization process so that we can identify the critical steps in this transformation.

We have found that time-resolving x-ray scattering studies are a valuable approach, especially when coupled with other in-situ techniques such as neutron scattering and ex-situ methods such as electron microscopy.

Understanding these processes is important to the optimization of polymer processing. As these materials are used in large quantities any modest gains are very significant. For example, the annual of polyethylene ~ 50 Million Tonnes and that for polypropylene ~ 25 Million Tonnes. The two polymers PE and PP account for ~ 65% of the thermoplastic market.

2. Experiment Approach

X-ray scattering methods provide a route to unambiguously determining the basic structural characteristics of polymeric materials. The penetration of X-rays means that these techniques are not restricted to thin films, as in the case of IR spectroscopy, or optically transparent materials, as in the case of optical microscopy. Complex materials including filled polymers, composites and strongly light scattering samples, such as semi-crystalline polymers, can be studied with ease. Moreover, the sample preparation required for x-ray scattering techniques is often minimal.

Wide-angle x-ray scattering techniques can provide direct information on key features such as crystallinity, preferred orientation, phase identification and compositional analysis. More detailed analysis can yield details of local chain conformations and packing arrangements in both crystalline and disordered polymers. Small-angle x-ray scattering techniques provide a route to information of a larger scale nature, particularly in multiphase materials such semi-crystalline polymers, block copolymers and blends. Quantitative details on crystalline lamellar size or on preferred orientation are just two examples of the structural parameters which can be obtained using this powerful technique.

We have set out to exploit these advantages by designing rheological stages [Nogales *et al.*, 2004] which enable wide-angle and small-angle x-ray scattering data to be recorded during flow and subsequent crystallization. Described in this work.

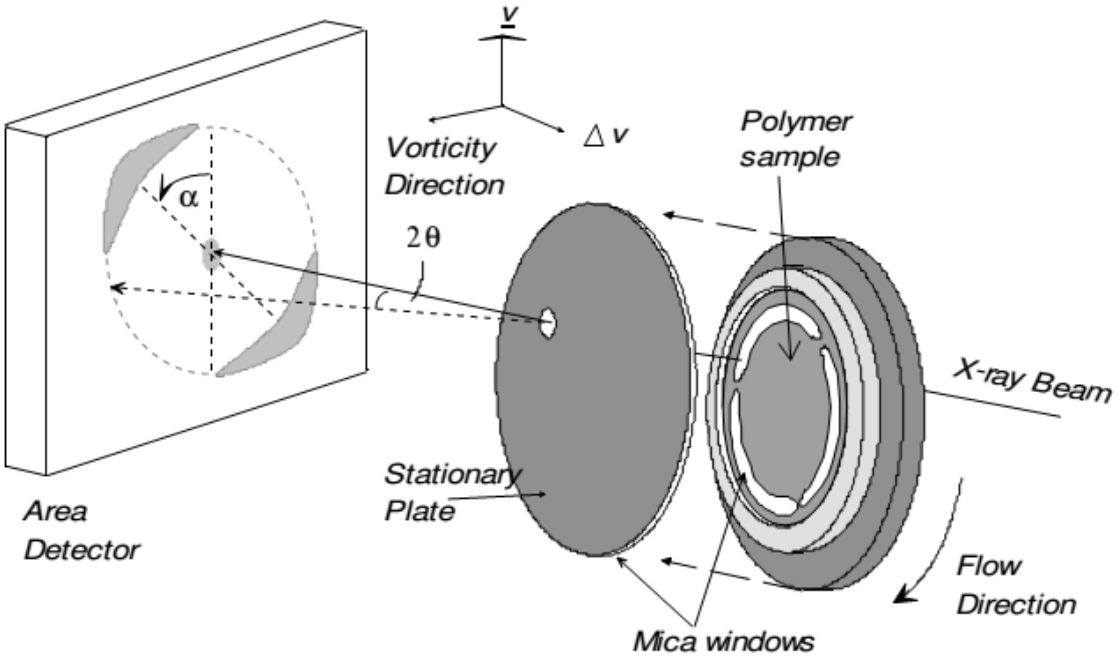

Figure.1: A schematic of the shear cell used for the in-situ time-resolving X-ray scattering measurements

