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Characterization of molecular orientation by differential scanning calorimetry

Part III *Injection blow moulding of polystyrene*

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Differential scanning calorimetry was used to study part quality from an injection blow moulding machine producing polystyrene thin-walled containers. Cavity-to-cavity, within cavity and shot-to-shot problems were detected. Multiple relaxation peaks observed in the temperature range T_g–T_{LL} had the relationship $T_j = 1.02\ T_i$ K, for $T_{LL} \geqslant T_j > T_i \geqslant T_g$ and $(j - i) = 1$. Based on some simple assumptions, a model was developed that allowed the multiple peaks be resolved between the injection moulding and blowing steps of the process and into a three-dimensional array.

1. Introduction

During the processing of polymers, changes occur that can dramatically influence the mechanical properties of the polymers. A good example is the biaxial orientation of brittle polystyrene at temperatures above its glass transition. It is intuitively reasonable to expect that the stress imposed to give orientation and the temperature of the imposition, should be measurable. If a suitable technique could be developed, it should be possible to measure the stress recovery by differential scanning calorimetry (DSC) and one would expect the enthalpy to be proportional to the recoverable strain or orientation of the sample.

In Part I we discussed the $T_g - T_{LL}$ region where T_{LL} is the liquid–liquid transition temperature [1], while Part II discussed the effects of injection moulding and biaxial orientation of polystyrene [2]. In Part III, we examine the effects of imposing stresses in three directions during the injection blow moulding process.

2. Experimental procedure

2.1. Injection blow moulding process

The injection blow moulding process (IBM) is composed of a number of steps to produce hollow plastic articles. In Step 1, a molten polymer is injected into a cavity on to a core to form a parison. In Step 2, the parison on the core is separated from the mould cavity by moving the parison on the core, axially in a straight path away from the mould cavity and to a blow station to form the final shape. The final step is the injection of the article. Further details may be found in US Patent 4 540 543 [3].

Injection moulding imparts uniaxial orientation along the transverse direction, x, while the blow moulding gives biaxial stretching around the container periphery, y, and through the wall of the container, z. Some additional orientation may occur along the transverse direction, x, during the blowing step.

2.2. Differential scanning calorimetry

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 [1, 2].

Samples 5 mm diameter were stamped from various positions in the container wall and weighed into open pans. Prior to placing into the DSC furnace, a drop of silicone oil was added to ensure good contact with the surface of the pan as the sample changed dimensions during a temperature scan.

The glass transition temperature, T_g, does not occur at a single temperature but is, in fact, a temperature range of 15–20 °C in which the onset of motion on the scale of molecular displacements can be detected in a polymer sample. The fact that one temperature is reported as T_g, is a matter of convenience. In the present case, we have selected a midpoint temperature between two inflections of the base line recorded during the transition on the second scan [1].

3. Results

Fig. 1 shows a typical DSC scan of a sample taken from a fabricated thin-walled container. In this case three strong peaks are evident above T_g at 112, 119 and 126 °C together with a slope change around 150 °C. Overlaid on the first trace is the second scan which showed only the glass transition. Depending upon the particular sample and position within the sample, up to four peaks could be observed above T_g corresponding to molecular relaxations. Fig. 2 shows an example of three strong peaks occurring at 111, 119 and 135 °C, together with a shoulder at 125 °C.

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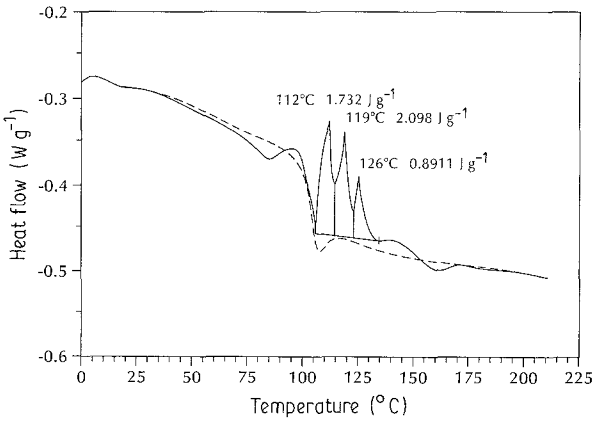

Figure 1 Typical DSC scan of container wall, showing three strong peaks.

