

Molecular Morphology of Petaloid Bases of PET Bottles: A Small-Angle X-ray Scattering Study

Tracey Hanley,^{1,2} David Sutton,^{1,2} David Cookson,^{1,4} Edward Kosior,^{3*} Robert Knott^{1,2}

¹Australian Nuclear Science and Technology Organisation, Private Mail Bag, Menai, New South Wales 2234 Australia

²CRC for Polymers, 32 Business Park Drive, Notting Hill, Victoria 3168 Australia

³Visy Industries, 5 Coronation Ave Kings Park, New South Wales 2148 Australia

⁴ChemMatCARS, Advanced Photon Source, Argonne, Illinois 60439

Received 5 Jun 2005; accepted 27 Jul 2005

DOI 10.1002/app.22757

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Small-angle X-ray scattering (SAXS) studies were undertaken to explore possible morphological explanations for poor mechanical strength in the petaloid bases of poly(ethylene terephthalate) (PET) bottles. The bottles were manufactured using a two-stage injection stretch blow molding process. Splitting of PET bottle bases under load is both inconvenient and expensive. In this study, SAXS data were collected with a 100 μm square X-ray beam to establish the molecular morphology as a function of position across the base topology. An amorphous region was identified in the base center (i.e., close to the injection gate of the preform)

with biaxially orientated, semicrystalline regions in the feet and valleys of the bottle bases. For bottles that had split under load, the transition between these two regions displayed uniaxial orientation that would lead to reduced mechanical strength in the circumferential direction. Reasons for this effect are explored. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 3328–3335, 2006

Key words: SAXS; polyethylene terephthalate (PET); petaloid base; orientation

INTRODUCTION

Petaloid bases are now standard features on two-stage injection stretch blow molded poly(ethylene terephthalate) (PET) bottles because of their stability and are used particularly for carbonated soft drink (CSD) containers. The manufacturing process is highly automated and, in the main, well understood. In Stage I, the PET bottle preforms are injection molded in batches of around 96 and cooled to room temperature so that the preform is virtually amorphous, although the area of polymer adjacent to the injection gate of the mold can be partially crystalline due to the proximity of the hot runner. In Stage II, the preforms are reheated to a temperature above the glass transition, but below the cold crystallization temperature and stretch blow molded into bottles of given design. The crystallinity and molecular orientation induced by this two-stage process are essential to impart the required mechanical properties (strength, optical clarity etc.).^{1–7} To manage this process in the commercial environment requires the enormous body of knowledge and know-how that has been developed in this field.

The present petaloid base motif (Fig. 1) is well established in commercial application, however as design techniques become more sophisticated, (particularly computational methods,⁸) further research and development can be expected. Currently, research into improvements is in progress⁹ with the aim to overcome some of the known limitations of the petaloid design.

One existing limitation is circumferential cracking of the petaloid base, a well-known phenomenon where the underlying causes are poorly understood.¹⁰ As part of an extended research program on the molecular structure of PET,¹¹ small-angle X-ray scattering (SAXS) techniques have been developed to investigate the morphology of PET chains under a range of controlled experimental conditions (e.g., temperature, shear, and chain composition) that model industry conditions. These SAXS techniques were used to explore the molecular organization of PET molecules in the petaloid bases of high quality bottles, and bottles that had split under load.

The packing pressure of the injection molded preform¹⁰ and the temperature of the preform during stretch blow molding³ are known to be important in determining the properties of the final product. For the packing phase, the hold time relates to the preform weight; during this phase the gate remains open allowing more material to be pushed into the mold cavity. During this stage, the preform is also being

Correspondence to: T. Hanley (Tracey.Hanley@ansto.gov.au).

*Present address: Closed Loop London, 1 Hobhouse Court, Suffolk St, SW1Y 4HH, London, United Kingdom.

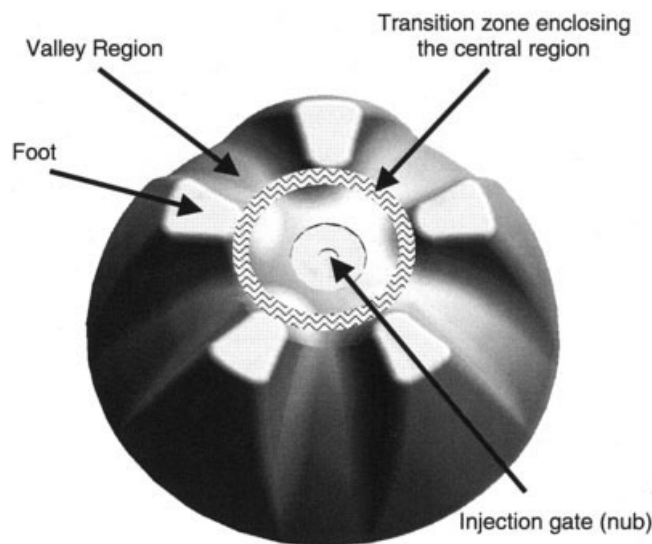


Figure 1 Engineering (rendered) drawing of a typical petaloid base of a bottle injection stretch blow molded from poly(ethylene terephthalate) (PET).

cooled in preparation for removal from the mold. Therefore, the longer the hold time, the more material is forced into the end of the preform that ultimately forms the base of the bottle. More efficient cooling to the body and neck of the preform allows these regions in the mold to resist the addition of more material.

