Small-angle X-ray Scattering Study of Shear-induced Crystallization in Polypropylene

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Introduction

The first-ever time-resolved small-angle x-ray scattering (SAXS) data collected on the ChemMatCARS beamline is presented here to indicate current beamline capabilities. The application of time-resolved SAXS techniques for the study of polymer crystallization has developed into a powerful experimental tool, capable of providing a wealth of structural information to assist in the description of this complex process. If industrial polymer processing techniques, such as injection molding, are to be understood and modelled effectively, the mechanisms of shear-induced crystallization need to be investigated. This work forms part of a research program to investigate the properties of commercial grades of polypropylene, with a view to ultimately predicting the properties of injection-molded (IM) parts. The program has both a theoretical [1] and an experimental approach, where the final morphology of IM parts have already been studied by using SAXS and wide-angle x-ray scattering (WAXS) [2, 3]. Many other groups have investigated the crystallization characteristics of polypropylene [4-8]. Current research on model polypropylenes indicates that the long relaxation times of high-molar-mass polymer chains play an important role in the degree of orientation for samples crystallizing after a step shear [9-11]. If industrial processing problems, such as shrinkage and warpage, are to be modelled and simulated accurately, many factors will need to be considered in future studies, including the effects of molar mass and molar mass distribution, rubber toughening components, and nucleating agents.

Methods and Materials

The ChemMatCARS beamline receives x-rays from an undulator source, where the full monochromatic beam has an estimated flux of 1013 photons/s at 8 keV with an energy bandpass of 10-4. The first optics enclosure (FOE) contains the beam conditioning equipment. It starts with a differential pump, which isolates the vacuum in the storage ring from the vacuum in the beamline. A Bremsstrahlung collimator then prevents the high-energy Bremsstrahlung gamma rays created in the storage ring from reaching the experimental hutch. Next, power-limiting apertures control the size of the x-ray beam and hence manage the power loading accepted by the monochromator. A Kohzu high-heat-load monochromator uses a water-cooled diamond (111) crystal to select the desired wavelength. A thermal dump then acts as a high-power beam stop to terminate the polychromatic wavelengths and protect the optics downstream. The first mirror has three coatings (Si, Rh, Pt) and acts as a low-pass filter to remove the high-order harmonics in the beam. The mirror also has the ability to provide focussing in the vertical plane. A second mirror is used for further harmonic rejection and realignment of the beam. Next, an integral shutter controls whether or not the x-rays are allowed to pass onto the experimental hutch. It can also act as a second thermal dump. The FOE ends with a specially polished and cooled x-ray-transparent beryllium window. This window isolates the vacuum in the FOE from the vacuum in the shielded beam transport. The sample position has a 1-m floor footprint for the insertion of user-supplied equipment (in this case, the shear cell) before the scattered x-rays pass through an evacuated flight tube onto the SAXS detector. A 1.3-Å (9.54-keV) x-ray beam was selected for this study.

For the polypropylene (PP) shear experiments, the PP pellets (Basell Moplen EP301K) were first melt-pressed to form bubble-free discs approximately 700 μm in thickness and about 15 mm in diameter. The PP disc was loaded onto the Linkam CSS450 shear cell in a horizontal position. The quartz plates of the shear cell were replaced with stainless-steel plates with windows of Kapton® film (125-μm thick) to increase x-ray transmission. The shear cell was aligned such that the 200×100-mm x-ray beam could pass through the centre of the 2.5-mm-diameter aperture, located 7.5 mm from the center of shear rotation. The polymer samples were melted at 210°C to erase any thermal/shear history. Once the PP was molten, the upper plate was lowered to the desired sample thickness (in this case, 500 μm). The shear cell was then placed in the x-ray beam path with the windows in a vertical position, such that the x-ray beam passed through the sample perpendicular to the shear direction. After 5 min at 210°C, the sample was quenched to the crystallization temperature of 130°C, at 30°C/min. A step shear was applied to the PP at a shear rate of 50 s^{-1} for 10 s. The cessation of the applied shear was regarded as time zero for the SAXS data collection.

A Bruker 6000 charge-coupled device (CCD) detector was used to collect the SAXS data. The detector has a data collection area of 94×94 mm^2, with a pixel size of 92 μm. The detector was located symmetrically at a distance of 1870 mm from the sample position, enabling a d-spacing in the range of 40 to 1100 Å to be studied. A 2-mm-diameter beam stop protects the detector from the direct x-ray beam. Data were collected for 6 s per frame followed by a 4-s wait period, but because of a read-out time of about 3 s, the average time between frames was approximately 13 s. Exact frame times were captured from the file header information and used to create the time axis. The program FIT2D was chosen to display the image files.