Figure 1 shows the essential features of the x-ray shear cell. The polymer is held between two mica discs which are supported by metal\ plates with appropriate apertures to allow the transmission of the x-rays. The whole assembly is mounted within a heating stage equipped with electrical heaters which are controlled using a Eurotherm PID Controller. Defined cooling was achieved by the use of a flow of cooled nitrogen gas together with appropriate electrically operated valves coupled to the Eurotherm controller. Quiescent temperature conditions were calibrated using the melting points of simple organic compounds. The cooling conditions were calibrated by comparing isothermal crystallization rates (without shear) for different temperatures with those recorded on equivalent samples in a DSC.

Using the intense flux available on the fixed wavelength beam-line 16.1 at the Daresbury Synchrotron Radiation source, real-time data were collected using the Area X-ray Imaging System (AXIS), developed at The University of Reading. A time resolution of ~1 s was possible with this arrangement. The small X-ray beam diameter of ~ 0.3 mm enabled the diffraction patterns to be obtained from defined volumes of material which had been subjected to more or less constant shear rate [An et al., 2006].

The internal morphology of the resultant samples, after cooling to room temperature, was examined in the TEM, following permanganic etching [An et al., 2006]. Samples were typically etched for four hours using a 1% solution of potassium permanganate dissolved in an acid mix containing 5 parts concentrated sulphuric acid to 2 parts orthophosphoric acid to 1 part water. The procedure removes sufficient material from the surface of the samples to eliminate any surface specific morphologies. After etching, samples were replicated using a standard two stage replication procedure; care was taken to ensure that replicas were taken from areas equivalent to those from which X-ray data were collected (ie at the same radial distance from the centre of the sample). All the replicas were shadowed radially and examined using a Philips EM301 operating at 80 kV.

3. Materials

We have used these tools to study a wide range of polymer systems including, polyethylene, polypropylene, polycaprolactone and polycarbonate. In this work, we focus on a typical broad molecular weight linear polyethylene (LPE) resin supplied by BP Chemicals, with a broad molecular mass range, with MW= 312,000 and MN = 33,000. The other polymer was a branched polyethlene (BPE) with a branching level of ~0.06 and was supplied by Borealis Polymers, and was characterised by much lower molecular masses; MW= 76,800 and MN= 11,300.

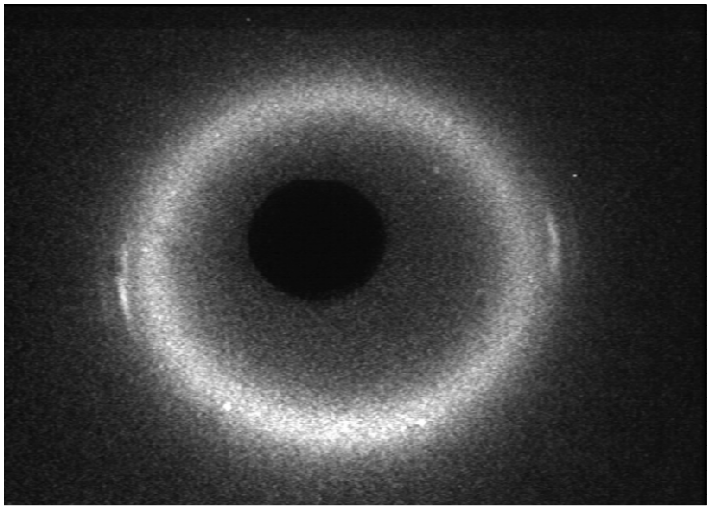

Figure.2: A time-resolved WAXS pattern for a 20% LPE/BPE Blend which has been sheared in the melt and then quenched to an isothermal crystallization temperature. The pattern is one of a series and corresponds to the very early stages of crystallization where the crystallinity is < 0.1%. The sharp peaks correspond to the (110) and (200) Bragg reflections.