Preform reheating for the stretch blow molding phase also plays a significant role in defining the ultimate performance of the bottle. Reheating is normally achieved using infra-red radiation supplied by an array of lamps in conjunction with convection. The aim of the reheating process is to raise the temperature of the preform body into the range of 90–115°C. This range is warm enough to avoid pearlescence (stress-whitening due to microvoiding) but below the cold crystallization temperature that would produce haze in the bottle. Axial temperature profiling is controlled so that both ends of the preform remain cooler while the body reaches ideal temperature. The neck above the support ring must remain cool to prevent distortion of the bottle closure region, while the bottom end of the preform must remain cooler to withstand the force of the stretch rod. The temperature profile along the body may vary to reflect any tapering in the thickness of the walls. Clearly the temperature profiling at the base of the preform during the stretch-blow phase will have a major contribution towards the final morphology of the petaloid base. The likelihood of failure by cracking is directly related to the polymer morphology of the petaloid base, hence both phases of the production process can significantly influence cracking susceptibility.

It is known that the routine two-stage injection stretch blow molding production process should lead

to an amorphous region in the center of the bottle base (although the nub region from the gate itself is semi-crystalline). This central region is immediately followed by a biaxially oriented region in the feet and valleys, which progresses into the bottle wall. The residual stresses in the base material have been calculated using the Abaqus Simulation Software,⁹ and the stress calculations indicate maximum stress is present in the valley regions. Lyu et al.¹² have used computer modeling to study crack formation in the base and concluded that cracks were formed in regions with inadequate strength. These regions resulted from insufficient stretching of the polymer, such that strain hardening did not occur, basically as a consequence of a coarse base design. The base cracks were also shown to result from crazing that occurred because of the maximum principle stress being located in the valleys and the crazing strongly affected the crack formation.

To illustrate, in a typical 2-L CSD bottle, the thickness of PET in the walls is 0.35 ± 0.1 mm, while the thickness over the central region of the base is 2.1 ± 0.4 mm. In the transition region between the base center and either the foot or valley, the thickness is reducing as the material is being stretched. A reduced thickness leads to a reduced strength of the base until the material is stretched far enough for strain hardening to occur, and at this point there is a dramatic increase in the overall strength, which compensates for the reduction in thickness. Obviously there remains a suspect region where the material is thinning but strain hardening and subsequent crystallization is yet to take place.

Lyu et al.¹³ produced a further study that concluded the key design parameters affecting circumferential cracking in the bottle base were foot length, valley width, and clearance (the height difference between the gate position and the surface on which the bottle stands). Computer simulations were used to find the optimum values for design parameters that reduced the principle stress concentration, and these values were then used to design a new base, which resulted in increased crack resistance.⁹ For the present study, no attempt was made to explore any skin/core effects, although research by Everall et al.¹⁴ indicated that skin/core effects were important. In a study using polarized attenuated total reflection FTIR spectroscopy¹⁴ on bottle walls, complex orientation patterns and gradients were shown to exist in the skin/core regions that depended on preform and mold design. It was shown that the differences in hoop extension for the inner and outer surfaces of a bottle wall are significant for overall morphological properties. Typical values are approximately 5 and 4 for the inner and outer walls respectively, of a 2-L bottle. The different geometry of the base means that there is unlikely to be any significant differences in hoop extension between inner and outer surfaces until the base starts to curve

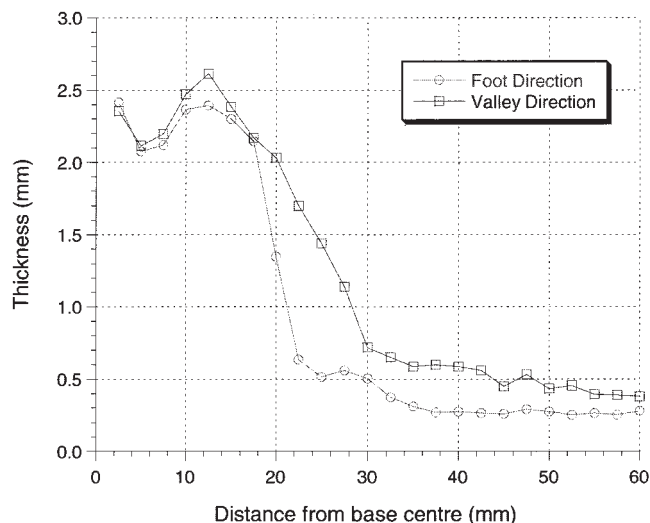


Figure 2 A plot of PET thickness versus distance from base centre as measured for a typical 2-L CSD bottle.

into the bottle wall, well beyond the transition region of interest. However, differences may exist due to rapid cooling of the skin during the injection molding process, which freezes the skin while the core material is still flowing into the mold.

