Conclusions

(1) There is a surprising analogy between the viscous behaviour at a vanishing shear rate in the melt and the thermal properties of fusion of PEO fractions and blends. In fact the critical parameters M_c and ν_c relative to the entanglement coupling concept are very close in value to those at which presumably the PEO chains pass from chain extended to chain folded crystals (M_c' and ν_c'). This could be due to the nature of the chain, i.e. to its internal flexibility which beyond a certain length can give rise to folded chains (entanglements in one case and folded chain lamellae in the other). Of course this fact could be due to coincidence and have no physical meaning.

(2) The viscosity data seem to show compatibility of the fraction in the blends over the entire range of composition in the melted state, since ΔE^* results are independent of molecular weight and concentration.

(3) The d.s.c. data show compatibility of the PEO fractions in the solid state since there is a unique melting peak on the entire range of composition of the blend.

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X-ray diffraction of processed poly(vinyl chloride)

X-ray diffraction traces have been obtained for both commercial PVC[1–3] and for materials having a higher level of syndiotacticity and crystallinity[4–7].

Mammi and Nardi[4] have discussed the X-ray diffraction patterns obtained for oriented PVC fibres, and more recently Brady and Jabarin[3] have reported the changes in the wide-angle X-ray diffraction pattern of poly(vinyl chloride) introduced by uniaxially stretching at 23°C to the 'natural' draw ratio. This work prompts us to report some X-ray diffraction studies on PVC samples prepared by injection moulding, compression moulding and drawing above and below T_g.

Compression moulded sheets were prepared from a blend of 100 parts 'Corvic' D55/09 suspension polymer with 3 parts of a liquid organotin stabilizer ('Stanclere' T126). The blend was prepared using a Fielder mixer and moulded at 200°C for 10 min. The sheet was cooled in the mould to 40°C, cooling time being 20 min. Dumbell test pieces cut from the sheets were uniaxially oriented at a range of temperatures using an Instron tensile tester. The stretching rate used was 0.1 mm/min and the draw ratio was maintained constant at approximately 1.5 for all temperatures.

Injection moulded plaques were prepared using a Bipel injection moulding machine with the mould temperature at 40°C. The compound contained 'Breon' MSO/50 mass PVC polymer, 'Stanclere' T126 stabilizer, lubricants (wax OP and calcium stearate) and processing aid (Paraloid K 120N).

Microscopical examination shows that sections cut through PVC injection moulded plaques have highly oriented 'skins', and a 'core' region in which the orientation is considerably less[8]. Samples of skin and core were prepared.

The X-ray diffraction measurements on all samples were made with Jeol DX-GE-2S generator and a DX-GO-S vertical goniometer using Ni-filtered CuKα radiation in an air atmosphere. Reflectance mode measurements were made using rectangular samples (27 x 12 mm) not less than 0.60 mm thick. For the stretched samples, measurements were made with the orientation direction at 0°, 45° and 90° to the plane containing the X-ray beam. Plots of intensity in arbitrary units *versus* diffraction angle, 2θ, were obtained over the range 12°–46° 2θ.

Figure 1 compares X-ray diffraction patterns for processed samples with that obtained for a compression moulded sample drawn at room temperature. The trace obtained for the compression moulding is similar to those previously reported[1–3] for PVC. For the injection moulded skin sample a significant increase in the peak at 17° 2θ compared with the compression moulded sample

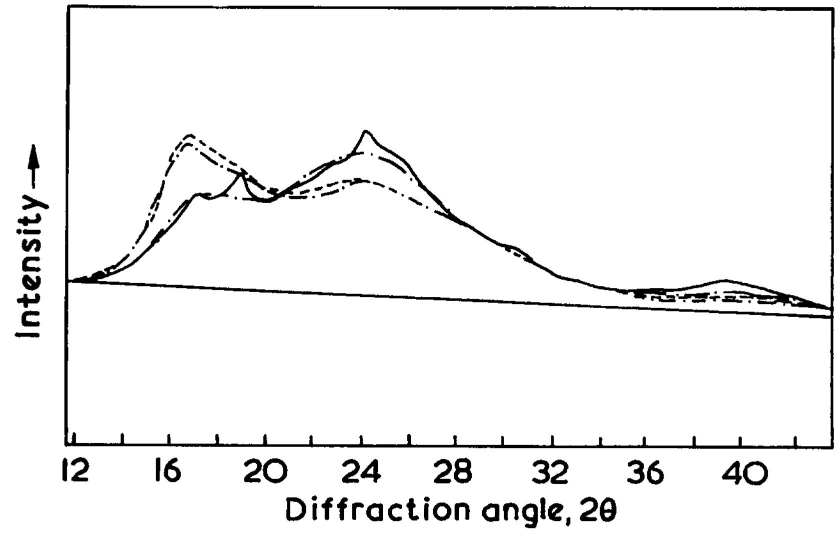

Figure 1 X-ray diffraction patterns for samples prepared by different processing techniques: ——, compression moulded at 200°C; — — — , injection moulded skin; —·—·—, uniaxially stretched at 23°C; —·—, injection moulded core

