Structural order in oriented PVC mouldings

J. C. Vyvoda, M. Gilbert and D. A. Hemsley
Institute of Polymer Technology, University of Technology, Loughborough, Leics, UK
(Received 15 May 1979; revised 15 June 1979)

The structural changes occurring upon drawing and annealing of compression and injection mouldings of commercial poly(vinyl chloride) were studied by wide-angle X-ray diffraction. Low temperature drawing appears to lead to a reduction in 3-dimensional order and an increase in oriented 2-dimensional order. The degree of order of drawn and annealed PVC depends on draw ratio, annealing temperature and the restraint during annealing. The maximum in 2-dimensional order occurs on annealing at 110°C. Tensile yield stress is significantly increased by the drawing process and it was shown that the anisotropy of this mechanical property decreased upon annealing. This could not be explained by the reduction in amorphous orientation alone. Electron microscopy of the fracture surfaces shows a structure which appears to be related to the drawing and annealing process.

INTRODUCTION

The important commercial polymer poly(vinyl chloride) (PVC) is considered to be about 55% syndiotactic. X-ray diffraction has indicated the existence of crystallinity in the range of 5 to 10%[1] for unannealed polymer. Thermal treatment of semicrystalline polymers is known to affect the crystallinity, particularly when this is carried out above T_g[2,3]. Ohta, Kajiyama and Takayanagi[4] determined crystallinity of PVC from d.s.c. thermograms and obtained a maximum value of 5.7% for an annealing temperature of 130°C. Less conventional polymers such as low molecular weight PVC prepared in the presence of chain-transfer agents were shown[5] to yield up to 44%. Baker, Maddams and Preedy[6], using highly syndiotactic samples made by the urea clathrate method, reported 63% crystallinity which increased upon annealing and finally reached a value of 76–78%.

Recently Lemstra, Keller and Cudby[7] reported an unusually high X-ray crystallinity (the percentage of crystallinity was not expressed in this work) from the diffraction pattern of a commercial material. This was obtained via a novel thermoreversible gelation method. They identified two structures designated A and B. Structure A was obtained by stretching the PVC gel without further annealing and exhibited sharp meridional arcs corresponding to the spacing 5.2 Å. Two equatorial arcs corresponding to 5.4 and 4.7 Å were observed together with a broad 3.64 Å circular halo. Upon annealing under constant load at 100°–110°C the 5.2 Å reflection initially increased in prominence but eventually disappeared above $T = 130$°C and structure B was obtained. They concluded that the unexpectedly high level of crystallinity in PVC can be achieved only by the route of gel formation. However, Ohta and coworkers[4] obtained well-defined wide-angle X-ray crystalline patterns of PVC stretched 2.6 times at 60°C and subsequently annealed at 105°C. Recently Brady and Jabarin[8] and Gilbert and Vyvoda[9] have observed an increase in the intensity of the 17° (2θ) peak in the wide-angle X-ray diffraction pattern of PVC uniaxially-drawn at room temperature. The latter authors suggested that, in addition to orientation, there was development of two-dimensional order perpendicular to the chain direction. Mammi and Nardi[10] have reported a strong reflection at 17.5° (2θ) in 500% stretched PVC fibre and indicated the presence of a nematic mesomorphic phase.

Yeh and Lambert[11] and Yeh and Geil[12] have shown that isotactic polystyrene and poly(ethylene terephthalate) can be crystallized by stretching polymer films followed by subsequent annealing at higher temperatures. The transformation from an essentially fibrillar morphology (obtained by strain-induced crystallization) into a lamellar morphology by additional treatment can occur[13]. This transformation can be either irreversible or reversible with temperature, depending upon whether the stretched polymer is thermally treated above or below the original stretching temperature. Yeh[13] demonstrated that the resulting morphology depends greatly on annealing conditions, i.e. whether the annealing is carried out with the specimens free or restrained and on the magnitude of the applied strain.

In this work we present results of wide-angle X-ray diffraction studies of commercial poly(vinyl chloride). The samples were prepared by injection and compression moulding with subsequent stretching and annealing treatments. Comparatively high levels of order obtained by these treatments and not yet reported in the literature are discussed together with their effects on mechanical properties.