EXPERIMENTAL

PET bottles were randomly selected from (i) a batch of high quality bottles (2 L capacity) and (ii) a batch of split bottles (2 L capacity). The bases were cut from the bottles to provide a clear path for the X-ray beam in transmission mode. No other sample preparation was required.

The bottles were manufactured by Visy Industries from commercial grade PET using two stage injection stretch blow molding process operating under standard industry conditions. The split bottles were obtained after they had split under load of carbonated soft drink (CSD) in a factory environment.

Measurements of thickness of the PET in 2-L CSD bottles and corresponding preforms at various positions along the bottle walls and bases were made using vernier calipers. The measurements were repeated for several different samples and at many locations. The average values through both the valley and foot directions for 2-L CSD bottles are represented graphically in Figure 2, while the average values for the corresponding preforms are shown in Figure 3.

Data were collected on the SAXS instrument on the 15-ID-D beamline ChemMatCARS (Advanced Photon Source, Chicago, IL).¹⁵ An X-ray beam with a wavelength of 1.3 Å (9.54 keV) was selected. The 2D SAXS patterns were collected using a Bruker 6000 CCD detector (active area $94 \times 94 \text{ mm}^2$ with a pixel size of 92 μm), which was located 1887 mm from the sample

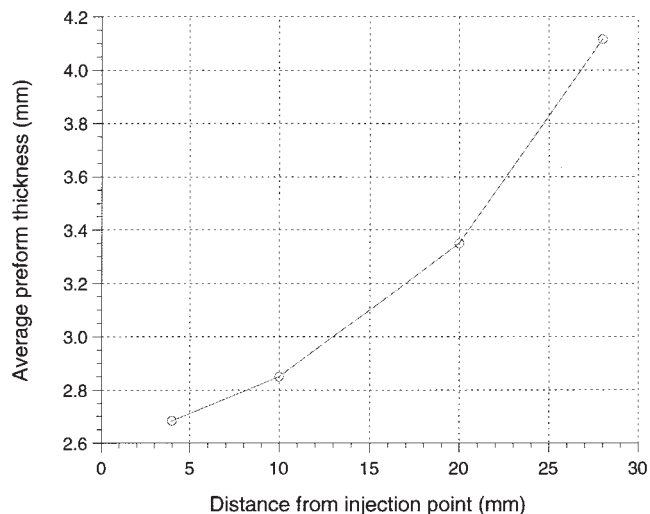


Figure 3 A plot of PET thickness versus distance from injection point as measured for an injection molded preform.

position. This geometry enables a d -spacing in the range of 40 to 1100 Å (i.e., molecular dimensions) to be studied. The d -spacing is derived from Bragg's law ($\lambda = 2d \sin \theta$; where λ is the wavelength of the incident radiation, and 2θ is the scattering angle) and is inversely related to the scattering vector, q ($q = 4\pi \sin \theta / \lambda$). The q is, in turn, related to the position of the

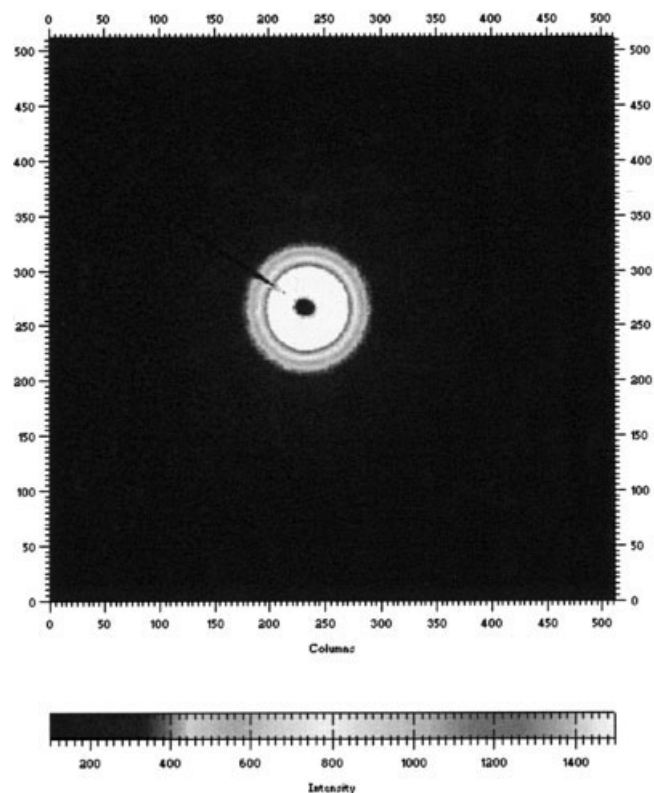


Figure 4 Typical SAXS pattern for an amorphous polymer obtained from a petaloid base close to the centre.

