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Characterization of molecular orientation by differential scanning calorimetry

Part II *Injection-moulded and biaxially oriented polystyrene*

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Differential scanning calorimetry was used to study the injection moulding and biaxial orientation of polystyrene. Single exothermic peaks were observed for uniaxial orientation, whereas multiple relaxations were observed for biaxial orientation. The temperatures of the relaxations followed the general relationship

$$T_j = 1.02\, T_i\,(\mathrm{K})$$

where $T_j > T_i \geqslant T_g$ and $(j-i) = 1$. In the case of injection-moulded samples, the overall dimensional shrinkage did not correlate with the enthalpy determined by differential scanning calorimetry, indicating nonaffine behaviour between dimensional and molecular orientation.

1. Introduction

The end-use properties of fabricated parts produced from thermoplastics are affected by the degree, type and homogeneity of orientation of the mass molecular chains. The presence of orientation may be beneficial, as in the case of biaxially oriented polystyrene (OPS), or detrimental as in the case of the uniaxial orientation generally experienced in injection moulding. In most cases, the commonly used physical methods of polymer characterization [1] cannot be used to investigate orientation, and one normally has to resort to birefringence, small-angle neutron scattering or infrared dichroic measurements. Another possible technique lies in the use of differential scanning calorimetry (DSC).

The processing of thermoplastics involves heating, moulding, forming and cooling. During these stages, energy is imparted which causes the polymer chains to orientate. If the part is cooled sufficiently quickly below the glass transition temperature, T_g, the strain will be frozen in. It is reasonable to assume that on reheating to above T_g, this strain will be released and an exotherm may be detected by DSC.

In Part I of this study [2] we discussed the controversy surrounding the T_g–T_{LL} region. In Part II, we investigate the use of DSC to measure uniaxial orientation as shown by injection moulding and biaxial orientation produced in oriented polystyrene sheet (OPS). Part III will examine injection blow moulding of polystyrene.

2. Experimental procedure

A number of commercially available polystyrenes (Table I) were injection moulded into cold drink cups on a two-cavity, Husky moulding machine, operating under a 6 s total cycle.

TABLE I Polystyrene characteristics

	Melt flow rate (g per 10 min)	Average mol wt g mol^{-1}	Mol wt distribution
Styron† 667	8	215 000	2.6
Styron 666 APR*	9	195 000	2.3
Styron 685D	1.4	300 000	2.3
Styron 675 APR*	9	195 000	2.3

† Trade mark, Dow Chemical Co.
* Differs in additive package.

The biaxially oriented sheet was obtained as commercial product using Styron 685D. All samples were studied by means of a DuPont 910 DSC cell/base with a DuPont 9900 data/control station. Details may be found elsewhere [2]. Samples of 10–20 mg were contained in standard open pans containing one drop of silicon oil to maintain thermal contact during shrinkage.

Two consecutive heating scans in the DSC were made on each sample at a scanning rate of 20° min^{-1} from − 10° to 210 °C. Free cooling of the sample was undertaken between scans. Both scans were important, the first being more representative of the structure of the fabricated sample, while the second, and sometimes a third scan, was necessary to reveal structural effects in an annealed sample. Each sample was tested a number of times.

3. Results

3.1. Injection moulding

In Figs 1 and 2 are shown some typical stored-energy-release curves at constant injection rate and different

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melt temperatures, and at constant temperature and varying injection rates. Generally a very broad peak was obtained between T_g and approximately 200 °C. One difficulty was the determination of the start and end points of the exotherm. We chose to superimpose the second scan, which represented the relaxed polymer, over the first scan (Fig. 3). The area difference between the first and second scans was taken as the stored energy of the fabricated point. Fig. 4 shows the enthalpy against injection moulding temperature, at two different injection rates. As might be expected, molecular orientation ($\equiv \Delta H$) decreased with increasing temperature and followed a similar trend for overall dimensional shrinkage (Fig. 5). There was very little correlation between overall shrinkage and ΔH. This was not surprising, as it has been found that polymer chains do not deform affinely to external dimensions for cases of greater than 75% shrinkage [3].

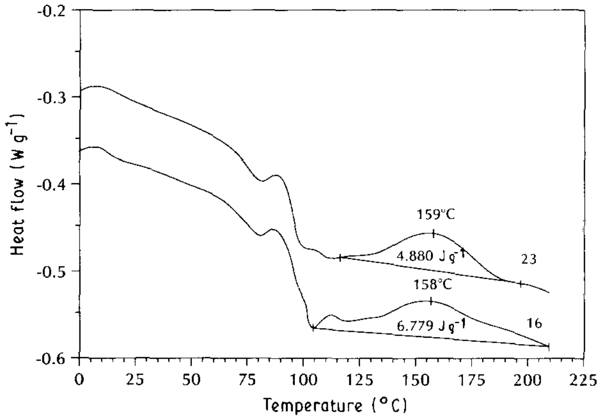

Figure 1 DSC scan of Styron 667, moulded at constant (low) injection rate and 290 °C (sample 16) and 315 °C (sample 23).