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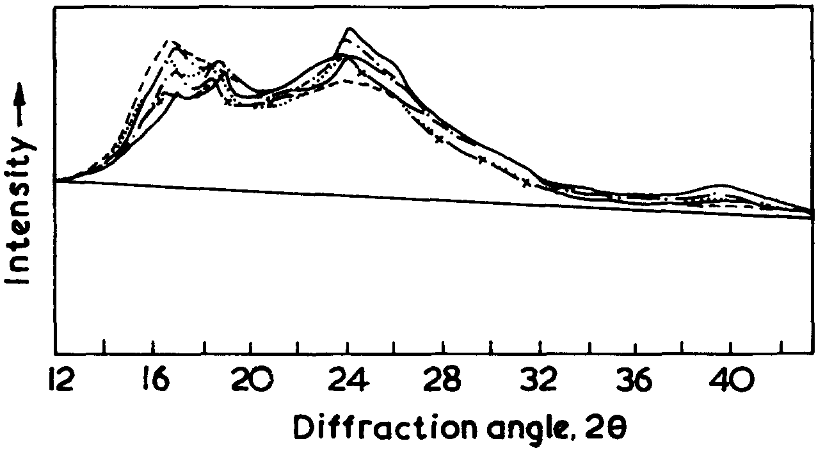

Figure 2 X-ray diffraction patterns for polymers uniaxially drawn at different temperatures: ——, compression moulded; – – –, 23°C; —·—, 50° C; • • • • •, 85°C; —•—•—, 110°C; —x—, 150°C

is observed.

The 2θ peaks at 24.1° and 39.6° are considerably reduced. An almost identical diffraction pattern was obtained for the sample uniaxially drawn at room temperature.

Mammi and Nardi[4], and Baker, Maddams and Preedy[7] have examined the various reflections which give rise to peaks in the 16°–18° 2θ range and the 24°–26° 2θ range. The latter workers have suggested that the former are mainly a measure of two-dimensional order perpendicular to the chain direction, while the latter are a measure of three-dimensional order. They have shown that during the annealing of highly syndiotactic PVC at elevated temperatures the total crystallinity increases, while the ratio of the area under the 17° 2θ peak to the area under the 24° 2θ peak decreases, and therefore suggest that two-dimensional order initially forms more rapidly than the wholly crystalline phase, but can subsequently be converted to it.

It seems reasonable to attribute the relatively large peak at 17° 2θ obtained for the skin of an injection moulding to two-dimensional order. As polymer flows into the mould and comes into contact with the cold mould surface, it cools rapidly. Molecules are frozen at the mould surface then oriented by shearing caused by flow of additional material into the mould.

It has already been shown that skins are highly birefringent and exhibit considerable shrinkage on subsequent heating. The present work suggests that, in addition to orientation, there is development of two-dimensional order perpendicular to the chain direction. Comparison of traces in *Figure 1* implies that the structural arrangement in the skin sample is very similar to that obtained for a sample of PVC drawn at room temperature.

The effect of draw temperature on the X-ray diffraction pattern is shown in *Figure 2*. In this Figure results plotted were obtained for samples with their draw direction at 0° to the plane of the X-ray beam. Similar results were obtained if the sample was arranged with its draw direction at 45° or 90° to this plane. As the draw temperature is increased, the ratio of the peak at 17° 2θ to the peak at 24° 2θ decreases. This is consistent with the lower level of orientation achieved at higher temperatures. The sample drawn at 150°C has an X-ray diffraction pattern very similar to the compression moulded sample, suggesting that there is little residual orientation in samples drawn at higher temperatures.

The X-ray diffracton trace obtained for the core of the injection moulding is considerably different from that obtained for the skin. In terms of relative peak heights in the two angular regions it is rather similar to the compression moulding. However, the peaks are much broader and the peak in the 17° 2θ region is not resolved into two, suggesting that the injection moulded core is less crystalline than the compression moulding.

It appears that it may be possible to use this X-ray method to assess the level of two-dimensional order in injection moulded PVC samples. Further work is concerned with investigating the effect of varying draw ratio on the X-ray diffraction pattern.

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