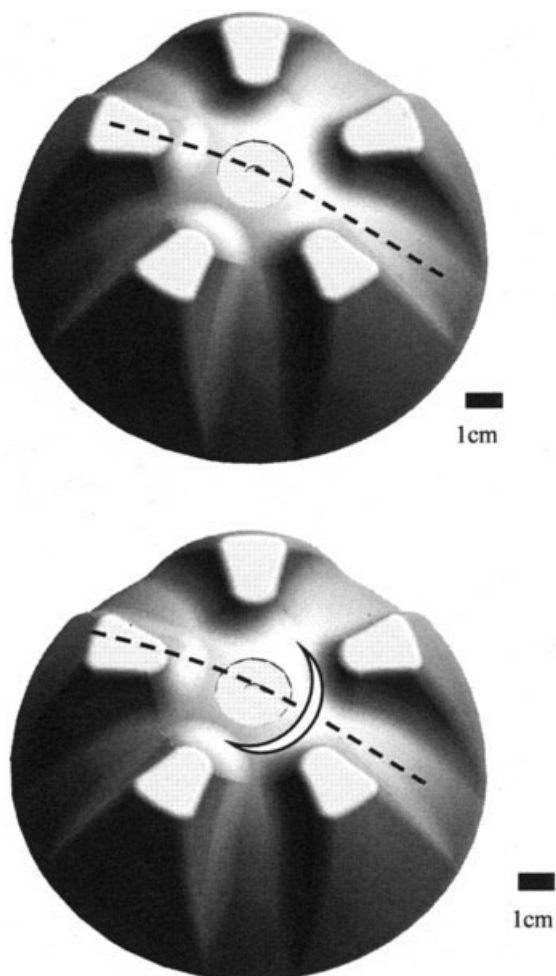


Figure 5 Petaloid base of (a) a high quality bottle, and (b) a split bottle (with the circumferential split shown in cartoon), with the diameter indicated for the X-ray beam scan.

scattered X-ray on the 2D detector with $q = 0 \text{ \AA}^{-1}$ at the center of the detector. The total q range for the instrument configuration outlined above was $0.007 < q < 0.3 \text{ \AA}^{-1}$.

A typical 2D SAXS pattern is shown in Figure 4; the computer software Fit2D¹⁶ was used to manipulate and display the SAXS patterns. The color-coded intensity scale (counts per pixel) is indicated across the bottom of the image. A beamstop is located on a supporting arm (upper left quadrant of the image) to prevent permanent damage of the detector by the intense beam of X-rays. The beam was $100\text{-}\mu\text{m}$ wide and $100\text{-}\mu\text{m}$ high, and the intensity of the incident beam is estimated to be approximately 1×10^{12} photons sec^{-1} . The petaloid base was mounted on an X-Y translation stage and the beam scanned down a diameter of the base (Fig. 5). Data were collected for 10 s intervals.

The SAXS intensity was not placed on an absolute scale and since the sample thickness varies over the base, the SAXS data are used to highlight qualitative differences in crystallinity and orientation.

RESULTS

Figure 4 is a typical 2D scattering pattern from an isotropic amorphous polymer. The symmetry of the SAXS pattern indicates that there is no preferred orientation of the molecular chains. There is very little scattering except very intense scattering at very low q (i.e., close to the beamstop) due to density fluctuations which occur randomly in all samples. By contrast, Figure 6 is a pattern from a biaxially oriented crystalline polymer. There is an intense amount of q -dependent scattering with two axes of symmetry apparent.

Figure 7 is a sequence of 2D SAXS patterns as a function of position across a diameter of a high quality bottle. The patterns clearly show the biaxial orientation of the PET crystallites across a foot and down a corresponding valley, also shown are the SAXS patterns near the center of the base illustrating typical isotropic scattering from amorphous polymer. There is an amorphous region starting from the center and extending circumferentially to approximately 19 mm distant from the center where biaxial orientation and crystallization of the polymer commence. The extent of the orientation and crystallinity depends upon the geometry of the base, and it can be seen that there is an abrupt change from the amorphous region to the crystalline regions. The most biaxially oriented regions of