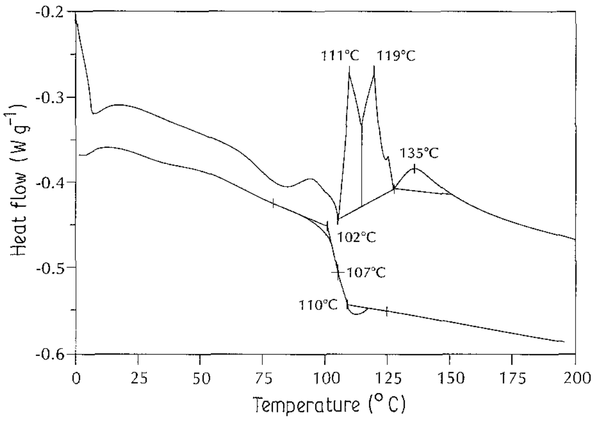

Figure 2 DSC scan of container wall, showing peaks and shoulder.

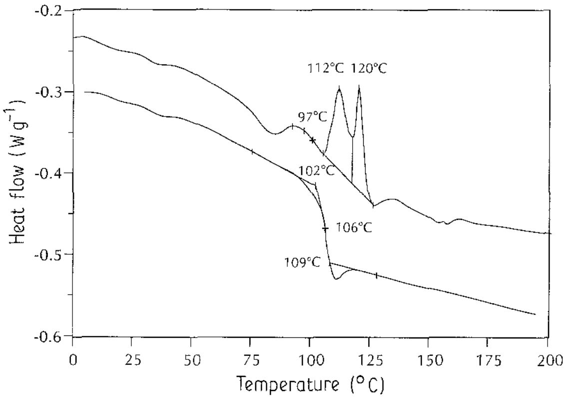

Figure 3 DSC scan of container wall.

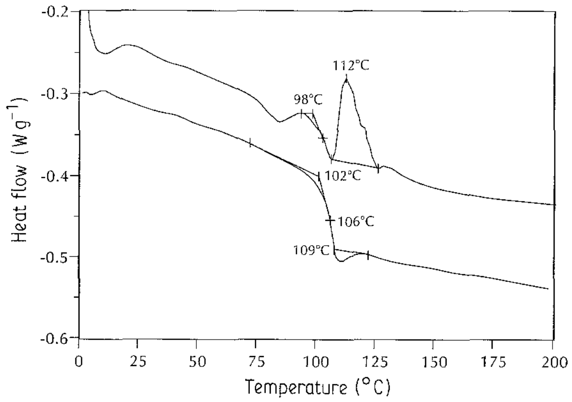

Figure 4 DSC scan of container wall.

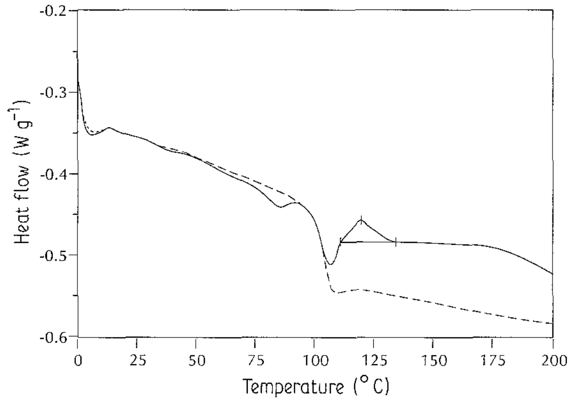

Figure 5 DSC scan of injection moulded container wall.

Further examples are shown in Figs 3 and 4. In all cases the peaks had disappeared on the second temperature scan, indicating that they were due to molecular orientation.