Blends of these two polymers ranging in composition from 5-20% LPE were examined during the course of this investigation. All the blend samples described here were prepared by solution processing, using xylene as a co-solvent. Appropriate masses of each polymer were first dissolved in xylene at 140 oC to give a 1% w/v solution and, then, recovered by precipitation in an excess of cold methanol, followed by filtration and vacuum drying.

4. Results

Figure 2 shows a snapshot of the wide-angle x-ray scattering taken at an early stage of crystallization following shear flow in the melt phase. It is clear that the crystals have a very strong preferred orientation. Note that both the 110 and 200 reflections are most intense on the equatorial section indicating a fibre type alignment of the crystals. It is possible that these correspond to the shish in the shish-kebab type morphology. We can use the wide-angle scattering data to evaluate the level of crystallinity during the crystallization process and this is shown in Figure 3.

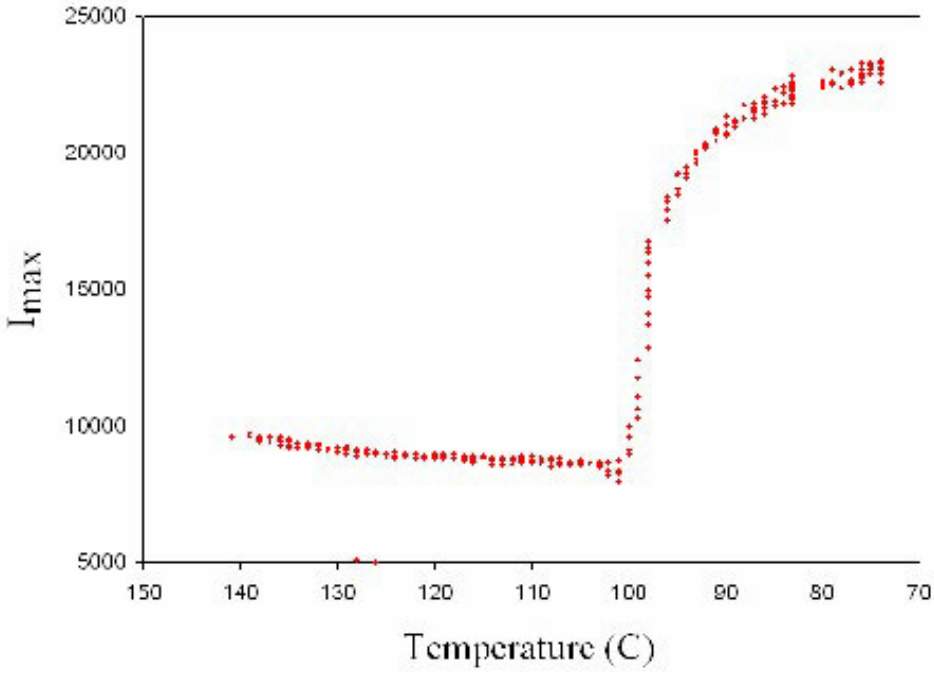

Figure.3 A plot of the crystallinity against temperature for a sample of 20%LPE/BPE blend which has been sheared in the melt and then quenched to an isothermal crystallization temperature.

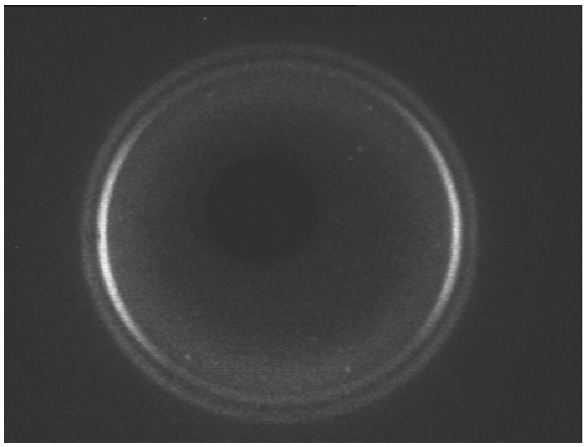

Figure.4 A time-resolved WAXS pattern for a 20% LPE/BPE Blend which has been sheared in the melt and then quenched to an isothermal crystallization temperature.