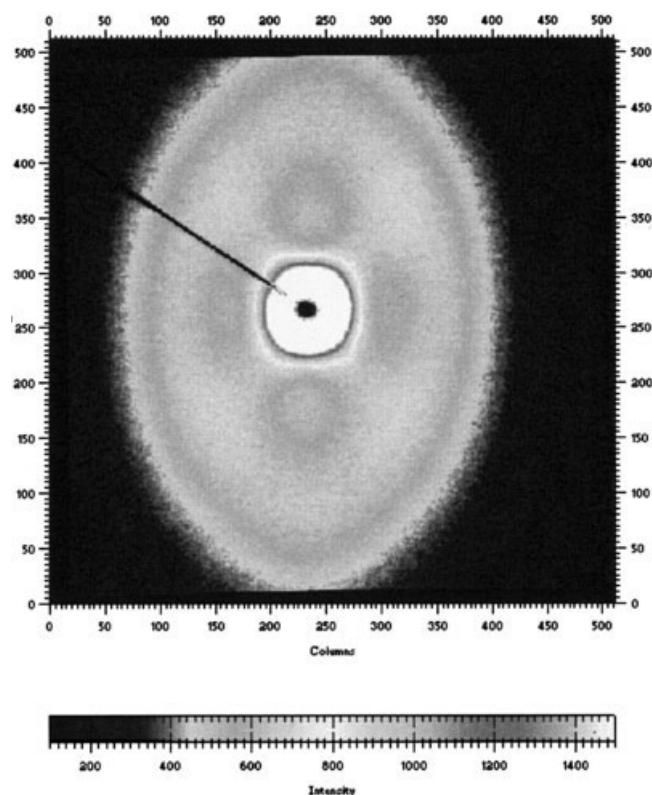


Figure 6 Typical SAXS pattern for a biaxially oriented polymer obtained from a petaloid base in the valley between the feet.

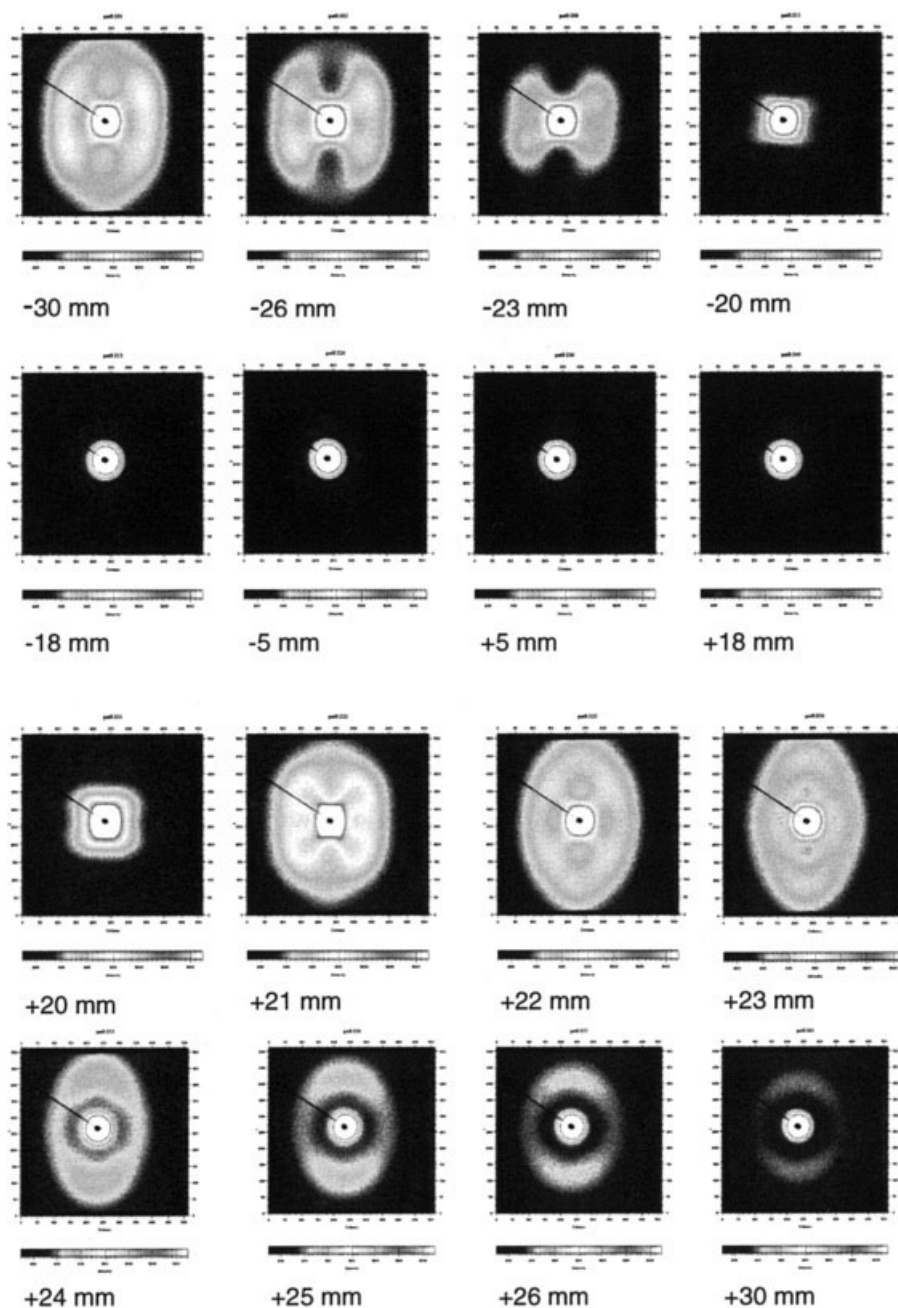


Figure 7 A sequence of SAXS patterns obtained from a scan across the diameter of a high quality PET bottle. Centre is the origin (i.e. 0 mm), and distances from centre through the valley are $-ve$, distances from centre over the foot are $+ve$.

the base are in the valley and the initial rise to the foot region. In the middle of the foot, the orientation becomes more circular and less crystalline, indicating that the stretch in this region is more uniaxial (or less biaxial). However crystalline lamellae are still present in this region.