In order to separate the two-stage process into the injection moulding cycle and blow moulding cycle, the process was interrupted and preforms collected. Single peaks were obtained, corresponding to the uniaxial orientation of the injection moulding process, Fig. 5. Table I gives some typical data for a series of containers and preforms in which samples were taken 3 cm from the lip. It is noted that the average peak temperatures are very consistent in spite of the fact that the containers were selected from a number of different cavities and produced on two machines

TABLE I Typical average data for peak temperatures and associated enthalpy, ΔH (area under peak) for moulded containers

Sample	T_g[a] (°C)	T_1 (°C)	ΔH_1 (J g^{-1})	T_2 (°C)	ΔH_2 (J g^{-1})	T_3 (°C)	ΔH_3 (J g^{-1})	T_4 (°C)	ΔH_4 (J g^{-1})
Container 1 16 cavities	106.0 ± 0.3	110.8 ± 0.7	1.9 ± 1.2	118.6 ± 1.4	1.4 ± 1.1	125.0 ± 2.8	1.4 ± 1.3	137 ± 12	0.5 ± 0.4
Preform 1 18 cavities	106.2 ± 0.6	114.2 ± 2.1	2.9 ± 1.9						
Container 2 14 cavities	105.8 ± 0.6	110.9 ± 0.8	1.4 ± 0.5	118.9 ± 1.0	1.0 ± 0.6	123.9 ± 3.2	0.7 ± 0.6	135 ± 1.0	0.4 ± 0.5
Preform 2 8 cavities	105.2 ± 0.6	114.4 ± 1.4	1.5 ± 1.4						

[a] Determined from second scan.

under various conditions. The standard deviation is a reflection of the consistency of the fabrication process.

3.1. Separation of peaks

Orientations in polymers are only obtained by applying deformation in one or in two perpendicular directions, at a suitable temperature. When the temperature is too low, i.e. when the polymer is in the glassy state, such deformations will lead to rupture or, if possible at all, require excessively high stresses. At too high temperatures, namely in the pure viscous state, deformations can be easily applied but will not result in molecular orientations because of rapid relaxation. Suitable conditions are those where the relaxation rate is exceeded by the rates of deformation and cooling. For amorphous polymers this is the case in a temperature range between the glass–rubber transition point, T_g, and a somewhat higher value. It is suggested that this is the liquid–liquid transition temperature, T_{LL}. Previously it was shown [1] that the T_g for sample 685D was 105 °C and T_{LL} was 160 °C. All exothermic peaks were observed within this temperature range.

For separating the DSC peaks into their component parts, it is necessary to make some simple assumptions. Let us assume the orientation be considered as a rectangular Cartesian system of coordinate axes *xyz*: *x* is the longitudinal direction, the direction of flow during injection of the preform, *y* the transverse or peripheral direction and *z* the thickness. Both *x* and *y* are under tension while *z* is under compression.

From dimensional considerations, we assume that the polymer chains follow affinely the external deformation of the preform [4] during the blowing cycle, Table II. We further assume that each exothermic peak corresponds to the energy impacted during three-dimensional stretching, in addition to that already imparted during the injection step at T_x.

Each peak may be removed by a step-wise annealing process, Fig. 6. Considering the example shown, three peaks were evident at $T_1 = 112\,^\circ\mathrm{C}$, $T_2 = 119\,^\circ\mathrm{C}$ and $T_3 = 126\,^\circ\mathrm{C}$. On annealing at 113 °C for 2 min, T_1 was removed. However, a peak appeared at $T_4 = 135\,^\circ\mathrm{C}$, while the total energy of the system ΔH_T, remained constant. Because both the *x* and *y* directions are in tension, if constant volume is maintained, the first step annealing results in an increase in thickness, *z*, and it is reasonable to assume T_4 is associated with this change. Further annealing experiments were undertaken at peak temperature + 1 °C to remove progressively each orientation peak. At a temperature $\geqslant 160\,^\circ\mathrm{C}\ (\equiv T_{LL})$ all peaks had been removed; trace 5, Fig. 6.