Results

The resulting SAXS images for the shear-induced crystallization of PP are shown in Fig 1. The color scale of each image has been optimized to highlight small changes in the scattered x-ray intensity. The beam stop and its support arm are clearly visible, casting a black shadow onto each image. The scattered x-rays remain isotropic until at least 13 s after the cessation of shear. By 26 s, large streaks appear in the meridional plane (flow direction), while there is also a small increase in scatter in the equatorial direction. The meridional streaks are oriented at about 5° to the horizontal plane, which is attributed to the curvature of the shear path seen within the aperture of the shear cell, implying that the smaller x-ray beam may not be located in the absolute center of this aperture. The large increase in meridional scatter is attributed to the creation and orientation of semicrystalline lamellae. These lamellae have become oriented perpendicular to the flow direction. The small increase in equatorial scatter was also observed in other samples in this study, and it has been attributed by Somani et al. [12] to microfibrillar structures oriented parallel to the flow direction. The image acquired at 39 s shows that there was a significant increase in scattering in all directions, while in the meridional plane, the streaks have developed into lobes that exhibit 180∞ rotational symmetry. The next image at 51 s indicates that there has been an increase in the ordering of lamellae perpendicular to the flow direction, while a ring at the dominant scattering vector (q) can be seen most of the way around the image. The structure of the scattered intensity in the meridional peaks appears to get coarser from about 64 s onward; the shape in the teardrop-like peaks remains virtually unchanged. The final coarsened SAXS image collected at 2421 s, after cessation of shear, indicates that a significant number of lamellar-like structures with a long period of about 265 Å become oriented perpendicular to the flow direction. A full ring at about

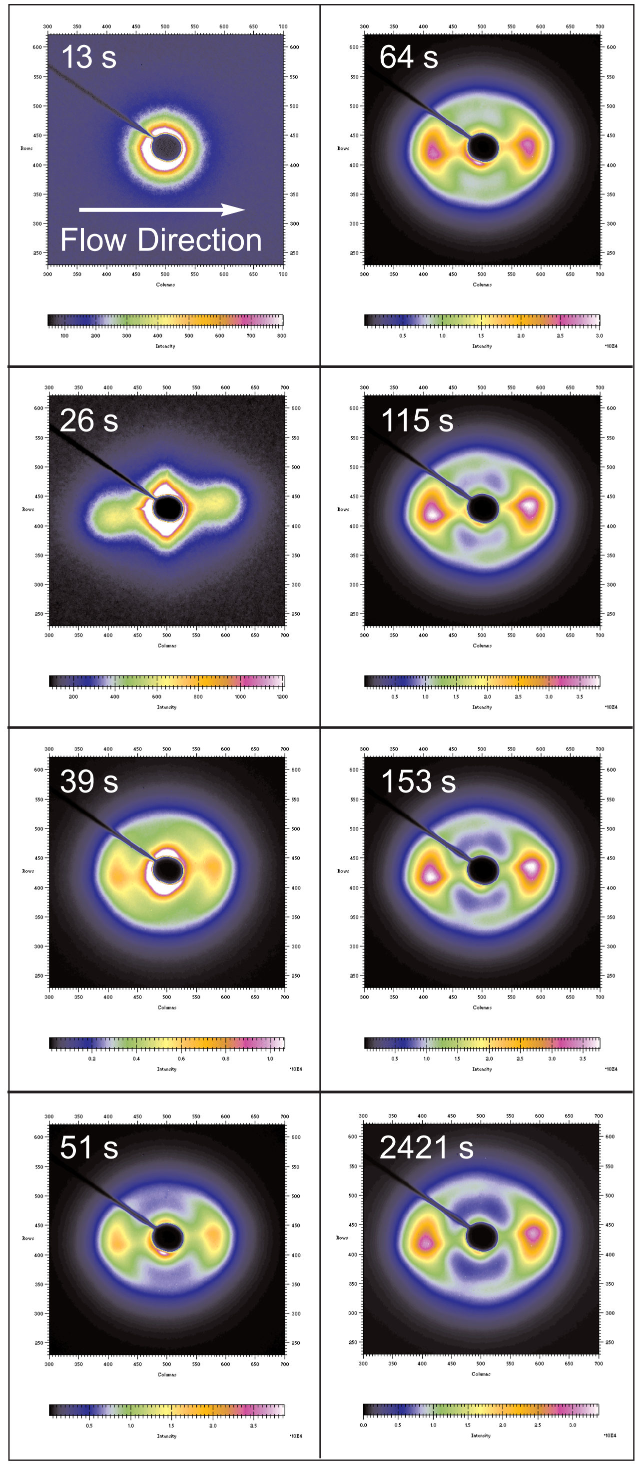

FIG. 1. A selection of SAXS images for the shear-induced crystallization of polypropylene.

this q value is present, however, which indicates that similar structures have formed with all orientations. The step shear has induced nucleation and growth, giving preferred lamellae orientation. Further studies confirm that the application of shear increases the crystallization kinetics with respect to crystallization under quiescent conditions.

Discussion

The first-ever time-resolved SAXS study on the ChemMatCARS undulator 15-ID-D beamline was successfully completed. The extremely intense x-rays from a third-generation synchrotron coupled with a high-resolution 2-D SAXS detector produced a series of SAXS images of exceptional quality and detail. The only drawback to the existing setup is the read-out time for the CCD detector, which, at about 3 s, limits the study of faster processes, even when the scattered count statistics may well be sufficient from a much shorter exposure time. The SAXS images following the shear-induced crystallization of polypropylene exhibit a high degree of anisotropy, with maxima in the meridional plane indicating lamellar-like structures oriented perpendicular to the flow direction. The images also exhibit 180° rotational symmetry.

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