Figures 8 and 9 form a similar sequence for a bottle that had split under load. Figure 8 shows the SAXS patterns for the scan across the foot (excluding the split) while Figure 9 shows the patterns for the valley (including the split). The biaxial orientation is still

evident over the foot and down the valley, and the noncrystalline region is still present in the center of the base. However, the SAXS patterns for the central regions are not isotropic close to the beam stop, indicating a preferred orientation of the density fluctuations. This orientation is equally apparent for the whole of the central region in the base, indicating that there is circular alignment of the polymer chains without significant crystallization. In addition, the biaxial orientation is asymmetric in both the foot and the valley and occurs preferentially in one direction (Fig. 8, +20

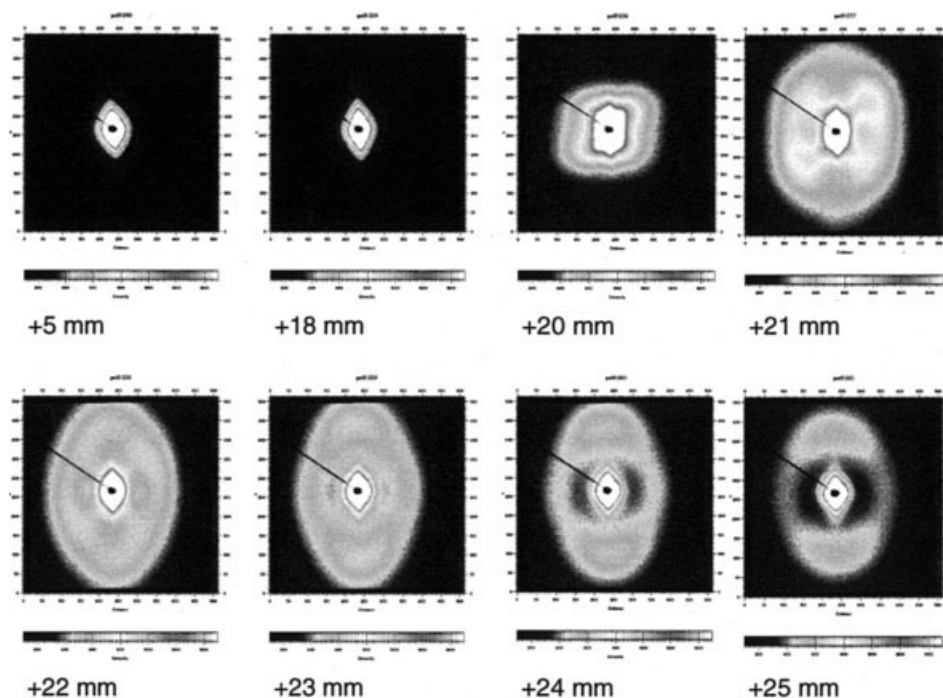


Figure 8 A sequence of SAXS patterns obtained from a scan across the foot of a PET bottle that had split under load (opposite side to the split). Centre is the origin (i.e. 0 mm), and distances from centre over the foot are +ve.

and +21 mm) prior to enhancement of the second direction, which leads to a more symmetric distribution (Fig. 8, +22 mm and +23 mm).

The split in the base starts at approximately 21 mm from the center (Fig. 9) and is approximately 3 mm wide. It appears that the crack occurs (in this particular bottle) not directly on the edge of the amorphous region, but where the biaxial orientation and crystallinity begins (the so-called transition region). Visual inspection of a small batch of similar bottles suggests that the initial crack occurs in a similar position. Note that the crack propagation occurs around the circumference in the same direction as the preferred orientation of the polymer chains.

DISCUSSION

The molecular orientation observed in a split bottle has a magnitude of a large size-scale (i.e., low q , close to the beamstop) and therefore correlates more to a preferred orientation of polymer chains aligning in the circumferential direction. The presence of this uniaxial orientation of the polymer persists throughout the base and is aligned circumferentially, which is the same direction as the split. Therefore circumferential splitting in a PET bottle for CSD strongly correlates with the circumferential orientation observed by SAXS. Note that the uniaxial orientation is observed in regions remote from the split and is therefore unlikely

to be caused by mechanical deformation of the splitting process.