TABLE II Dimensions of preform and model container 1

	Preform	Container	Draw ratio
x	10	10.7	1.07
y	8.48	21.05	2.48
z	0.117	0.033	– 3.55

DSC average data

Preform: $T_x = 115\,^\circ\mathrm{C}$, $\Delta H_x = 3.15\ \mathrm{J\,g^{-1}}$

Container: $T_1 = 110\,^\circ\mathrm{C}$, $\Delta H_1 = 1.86\ \mathrm{J\,g^{-1}}$
$T_2 = 119\,^\circ\mathrm{C}$, $\Delta H_2 = 1.35\ \mathrm{J\,g^{-1}}$
$T_3 = 125\,^\circ\mathrm{C}$, $\Delta H_3 = 1.42\ \mathrm{J\,g^{-1}}$
$T_4 = 135\,^\circ\mathrm{C}$, $\Delta H_4 = 0.53\ \mathrm{J\,g^{-1}}$
$\Delta H_T = 5.16\ \mathrm{J\,g^{-1}}$

From dimensional changes, the *x* direction was increased by 7%, the *y* direction 148% and the thickness, *z*, was reduced by 72% during the blow step. If the extra enthalpy gained in the blow moulding step was proportional to these dimensional changes, the ΔH_x was increased by 3%, ΔH_y by 65% and ΔH_z by 32%. For the model container 1, $\Delta H_T = 5.16\ \mathrm{J\,g^{-1}}$ and for the preform $\Delta H_x = 3.15\ \mathrm{J\,g^{-1}}$, Table III. On average, ΔH associated with the blowing step was the difference, $2.01\ \mathrm{J\,g^{-1}}$. Based on the dimensional considerations: ΔH_x was increased by $0.06\ \mathrm{J\,g^{-1}}$ ($2.01 \times 3\%$), ΔH_y by $1.31\ \mathrm{J\,g^{-1}}$ ($2.01 \times 65\%$), and ΔH_z by $0.64\ \mathrm{J\,g^{-1}}$ (2.01×32).

For the blown container

$$\begin{aligned} \Delta H_x &= 3.15 + 0.06 = 3.21\ \mathrm{J\,g^{-1}} \\ &\equiv \Delta H_1 + \Delta H_2 \end{aligned} \qquad (1)$$

which leaves $1.95\ \mathrm{J\,g^{-1}}$ (5.16–3.21) unaccounted for.

We have shown that $\Delta H_z \equiv \Delta H_4 = 0.52\ \mathrm{J\,g^{-1}}$, and therefore

$$\begin{aligned} \Delta H_y &= 1.95\text{–}0.53 = 1.42\ \mathrm{J\,g^{-1}} \\ &\equiv \Delta H_3 \end{aligned} \qquad (2)$$

In summary

$$\Delta H_x \equiv \Delta H_1 + \Delta H_2 = 62.2\%\ \Delta H_T \qquad (3)$$

$$\Delta H_y \equiv \Delta H_3 = 27.5\%\ \Delta H_T \qquad (4)$$

$$\Delta H_z \equiv \Delta H_4 = 10.3\%\ \Delta H_T \qquad (5)$$

TABLE III Dimensions of preform and model container 2 and associated enthalpies

	Dimensions (cm)			
	Preform	Container	Draw ratio	% Change
x	10.9	12.2	1.12	11.9
y	10.0	21.8	2.18	118
z	0.106	0.0355	– 2.99	– 66.5

DSC Average data

Preform: $T_x - 114\,^\circ\mathrm{C}$, $\Delta H_x = 2.16\ \mathrm{J\,g^{-1}}$

Container: $T_1 = 111\,^\circ\mathrm{C}$, $\Delta H_1 = 1.38\ \mathrm{J\,g^{-1}}$
$T_2 = 119\,^\circ\mathrm{C}$, $\Delta H_2 = 0.974\ \mathrm{J\,g^{-1}}$
$T_3 = 124\,^\circ\mathrm{C}$, $\Delta H_3 = 0.72\ \mathrm{J\,g^{-1}}$
$T_4 = 135\,^\circ\mathrm{C}$, $\Delta H_4 = 0.48\ \mathrm{J\,g^{-1}}$
$\Delta H_T = 3.49\ \mathrm{J\,g^{-1}}$

