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Residual orientation in injection micro-molded samples

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Abstract

The orientation of polymer chains after injection molding is usually studied using techniques that measure the average orientation of molecular segments. Small-angle neutron scattering (SANS) is a technique for measuring the overall chain orientation and is very sensitive to molecular anisotropy. In this study, a blend of a commercial general-purpose polystyrene and deuterated polystyrene was injection micro-molded under a variety of molding conditions. SANS was then used to measure the residual orientation of the deuterated chains. As expected, the molecular orientation decreased with increasing mold temperature and increased with decreasing mold thickness. However, for these micro-moldings, the residual orientation decreased with increasing injection velocity. The measured orientation also appears to be Q-dependent indicating that the average residual orientation of short-chain segments may not necessarily reflect the overall chain conformation.

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1. Introduction

Injection molding is one of the most widely used methods for producing shaped objects out of polymeric material. Injection-molded objects often have residual macromolecular orientation induced during the injection cycle. This orientation varies along the length and also through the thickness of the sample and can have a significant impact on the mechanical and optical properties of the finished article.

Studies of residual orientation in injection-molded samples usually use techniques such as optical birefringence, IR dichroism and X-ray Scattering. These techniques usually measure the average orientation of individual segments of the polymer chain; for example, IR dichroism may be used to measure the average orientation of a C–C bond along the backbone of a polyolefin chain. This average segment orientation is then used to infer the extent of overall chain orientation.

Small-angle neutron scattering (SANS) can be used to measure monomer–monomer interactions over much longer distances, with the length scale inversely related to the scattering angle. SANS is an excellent tool for directly measuring the overall dimensions of the polymer chain [1], rather than inferring the chain orientation from the average segment orientation.

SANS has only rarely been used to examine chain conformation in injection-molded specimens [2]. In the cited study, the authors compared SANS results with optical birefringence for injection-molded polystyrene and found a good correlation at high orientation. However, at low levels of orientation measured by SANS, the samples displayed no measurable birefringence.

2. Sample preparation

A partially deuterated blend of polystyrene was prepared by solution blending. Deuterated polystyrene (4% w/w) was blended with commercial general-purpose polystyrene in chloroform (2% w/w) then precipitated in excess methanol. The precipitate was filtered and dried before

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Table 1
GPC polystyrene molecular weights

	M_n	M_w
Polystyrene-h8	91,060	195,400
Polystyrene-d8	91,000	127,000

Table 2
Flow front speed

Injection pin velocity (m/s)	0.7 mm mold	1.0 mm mold
0.15	0.30	0.21
0.35	0.70	0.49
0.55	1.10	0.77
0.75	1.50	1.05

Table 3
Thermal conditions

	Melt temperature (°C)	Mold temperature (°C)
Polystyrene (cold)	190	50
Polystyrene (hot)	200	65

pelletization using a capillary viscometer to produce the extrudate. The commercial polystyrene was put through the same solution/precipitation process to produce the matrix samples. The average molecular weights of the two polymers are shown in Table 1.

Samples were injection molded into flat plates using a Battenfeld Microprocessor 50. The flat plate dimensions were $14 \times 26\,\mathrm{mm}^2$ with a thickness of 0.7 or 1.0 mm. The flat plate section was preceded by a simple 45° fan gate to produce a flat flow front. The injection molding conditions were varied to produce a number of samples at different injection speeds and with different thermal histories. The injection molding conditions are shown in Tables 2 and 3.

3. Data collection and analysis

SANS data were collected at the NIST Center for Neutron Research. Samples were run on the NG1 (SANS) beamline with a Q range of 0.005–0.080 Å^{-1}. The center of each sample was illuminated with a 6.2 mm diameter beam with the beam parallel to the thickness (z-axis) of the sample and perpendicular to the flow direction (y-axis).

The NG1 beamline was calibrated using silica standards and the scattered intensity was converted to differential scattering cross-section. A number of matrix samples were run to evaluate any structural scattering due to the matrix (such as void scattering) and to determine the level of incoherent scattering.

The measured scattering anisotropy can be expressed as an eccentricity (ε) that is equal to the ratio of the radii of gyration calculated for data binned into sectors along the x- and y-axes [4]. The closer the eccentricity is to unity, the lower the orientation. The eccentricity can also be extracted directly from the 2D data using an elliptical analysis technique.

In this case, the expected Rg for the unperturbed deuterated polymer is 93 Å [3] meaning that the Guinier region ($Q\,\mathrm{Rg}<1$) is for data below $Q = 0.0107\,\text{Å}^{-1}$. However, we saw significant scattering from the matrix samples for $Q < 0.010\,\text{Å}^{-1}$ (the scattering intensity for the matrix samples was approximately half that of the deuterated samples) so elliptical binning has been employed to calculate the eccentricity of the samples as described by Bradford et al. [4].