EXPERIMENTAL

Materials and sample preparation

Breon M80/50 mass PVC polymer was dry-blended in a Fielder mixer. The injection-moulding compound contained 3 parts per hundred (w/w) of Stanclere T126 stabilizer, 0.5 parts of calcium stearate, 0.75 parts of wax OP and 4 parts of Paraloid K 120N as a processing aid. Samples were prepared using a Bipel injection-moulding machine with a mould temperature of 40°C. The compression-moulding compound contained three parts of Stanclere T126 liquid organotin stabilizer only. The PVC powder was moulded at 200°C for 10 min followed by cooling under pressure to room temperature. The initial rate of cooling in the press was 19°C min^{-1}. For some X-ray diffraction studies a Shell commercial grade, Carinex DG 258, polystyrene was used. Samples were prepared by compression-moulding at 160°C

0032–3861/80/010109–07$02.00

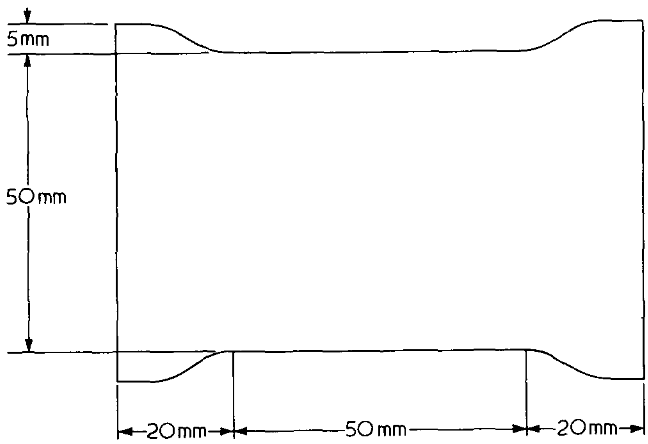

Figure 1 PVC dumb-bell used for stretching

for 10 min. again with subsequent cooling under pressure, to room temperature.

Stretching and annealing treatment

PVC dumb-bell shaped samples having the dimensions shown in *Figure 1* were uniaxially stretched to different draw ratios in the Instron testing machine using a straining rate of 0.1 mm min^{-1} at 70°C. The drawing temperature for the polystyrene control samples was 100°C. The stretching process for both materials was continuous since no 'neck' formation was observed under these conditions.

Some samples were subsequently annealed in an air oven without restraint, together with unstretched PVC as a control. The air oven was also used for the annealing of unrestrained injection-moulded specimens. An Instron tensile tester with environmental chamber was used for annealing restrained specimens.

X-ray diffraction measurements

PVC X-ray diffraction patterns were obtained with a Jeol DX-GE-2S generator operated at 40 kV, 30 mA with a vertical goniometer type DX-GO-S. Ni-filtered CuKα radiation was used in an air atmosphere. Reflectance mode measurements at ambient temperature were made using rectangular samples (27 x 12 mm) and the diffraction intensity in arbitrary units was obtained over the 2θ range 10°–47°. No correction for air scattering and variation of scattering intensity with 2θ was made.

The sample was not rotated while measurements were being made, but measurements made with the sample rotated to different angles within its own plane showed only minor variations which would not affect the results significantly. Transmission X-ray measurements were made with samples of 0.1 mm thickness and a sample to film distance of 5 cm. Scattered intensities were recorded photographically. X-ray diffraction patterns of polystyrene were obtained with samples 2 mm thick using transmission mode measurement. Diffraction intensity was obtained over the 2θ range 12°–30° and the resulting diffraction curves were essentially the same as described by Challa, Hermans and Weidinger[14].

Tensile properties

Since all the samples exhibited a well-defined yield point, tensile yield stress was determined at room temperature using the Instron tensile tester at 5 mm min^{-1} grip separation speed. Test samples (ASTM D638-72) were cut from drawn and annealed PVC and tested in directions both parallel and transverse to the stretch direction. Tensile yield stress was calculated using the area of the initial cross-section.