ΔH_x (container) $= 2.16 + (1.33 \times 6\%) = 2.24\ \mathrm{J\,g^{-1}}$

which leaves $3.49 - 2.24 = 1.25\ \mathrm{J\,g^{-1}}$

$$\Delta H_z \equiv \Delta H_4 = 0.48$$

$$\begin{aligned} \Delta H_y &= 1.25 - 0.48 = 0.77\ \mathrm{J\,g^{-1}} \\ &\equiv \Delta H_3 \end{aligned}$$

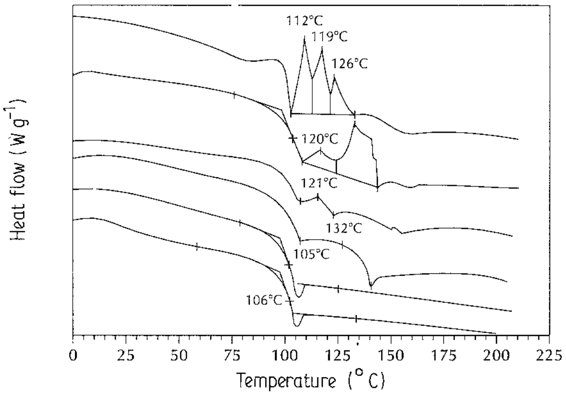

Figure 6 Step-wise annealing, showing removal of peaks in DSC scans.

Similar calculations for another model container 2 are given in Table III. In this case 64.2% of the enthalpy was in the *x*-direction, 22% in the peripheral, *y*, direction and 13.8% in the *z*-direction.

3.2. Application

Closer, examination of the data used for Table I in which samples were examined from different cavities, but at the same point within a cavity, showed a variation in both the enthalpy and number of peaks. This variation may be correlated with part appearance and properties. Corrective actions during the cooling cycle or placement of cooling lines may be undertaken. Aside from cavity-to-cavity differences, samples taken within a sample may indicate areas of too low, or too high, orientations. Fig. 7 shows the DSC traces obtained from three positions within one container. Both the lip and base areas of the container are reminiscent of the single, uniaxial orientation of the injection-moulded preform [2]. The middle area has developed some biaxial orientation as indicated by the presence of three peaks. Crush tests showed a break emitting from and perpendicular to the lip. On reaching the middle section of the container wall, the crack travelled in a peripheral direction, indicating a more balanced degree of orientation.

Flow lines may develop in a blown container through rapid relaxation of molecular orientation when temperatures are too high. When this occurs, a localized thickening of the *z*-direction may be detected and one would anticipate the lack of exotherm peaks. Fig. 8 shows an example of a part of a container that has developed flow lines compared with a part not showing flow lines. Flow line regions have a broad peak and lack the well-defined peaks exhibited by an acceptable sample.

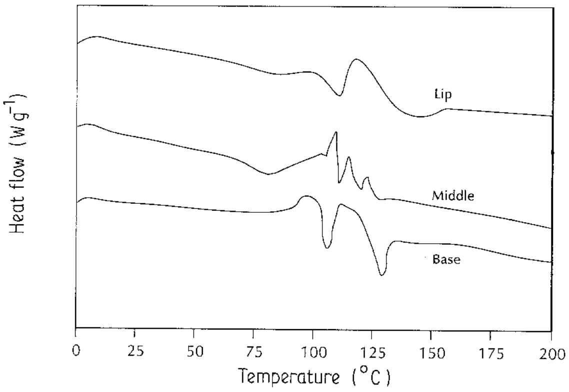

Figure 7 Profile of container wall.