It should be noted that the findings in this study are in basic agreement with those of Lyu and Pae⁹ who observed that cracks occur in the transition region because of thinning of the base but only in regions where the stretch ratio was not yet great enough to induce strain hardening and crystallization. Figure 9 shows that stretching and therefore thinning is induced at 18–20 mm from the center where biaxial SAXS patterns are just developing. The crack then occurs at approximately 21 mm, so it is highly likely that strain hardening has not yet been achieved in this region. Of course the alignment of polymer chains parallel to the crack propagation in this poor bottle only enhances the weakness in this high stress transition region. Comparing these observations to the base center and foot interface of the good bottle (Fig. 7), the biaxial orientation can be seen to develop quickly at 20 and 21 mm into a strong biaxially crystalline morphology at 22 mm, implying that strain hardening takes place by 22 mm to induce crystallinity. The fully amorphous central region inside 18 mm must be tough enough to withstand the stress build-up during this transition.

The question of how the central region of the cracked bottles became aligned remains. Consider first the thickness of the preforms as well as the central region of the blown bottle base (Figs. 2 and 3). The thickness of the preform at immediately either side of

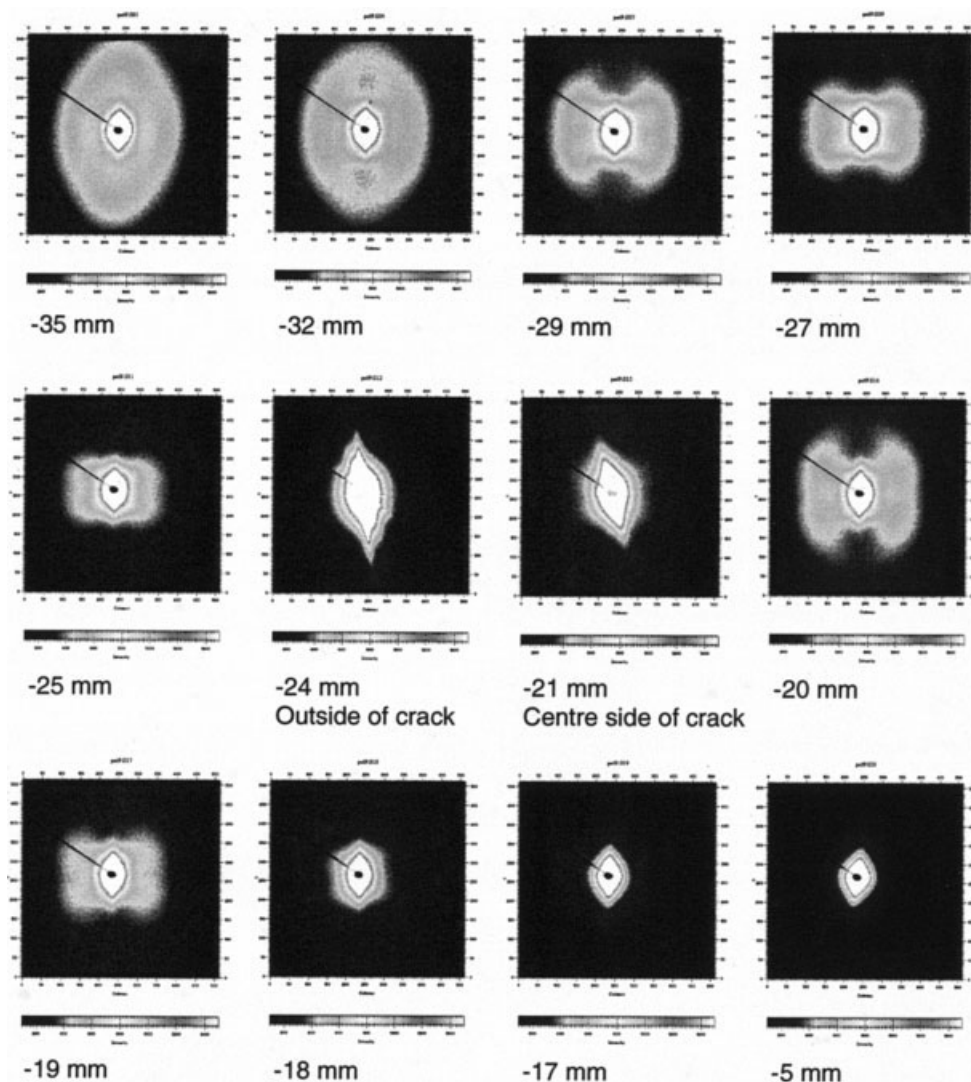


Figure 9 A sequence of SAXS patterns obtained from a scan across the valley of a PET bottle that had split under load (same side as the split). Split is 3 mm wide therefore distances from centre are distorted on far side of crack relative to uncracked sections. Centre is the origin (i.e. 0 mm), and distances from the centre through the valley are $-ve$.

the gate is approximately 2.7 mm, and this thickens to about 3 mm half way around the curve towards the side wall, which is at about 4.1 mm thick. The thickness in the central region of the bottle base up to a radius of 18 mm is 2.1 ± 0.4 mm, with the material starting to thin towards the edge of this region. It is likely that this central region in the bottle is formed from preform whose thickness is in the range 2.7–3 mm. Using the best and worst case scenarios, this implies that the minimum reduction in thickness seen in this region is about 7% while the absolute maximum possible reduction would be 43% at the very edge of the central region. Clearly from this simple analysis it can be concluded that this central region does experience some thinning during the stretch blow molding process, and that for good bottles it is known that this region is amorphous after processing. This means that poststretching, the polymer chains in

good bottles either have the time and energy to relax to a random state or stretching is not sufficient to induce molecular orientation.