Electron microscopy

Electron micrographs were obtained using a Cambridge S2A Scanning Electron Microscope. Fracture surfaces, prepared by impacting samples at liquid nitrogen temperature, were vacuum coated with gold prior to microscopic examination.

RESULTS

Uniaxial drawing of compression-moulded PVC

Cold-drawing improves tensile properties such as yield stress, modulus or ultimate tensile strength because of molecular alignment. Brady and Jabarin[8] reported an increase of 25% in the yield stress for PVC cold-drawn to its 'natural draw ratio'. However, no direct relationship between tensile properties, birefringence, enthalpy, shrinkage or 17° 2θ X-ray peak was reported.

Figure 2 compares the tensile yield stress and the intensity of the 17° 2θ peak (expressed as the ratio of the 17° 2θ intensity of the compression moulded drawn PVC and quenched PVC) as a function of draw ratio λ. The quenched PVC was prepared by heating the sample to 215°C for 5 min followed by chilling in ice/water mixture. The x-ray diffraction patterns of quenched PVC corresponded well to that obtained by Wenig[1] and Mammi and Nardi[10], i.e. the disappearance of the 110 reflection was attributed to the loss of crystallinity. As expected, tensile yield stress (*Figure 2*) increased significantly and reached 113 NM/m^{-2} for λ = 2.26. This represents an increase of 76.6% over the undrawn sample. It could be noted that above λ = 1.7 the yield stress increases more rapidly. The X-ray intensity ratio $I_{17°}/I_{17_q°}$ unexpectedly increased and the increase was linear with increasing draw ratio λ.

Figures 3a (obtained in the reflection mode) and *3b* (Obtained in the transmission mode) show the X-ray diffraction results for an unstretched specimen. Two sharp circular

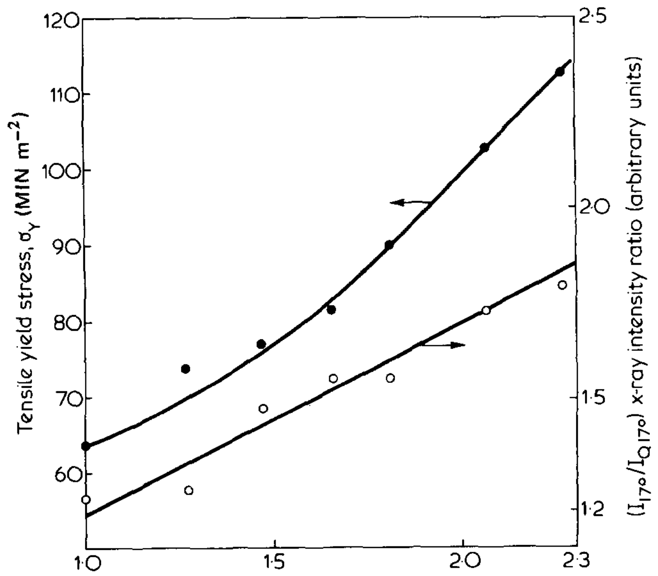

Figure 2 Effect of draw ratio on tensile yield stress and on X-ray intensity ratio