The pattern shown in Figure 4 is one of a series and corresponds to the final stages of crystallization after shearing for a high shear strain > 200su (product of shear rate and time).

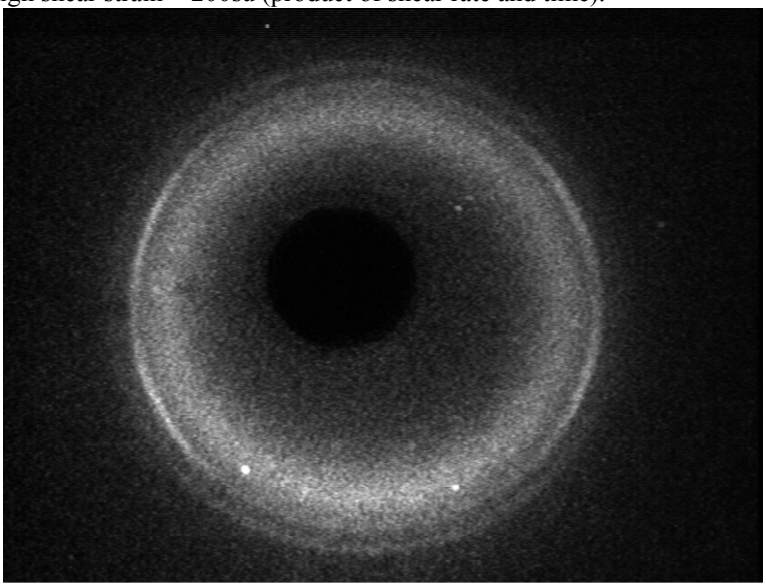

Figure.5: As in figure 4 but for a low shear strain < 70su.

Figures 4 & 5 show the final crystal textures for two different samples one subjected to high shear strain and the other to a low shear strains. The patterns in the very early stage of crystallization are the same for both samples and are equivalent to that shown in Figure 2. The change in shear strain led to the development of different lamellar morphologies. This is shown more clearly in the Figures 6 & 7 which show a series of azimuthal profiles for the patterns taken for the high shear strain sample. The sections shown correspond to the distribution of scattered at intensity for the 110 peak as a function of the azimuthal angle. The intensity is most intense throughout the sequence on the equatorial section (90 degrees) as was shown in the patterns in Figures 2 and 4. In contrast, the sequence of sections for the low strain sample reveals a change in crystal morphology as crystallization proceeds. Initially the scattered intensity is most intense at 90 degrees i.e. on the equatorial section but as crystallization proceeds, there is a distinctive switch in the pattern of crystal orientation. This can be seen more clearly in Figure 8 which shows the differences between successive sections shown in Figure 8. The patterns effectively reveal the scattering from the crystals which grew in that time slice.