For the cracked bottles, it is known that the polymer chains in this central region are circumferentially aligned but also noncrystalline. It is possible that the alignment happens during the stretch blow molding stage and that the morphology is fixed by quenching the temperature before the chains have time to relax. This is reasonable given that a cold stretch rod is in direct contact with this region and the material is stretched until it is also in contact with a cold mold. Clearly precise temperature control is required during this phase. Because of the absence of any crystalline scattering in the SAXS data, it is reasonable to conclude that whatever the stretching mechanism, the strain is obviously not great enough to induce crystallization.

Another potential source for the introduction of alignment into the central region of the bottle base is during the injection molding of the preform. If the packing pressure is too high or the hold time too long, then the preform can become over packed, which could introduce the alignment observed with SAXS.

The incidence of cracked bottles is reported to be much greater during the summer months. It is possible that the increased temperature during the period causes changes in morphology that further increase the stress throughout the critical transition region in the base, although it must be remembered that the bottles will still be well below the glass transition temperature. Of course, the pressure of the CSD in the bottle will also rise with temperature. A greater change in temperature means an increase in the "breathing" mechanism of the bottles which leads to greater stress in the transition zone. SAXS experiments that will provide some insight into this hypothesis are currently in progress.

CONCLUSIONS

Based on the extensive current knowledge of the two-stage injection stretch blow molding process, it is possible that the observed molecular orientation could arise from either stage of the injection blow molding process. It is therefore suggested that the problem lies with either over-packing during preform injection or hoop stretch during the bottle blow stage. Temperature control is known to be a vital parameter for both processes. The end result in this study is that base cracking was accentuated by the circumferential orientation of the polymer chains around the petaloid base.

The SAXS technique has been shown to provide valuable information on the molecular orientation in commercially produced bottles using the X-ray contrast between amorphous and crystalline regions.

Use of the ChemMatCARS Sector 15 at the Advanced Photon Source was supported by the Australian Synchrotron Research Program, which is funded by the Commonwealth of Australia under the Major National Research Facilities Program. ChemMatCARS Sector 15 is principally supported by the National Science Foundation/Department of Energy under grant number CHE0087817 and by the Illinois Board of Higher Education. The Advanced Photon Source is supported by the U.S. Department of Energy, Basic Energy Sciences, Office of Science, under Contract No. W-31-109-Eng-38. This research was carried out in the Australian Cooperative Research Centre for Polymers.

References

1. Cakmak, M.; Spruielli, J. E.; White, J. L. *Polym Eng Sci* 1984, 24, 1390.
2. Cakmak, M.; White, J. L.; Spruiell, J. E. *J Appl Polym Sci* 1985, 30, 3679.
3. Venkateswaran, G.; Cameron, M. R.; Jabarin, S. A. *Adv Polym Technol* 1998, 17, 237.
4. Ashford, E.; Bachmann, M. A.; Jones, D. P.; Mackerron, D. H. *Trans Inst Chem Eng* 2000, 78, 33.
5. Chevalier, L. *Plast Rubber Compos* 1999, 28, 385.
6. Chevalier, L.; Linhone, C.; Regnier, G. *Plast Rubber Compos* 1999, 28, 393.
7. Lu, W.; Debelak, K. A.; Witt, A. R.; Yang, C.; Collins, W. E.; Lott, C. *J Polym Sci Part B: Polym Phys* 2002, 40, 245.
8. MoldFlow website: <http://www.moldflow.com/stp/>
9. Lyu, M.-Y.; Pae, Y. *J Appl Polym Sci* 2003, 88, 1145.
10. Brooks, D. W.; Giles, G. A. *PET Packaging Technology*; Academic Press: Sheffield, 2002.
11. Hanley, T. L.; Forsythe, J.; Sutton, D.; Moad, G.; Burford, R.; Knott, R. B. *Polymer*, submitted.
12. Lyu, M. Y.; Kim, H. C.; Lee, J. S.; Shin, H. C.; Pae, Y. *Int Polym Proc* 2001, 16, 72.
13. Lyu, M. Y.; Kim, Y. H. *Int Polym Proc* 2002, 17, 279.
14. Everall, N.; MacKerron, D.; Winter, D. *Polymer* 2002, 43, 4217.
15. Sutton, D.; Hanley, T. L.; Knott, R. B.; Cookson, D. *J Synchrotron Res* 2004, 11, 505.
16. Hammersley, A. P. FIT2D V9.129, Reference Manual V3.1, ESRF Internal Report, ESRF98HA01T, 1998.