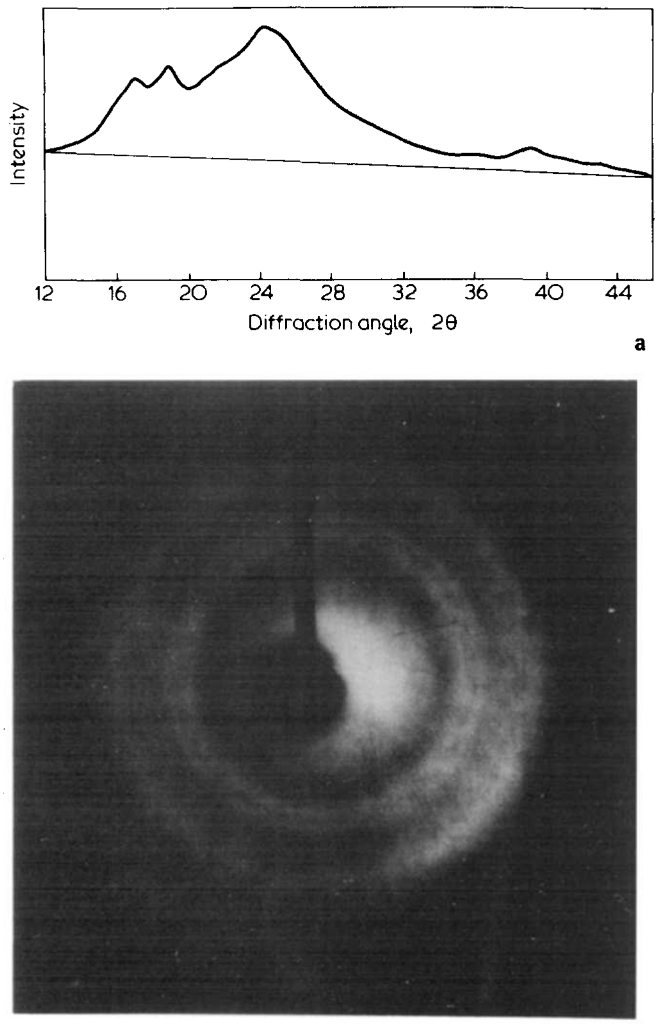

Figure 3 (a) X-ray diffraction pattern of undrawn compression-moulded PVC; (b) X-ray diffraction photograph corresponding to *Figure 3a*

halos in *Figure 3b* corresponding to the lattice spacings d = 5.19 Å and d = 4.6 Å can be discerned and a broader circular halo corresponding with d = 3.58 Å is also visible.

Figures 4a and *4b* show a diffraction trace and a photograph of a compression-moulded specimen drawn to $\lambda = 2.37$

A comparison of *Figures 3a* and *4a* shows a sharpening of the 17° 2θ peak on stretching. Peaks in this angular region have been shown[15] to be due to (010) (200) and (110) sets of planes. *Figure 4b* indicates that these planes are partly oriented in the stretched specimen.

Ohta *et al.*[4] have observed crystalline reflections from (010), (200) (d = 5.3 Å) and (110) (d = 4.8 Å) planes in a PVC sample for $\lambda = 2.6$ drawn at 60°C and also from (210) (d = 3.78 Å) and (201) (d = 3.67 Å) planes after annealing of drawn sample at 105°C. They found that there was no variation in birefringence upon annealing up to 170°C, at which temperature the crystalline reflections disappeared and therefore suggested that the PVC had crystallized during stretching and annealing. The linear relationship between $17^\circ/17^\circ_q$ ratio and the draw ratio λ (*Figure 2*) together with the presence of crystalline reflections (*Figures 4a* and *4b*) appear to be in accordance with the findings of Ohta and coworkers[4]. The presence of two-dimensional order as suggested by Baker, Maddams and Preedy[6] and indicated in earlier work[9] may in part be responsible for the significant increase of the tensile yield stress and increasing draw ratio λ.

In order to compare the drawing behaviour of a semi-crystaline polymer such as PVC with totally amorphous glassy polymer, atactic polystyrene was chosen. *Figure 5* shows an X-ray diffraction pattern of an undrawn compression-moulded sample of polystyrene together with a sample uniaxially drawn to $\lambda = 2.37$. Since polystyrene is brittle it could not be drawn at a lower temperature, hence a drawing temperature of 100°C was used. X-ray intensity was recorded over the 2θ range 12°–30° in transmission. The diffraction pattern obtained corresponded to the diffractograms of amorphous polystyrene sample as reported by Challa, Hermans and Weidinger[14]. No significant changes (*Figure 5*) in the X-ray intensity of the sample drawn to $\lambda = 2.37$ were observed when compared with the undrawn specimen. Diffraction patterns for lower draw ratios were similar and therefore not shown here. This is in sharp contrast with the stretching behaviour of PVC as discussed here.