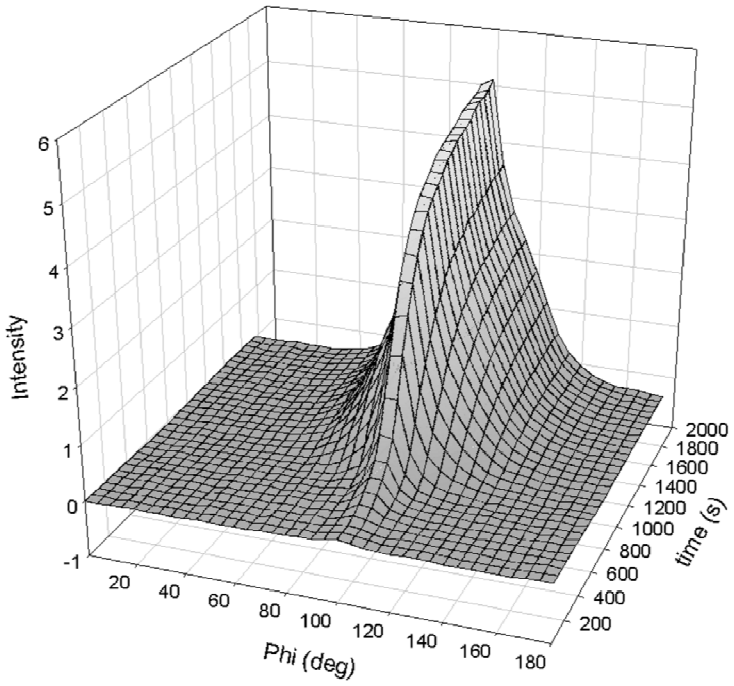

Figure.6: A series of time-resolved WAXS patterns (azimuthal sections) for the sample subjected to a high shear strain.

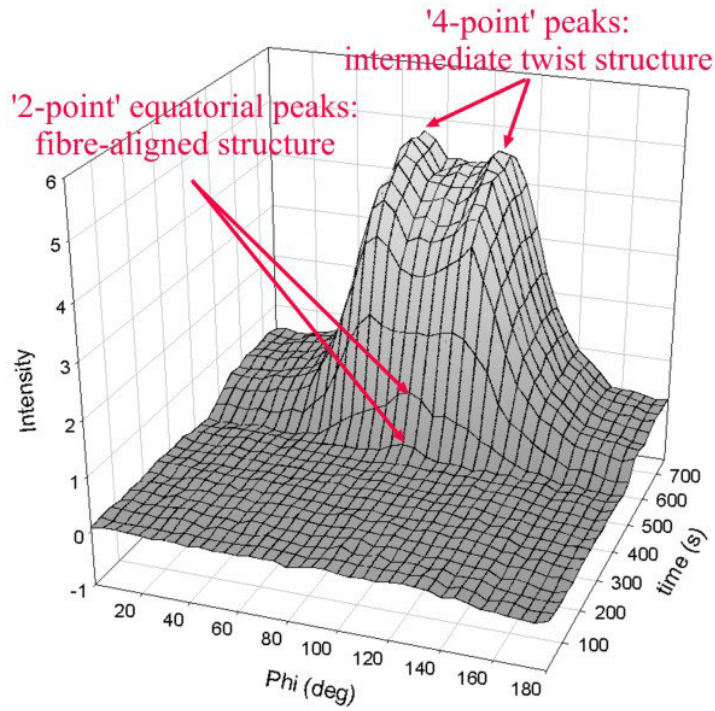

Figure.7: A series of time-resolved WAXS patterns (azimuthal sections) for the sample subjected to a low shear strain.