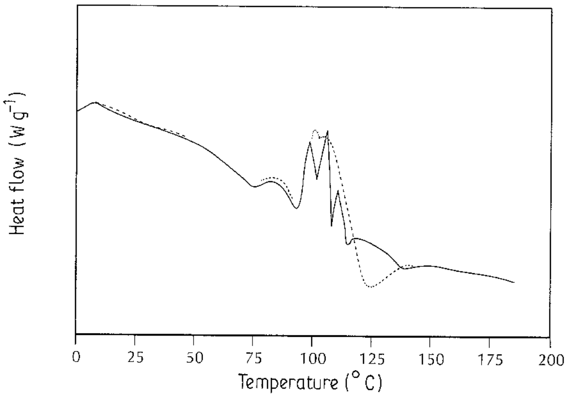

Figure 8 DSC scan of defective moulding: (——) good appearance, (· · · · ·) Flow Line.

4. Discussion

Studies on molecular orientation associated with uniaxially stressed samples have been previously reported. The process of injection blow moulding examined in this work was uniquely suitable for deforming hot polystyrene in a triaxial manner and freezing-in the stresses by rapid cooling. It has been demonstrated [4, 5] that chains deform affinely when their lengths are not too short and are given insufficient time to relax. Provided that the chain volume is assumed constant during deformation, the molecular draw ratio is found to be a linear function of the external draw ratio for draw ratio less than 3 [4]. The articles examined in this work met these requisites.

The data reported here indicate that multiple molecular relaxations may occur in polystyrene between the T_g and the so-called T_{LL} and follow the general equation

$$T_j = 1.02\, T_i\, \mathrm{K} \qquad (6)$$

for $T_{LL} \geqslant T_j > T_i \geqslant T_g$ and $(j - i) = 1$. Kato *et al.* [6] reported that thermal shrinkage of highly hot-drawn and quenched samples of poly(methyl methacrylate) and polycarbonates of bisphenol A show multiple relaxations around and above their T_gs. We have calculated their temperature relaxations to have a similar relationship, namely

$$T_j = 1.03\, T_i\, \mathrm{K} \qquad (7)$$

Drawing temperature, degree of drawing and cooling rate all affect orientation and the absence of exothermic peaks is a good indicator of process problems

Krimm [7], using X-ray scattering techniques, reported as early as 1953 that there appears to be a definite structural change occurring in polystyrene within the temperature range of about 90–160 °C, that might arise as a result of changes in configuration of the chain. Boyer [8] in a review article has summarized the evidence supporting the existence of a superglass transition process, which he termed a "liquid–liquid" transition, T_{LL}, temperature range.

The picture that emerges is of an amorphous polymer, above its glass transition temperature, in which the molecular chains are continuously wriggling from one conformation to another in response to thermal energy. The molecules are held together by temporary secondary bond cohesive forces which may lead to molecular segments entangling and disentangling with each other. This entangling gives rise to a temporary network structure. If a mechanical stress is imposed on such a system, it can respond in three distinct ways: (1) instantaneous elastic response: (2) retarded (conformational) elastic response: (3) viscous flow. In fact, the retarded elastic element must be expanded into a whole series of such elements, some with shorter and some with longer response times. In the injection blow moulding process only the short response times will be important within the temperature range T_g–T_{LL} and with draw ratios of less than 3:1, viscous flow appears to be of small consequence. However, the absence of exothermic peaks would indicate that viscous flow could not be discounted.

Based on this model the observations of multiple peaks occurring on a DSC scan, in the temperature region T_g–T_{LL}, are quite reasonable. The ΔH and temperature position are associated with the imposed stress during the process. Intuitively in the two-step injection blow moulding one might anticipate the four peaks detected. But their positions within the temperature range T_g–T_{LL} was unexpected, unless this is, in fact, the rubbery plateau region.

5. Conclusion

The combination of injection blow moulding and differential scanning calorimetry are ideally suited to investigate thermal relaxations in amorphous polymers. On the practical side, DSC may be used to investigate cavity-to-cavity problems, within cavity differences, shot-to-shot differences and determine ideal operating temperature ranges for the production of acceptable parts.

Acknowledgements

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