Annealing treatment of mouldings

(a) PVC annealed without external restraint – effect of temperature. Figures 6a and *6b* show wide-angle X-ray diffraction patterns of injection-moulded PVC specimens annealed without external restraint in an air oven at temperatures between 80° and 140°C. The diffraction pattern of the sample annealed at 80°C (*Figure 6a*) shows an en-

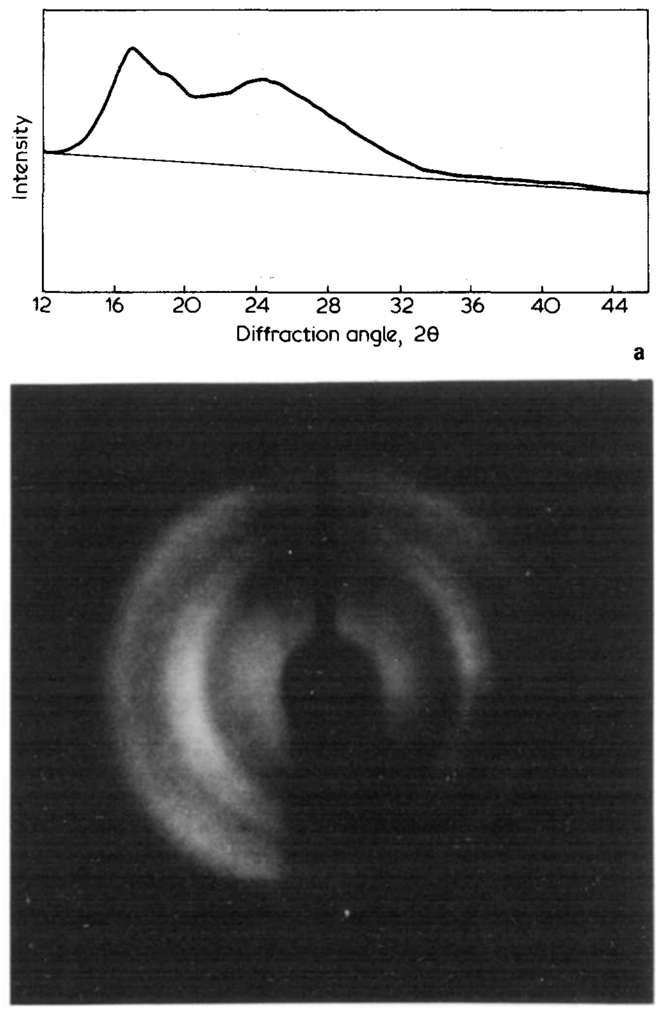

Figure 4 (a) X-ray diffraction pattern of compression-moulded PVC drawn to λ = 2.37. (b) X-ray diffraction photograph corresponding to *Figure 4a*

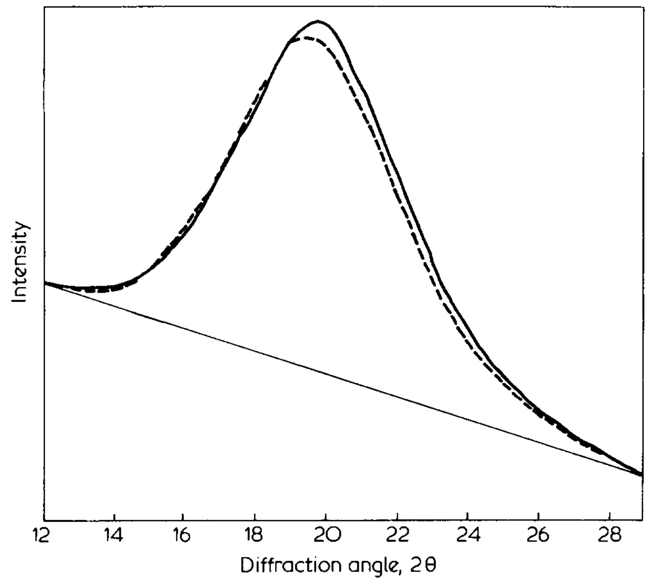

Figure 5 X-ray diffraction patterns of polystyrene. – – –, λ = 1.0; ——, λ = 2.37

and 18.6° 2θ peaks increase significantly with increased draw ratio. Furthermore, the peak centred at 23.9° 2θ progressively sharpened upon annealing. The estimated crystallinity of the sample drawn to λ = 2.65 was 20%.