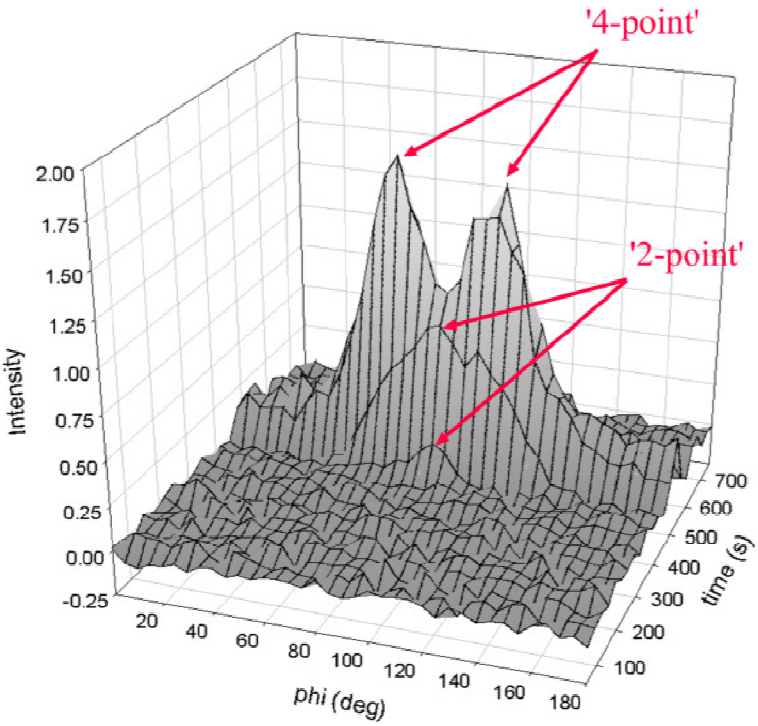

Figure.8 The differences between successive sections for the data shown in Figure 7.

The so-called four point pattern corresponds to a system of twisting or s-shaped lamellae. It is clear that without the time-resolving x-ray scattering data, we would not see this transition in crystal texture with time. The availability of this powerful technique allows us to map out the response of different resins to the shear flow history.

We can in part attribute this changing crystal orientation to the density of row nuclei. High shear strains even in the melt above the equilibrium melting point of the crystals still produce row nuclei. As the lamellae grow out from nucleating surface, they twist. If the row nuclei density is high then the lamellae only grow a short distance before they impact on other lamellae.

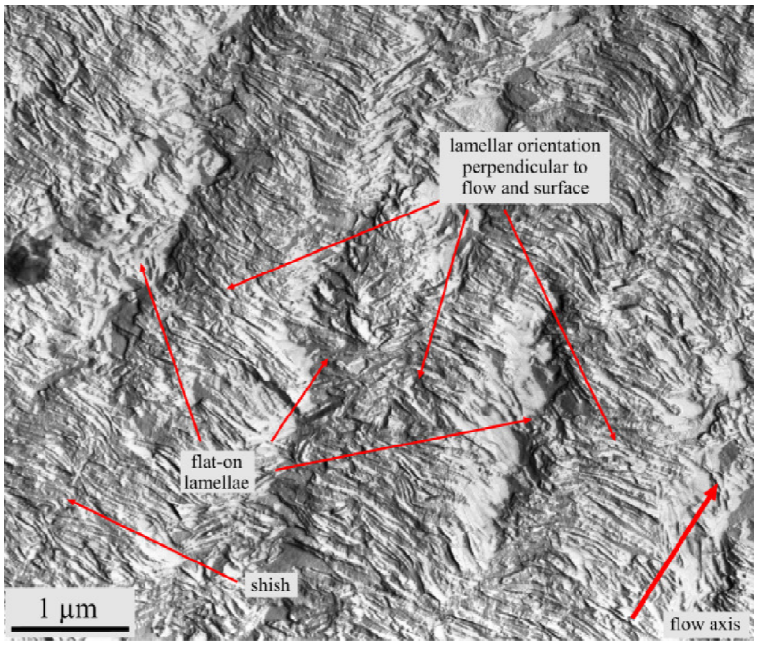

Figure.9: TEM micrograph of a sample subjected to a high shear strain showing a high density of row nuclei.

The flow axis is indicated by means of the bold arrow.