We can define a momentum space vector as

$$Q^* = (Q_y^2 + \varepsilon^2 Q_x^2)^{0.5}. \tag{1}$$

The eccentricity can be found by forming the data into bins of constant Q^* and minimizing the variance in detector cells from $0.015\,\text{Å}^{-1} < Q < 0.030\,\text{Å}^{-1}$:

$$\langle (C - \langle C \rangle)^2 \rangle, \tag{2}$$

where C is the count in each detector cell and $\langle C \rangle$ is the average detector count within the elliptical bins.

4. Results and discussion

The eccentricities for the polystyrene samples calculated using Eq. (2) are shown in Fig. 1. While other studies [5] have shown an increase in residual orientation with increasing injection velocity, we have found the opposite. Though the molds have a relatively large surface area for their volume and cool very rapidly, the fill-time is very short (<0.1 s). This increases the time for the polymer chains to relax after the flow has stopped and before the polymer solidifies. As expected, increasing the thickness of the part decreases the measured orientation.

The eccentricities presented in Fig. 1 are average eccentricities for Q between 0.015 and 0.030 Å^{-1} assuming that the deformation is uniform at various length scales.

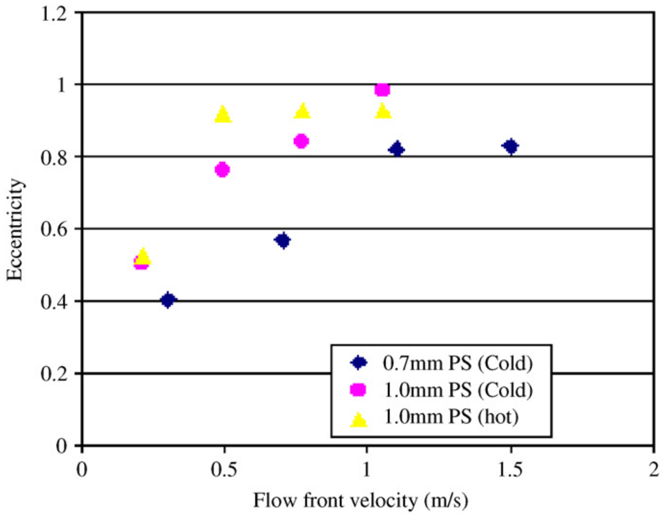

Fig. 1. Calculated eccentricity of polystyrene samples.

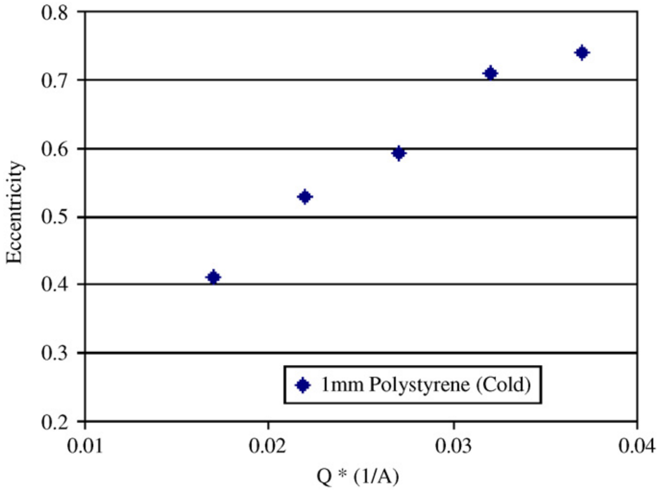

Fig. 2. Q-dependent orientation.

Bradford et al. [4] found that the measured orientation had a significant Q-dependence for hot stretched samples. Similarly in these samples if the eccentricity is calculated for smaller Q ranges (0.005 Å^{-1}) then the eccentricity is also revealed to be Q-dependent as shown in Fig. 2.

The Q-dependent nature of the eccentricity is consistent with previous SANS studies on hot-stretched polystyrene [4,6]. Previous studies have proposed that this Q-dependence comes from faster relaxation of short-chain segments than the chain as a whole. Assuming that the initial deformation is uniform, these data indicate that there is significant randomization at short length scales while the overall chain dimensions remain perturbed. The variation in orientation through the thickness of a sample would also produce a Q-dependent orientation however in that case one would expect to see an increase in orientation with increasing Q.

One of the implications of these results is that chains of different lengths may have a different residual orientation within a polydisperse matrix. This is an area we hope to explore in the near future by doping a single matrix with deuterated chains of different molecular weight. This is one area where SANS can provide data not available through other experimental techniques.

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