It has been shown previously by Yeh and coworkers[11–13] that isotactic polystyrene and poly(ethylene terephthalate) crystallize if stretched and subsequently annealed. Annealing temperatures of 155° and 175°C were used in the case of isotactic polystyrene and the annealing time varied from 1 to 20 min. The crystallization of drawn poly(ethylene terephthalate) was essentially complete[12] in 15 min at 180°C. In the present work the effect of crystallization time was studied and well-defined crystalline patterns were obtained after annealing injection-moulded specimens for 10 min at 90°C. Longer annealing times (up to 270 min) had no effect on the X-ray diffraction patterns. It appears, therefore, that strain-induced crystallization of PVC is a fast process and it is probable that crystalline structure is fully developed at the shorter times than 10 min, especially if heat transfer to the polymer is taken into account.

hanced 17° 2θ peak with a shoulder at ~18.7° 2θ and a broad peak centred at ~24.5° 2θ, together with smaller peaks at 30.6° 2θ and 39° 2θ. With increasing temperature the 17°–19° 2θ reflections are split into two distinct peaks centred at 16.9° and 18.6° 2θ and the broad peak at ~24° 2θ is significantly sharpened, with its maximum being centred at 23.9° 2θ. The intensities of all peaks increased progressively upon annealing up to 110°–120°C (*Figure 6b*) but at 140°C and above (not shown here) the intensity of all peaks decreased. Compression-moulded PVC was uniaxially drawn just below T_g. It has been observed that when annealed without restraint this failed to yield similar crystalline X-ray patterns. It has been shown previously[16,9] that mouldings consist essentially of a core between highly oriented skins. It would therefore appear that annealing of injection-moulded specimens has been done under conditions of intrinsic restraint, i.e. the oriented skins were effectively restrained by the core and chain relaxation was significantly prevented. Hence, it is clear that restraint is a necessary condition for this crystallization process.

(b) Annealing treatment with external restraint. In order to investigate the effect of external restraint and to compare the crystalline patterns with the patterns obtained under the conditions of intrinsic restraint, injection-moulded specimens were annealed in the temperature-controlled chamber of the Instron tester at 110°C. *Figure 7* compares the X-ray patterns of annealed specimens in the air oven without external restraint and in the Instron tensile tester. A considerable increase of intensities of all crystalline reflections is observed for the sample annealed with external restraint. A level of order of 30% was estimated from the diffraction pattern after separation of non-crystalline scattering using essentially the method of Rayner and Small[17]. No corrections for air scattering or for the change of Lorentz polarization and scattering factor with Bragg angle was applied. Therefore the true crystallinity value was probably higher.

(c) Effect of draw ratio λ. Figure 8 shows diffraction patterns of compression-moulded specimens drawn at 70°C to the draw ratios λ = 1.35, 2.00 and 2.65. The specimens were subsequently annealed at 110°C for 60 min with external restraint. It is evident that the intensity of 16.9° 2θ