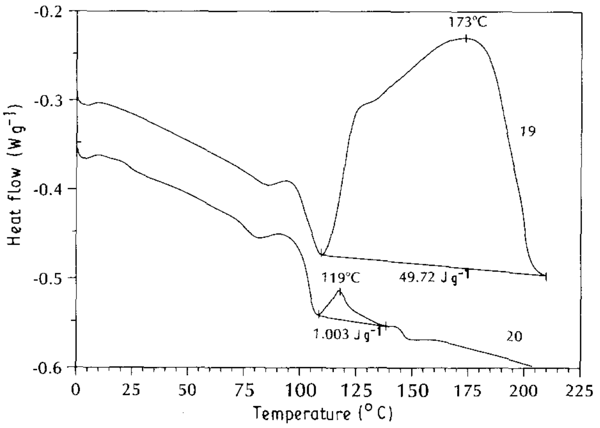

Figure 2 DSC scan of Styron 666 APR, moulded at constant temperature and low injection rate (sample 19) and high injection rate (sample 20).

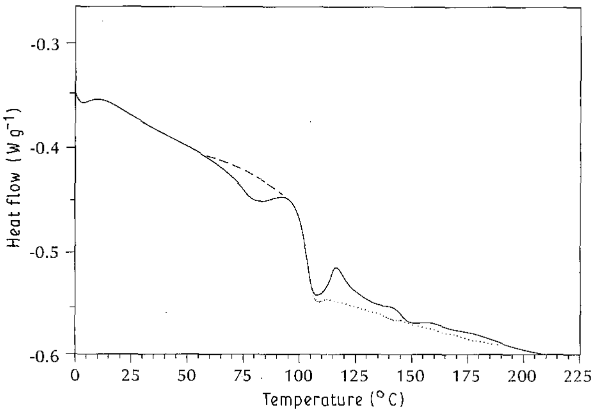

Figure 3 DSC scan of Styron 666 APR, showing second scan overlay (· · ·).

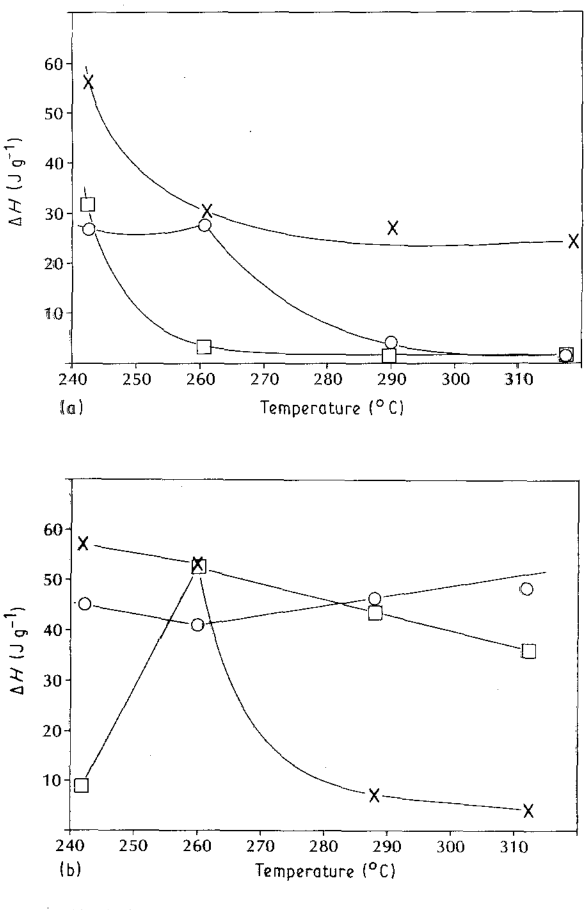

Figure 4 Enthalpy (ΔH) against moulding temperature at (a) high injection rate and (b) low injection rate. ×, Styron 667; ○, Styron 666 APR; □, Styron 675 APR.

The effect of injection speed was complex and depended on both the thermal and flow histories of the polymers.

3.2. Biaxial orientation

The biaxially oriented sheet (OPS) process for polystyrene consists of two parts. Firstly, a relatively thick sheet, 1 mm thick, is stretched in the machine direction between two sets of rolls at a draw ratio of approximately 2:1, followed by a further 2:1 transverse directional stretch by means of a tentering frame. The sheet is maintained between 100 and 140 °C during the latter stretch while it passes through a series of ovens. Typical DSC scans are shown in Fig. 6 for the uniaxial and biaxial stretch. The uniaxial stretch shows one smooth exothermic peak, similar to that found in the injection moulding process. The biaxial exothermic peak was broader and showed a number of shoulders, on either side of the peak, that followed the general relationship:

$$T_j = 1.02\,T_i(\mathrm{K})$$

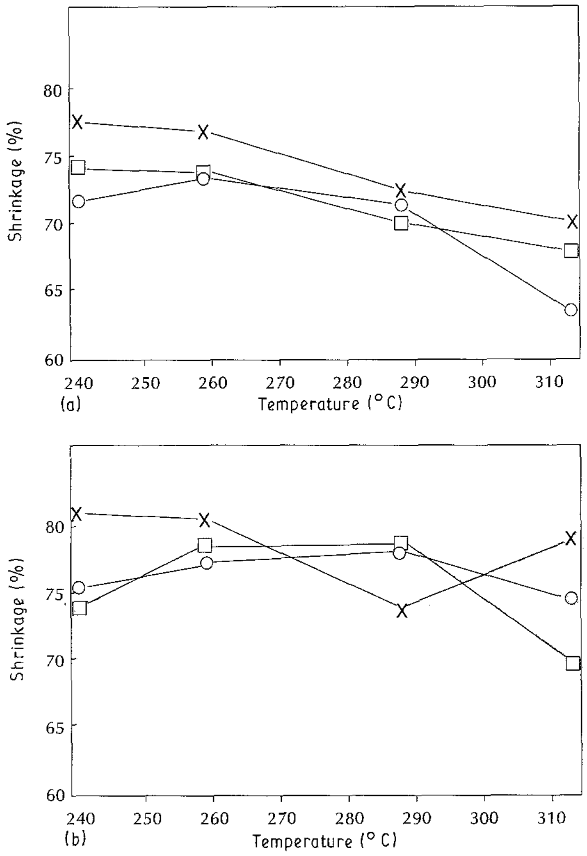

Figure 5 Shrinkage against moulding temperature at (a) high injection rate and (b) low injection rate. ×, Styron 667; ○, Styron 666 APR; □, Styron 675 APR.

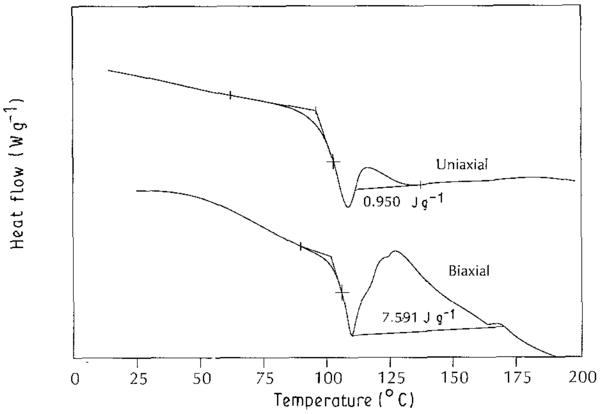

Figure 6 DSC scan of uniaxially and biaxially stretched polystyrene.

where $T_j > T_i \geqslant T_g$ and $(j - i) = 1$, when the temperature was expressed in (K). This relationship was also found to be followed in the injection-blow-moulding process [4] where the temperatures were more definitive.

4. Discussion

Houska and Brummell [5] recently reported the measurement of orientation in injection-moulded thermoplastics by transmission and reflection infrared spectroscopy, but failed to observe orientation in polystyrene. A partial explanation could be the sensitivity of the method, but more probably relaxation of the chains had occurred. As observed from our data, as the temperature of injection is increased, or more correctly the melt temperature, fewer residual stresses are induced because of the ability of the polymer chains to relax. The DSC technique measures an average enthalpy throughout the sample. In practice, there is a gradient throughout the sample thickness due to compressive stresses at the surface and tensile stresses in the inner layers.

In both injection moulding and uniaxial stretching in the OPS process, only single exothermic peaks were observed. In the second stretching step of the OPS process, the data showed a peak and two shoulders corresponding to apparently three molecular motions in the temperature range extending from the glass transition to the liquid–liquid transition, T_{LL}. As will be seen in an earlier report [4], the resolution of the shoulders into peaks depends on the rate and amount of deformation of the polymer.

The resolution of exothermic behaviours as determined by DSC, above T_g, into multiple peaks, indicates multiple molecular relaxations inherent in amorphous polymers. The act of orienting and cooling the polymers represses intra- and inter-molecular forces, which appear as exothermic peaks on reheating. The intensity of the peak was proportional to the amount of frozen-in stress, and at the minimum was observed as a step change in the DSC scan.

One inherent problem with the DSC technique is the decision whether to assign a change in base line to a molecular relaxation or to an experimental wobble. However, the method does provide insight into molecular processes that occur during the fabrication of polymers. In the present studies I have concentrated on the T_g–T_{LL} region, but believe valuable information should be obtained in other regions.

5. Conclusions

Differential scanning calorimetry (DSC) may be a useful technique for measuring molecular orientation in injection-moulded and biaxially oriented polystyrene. Molecular orientation is less than dimensional shrinkage when the polymer chains are stretched greater than 3:1.

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