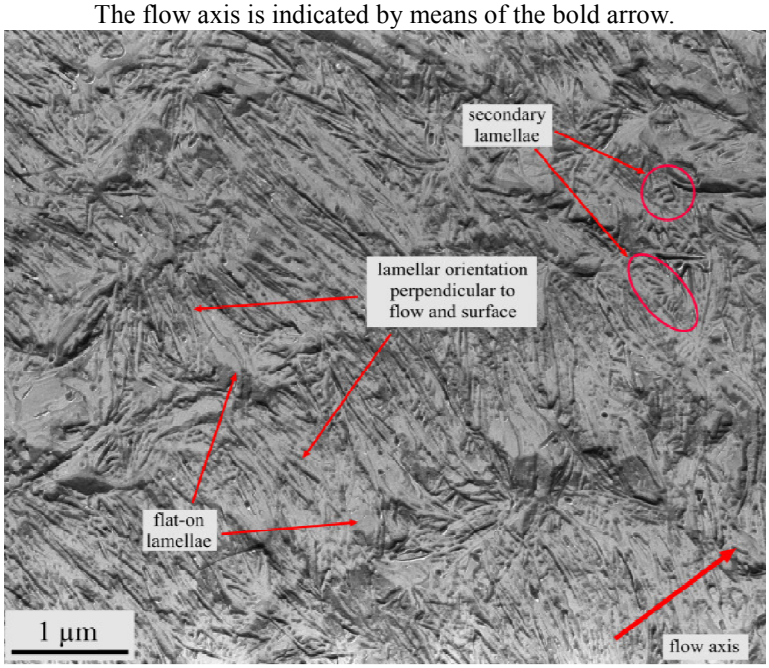

Figure.10: TEM micrograph of a sample subjected to a low shear strain. The flow axis is indicated by means of the bold arrow.

Figure 9 shows a TEM micrograph obtained from the internal surface of a sample subjected to a high shear strain. The high density of row nuclei can be easily observed together with a strong preferred orientation of the lamellae. In contrast, Figure 10 shows a TEM micrograph for a sample subjected to a low shear strain. The low row nuclei density and the mixture of lamellar orientations can be easily observed.

Conclusions

Time-resolving x-ray scattering provides a powerful approach to developing an understanding of the influence of shear flow on the subsequent crystallization of technologically relevant polyolefin resins.
The shear cell developed is particular effective in these studies.

The resultant crystal textures and hence properties are strongly dependent on the shear strain imposed in the melt. High shear strain in the melt leads to a high density of row nuclei which serve to template the subsequent crystal growth. The microscopy on the final samples provides a complementary technique which offers valuable information on the spatial distribution of the morphology.

These procedures are most useful in understanding the complex transformation from a polymer melt to a semi-crystalline solid during processing.

Acknowledgements

The x-ray scattering data shown here were obtained at the CCLRC Daresbury Synchrotron Radiation Facility and we thank the staff there is particular Anthony Gleeson for the their help in performing the experiments.

References

1. Nogales, A, Thornley, Sa, and Mitchell, Gr., 2004, “Shear cell for in-situ WAXS, SAXS and SANS experiments on polymer melts under flow fields”, J. Macromol Sci Phys; B, V 34: pp. 1161-1170
2. An, Y., Holt, J. J., Mitchell, G. R., and Vaughan, A. S., 2006, “Influence of Molecular Composition on the Development of Microstructure from Sheared Polyethylene Melts: Molecular and Lamellar Tinplating” , Polymer, V47 pp. 5643-5656.

The IISTE is a pioneer in the Open-Access hosting service and academic event management. The aim of the firm is Accelerating Global Knowledge Sharing.

More information about the firm can be found on the homepage:
http://www.iiste.org

CALL FOR JOURNAL PAPERS

There are more than 30 peer-reviewed academic journals hosted under the hosting platform.

Prospective authors of journals can find the submission instruction on the following page: http://www.iiste.org/journals/ All the journals articles are available online to the readers all over the world without financial, legal, or technical barriers other than those inseparable from gaining access to the internet itself. Paper version of the journals is also available upon request of readers and authors.

MORE RESOURCES

Book publication information: http://www.iiste.org/book/

Academic conference: http://www.iiste.org/conference/upcoming-conferences-call-for-paper/

IISTE Knowledge Sharing Partners

EBSCO, Index Copernicus, Ulrich's Periodicals Directory, JournalTOCS, PKP Open Archives Harvester, Bielefeld Academic Search Engine, Elektronische Zeitschriftenbibliothek EZB, Open J-Gate, OCLC WorldCat, Universe Digtial Library , NewJour, Google Scholar