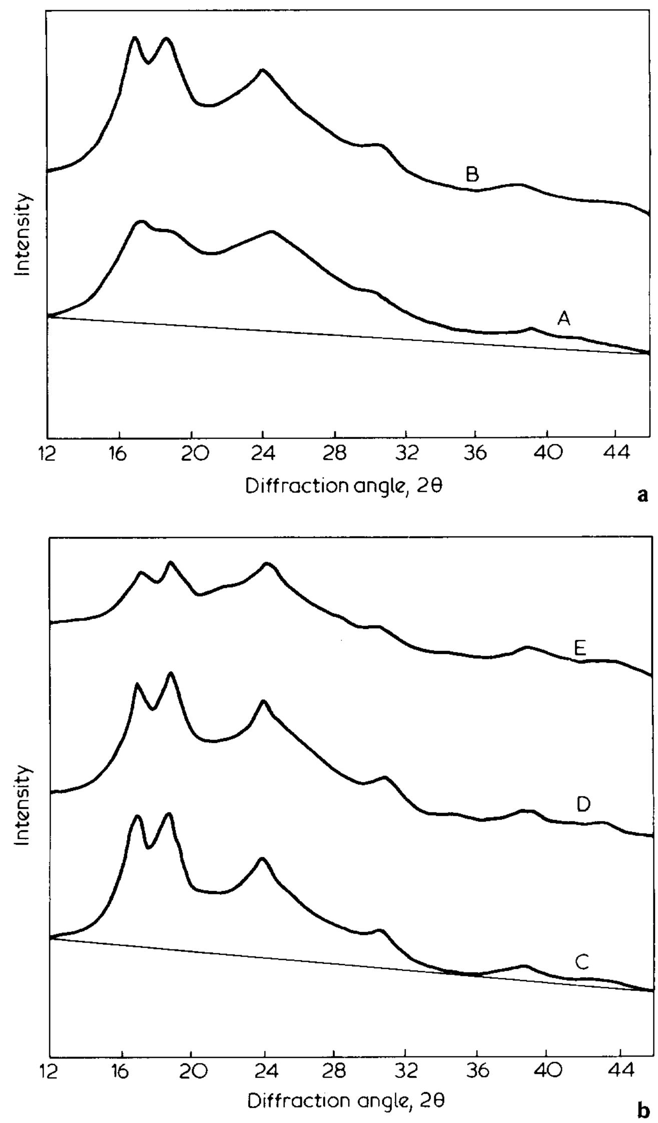

Figure 6a and *b* X-ray diffraction pattern of injection-moulded PVC annealed without restraint. A, 80°C; B, 100°C; C, 110°C; D, 120°C; E, 140°C

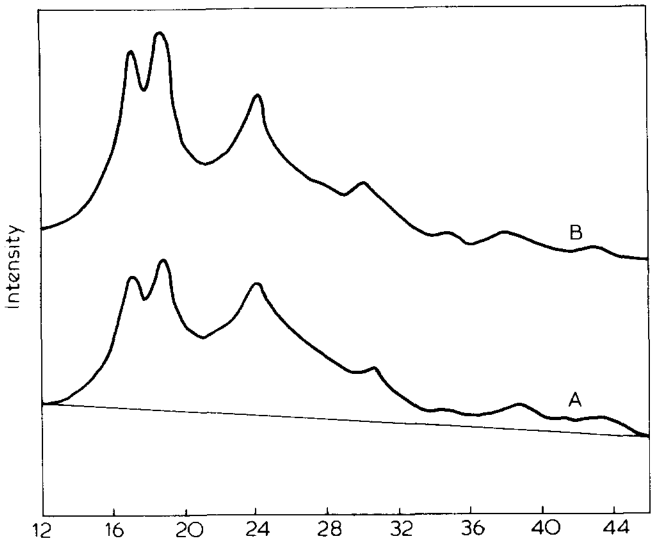

Figure 7 Effect of external restraint on X-ray diffraction patterns of injection-mouldings. A, unrestrained; B, restrained

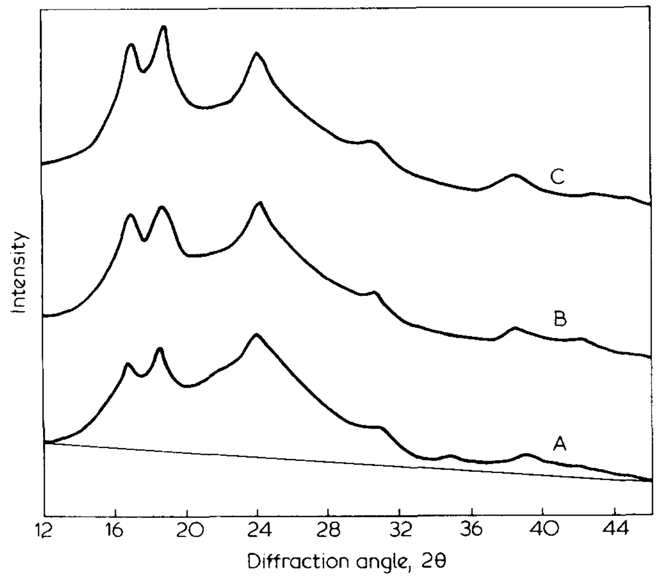

Figure 8 Effect of draw ratio on X-ray diffraction patterns of PVC compression-mouldings: A, λ = 1.35; B, λ = 2.0; C, λ = 2.65

Tensile properties

Annealing treatments of externally-restrained injection-mouldings discussed above have produced levels of order of about 30%. When the compression-moulded specimens were used, crystallinity of the order of 20% was achieved. It was expected that such changes would affect mechanical properties. Tensile yield stress has been found to be particularly sensitive to such treatment. Tensile yield stress was therefore measured parallel to, and perpendicular to the draw direction for drawn and drawn–annealed compression-moulded samples. The samples were annealed at 110°C for 60 min in the temperature-controlled chamber of the Instron tester. *Figure 9* shows plots of yield stresses vs. draw ratio, λ, up to λ = 2.5. For the drawn samples the yield stress increased significantly with the draw ratio in the parallel direction and decreased in the perpendicular direction. However, drawn-annealed samples were less anisotropic and in the perpendicular direction the tensile yield stress remained constant at about 64 MN m^{-2} until a draw ratio of 1.8 was reached.

The anisotropy does not appear to be solely due to amorphous orientation. Shrinkage measurements were carried out at 130°C for 3h for drawn and drawn-annealed specimens (λ = 1.6). The results were similar in the two cases (*Table 1*).

Scanning electron microscopy

Electron micrographs of untreated compression-moulded PVC were compared with those of similar specimens drawn and annealed. For this study no additives were used except the liquid organotin stabilizer. Fracture surfaces were examined in the scanning electron microscope as described earlier. *Figures 10a* and *10b* show the fracture surface of PVC drawn at 70°C to λ = 2.37 and 1.35, respectively. Both were annealed in the restrained state for 60 min at 110°C. No such texture is apparent in the untreated sample (*Figure 10c*). Yeh and Geil[12] observed ball-like structures (termed nodules) in their stretched poly(ethylene terephthalate). These structures aggregated and aligned on subsequent annealing at 180° or 260°C. Yeh and Lambert[11] and Yeh[13] observed lamellar morphology in isotactic polystyrene stretched and annealed in the restrained state. Gezovich and Geil[18] have reported large structures of 1 to 2 μm with

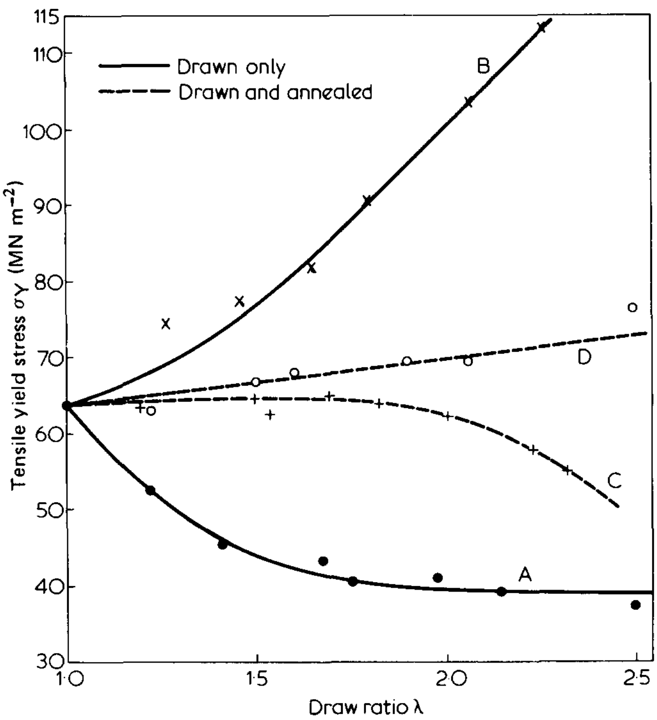

Figure 9 Tensile yield stresses of drawn and drawn and annealed compression-mouldings. Drawn: A perpendicular; B parallel. Drawn and annealed: C perpendicular; D parallel

Table 1

Sample	λ	% Shrinkage in draw direction	% Reversion
Drawn	1.68	29.0	42.6
	1.61	25.6	42.9
Drawn/annealed	1.69	31.5	45.7
	1.65	28.1	43.3

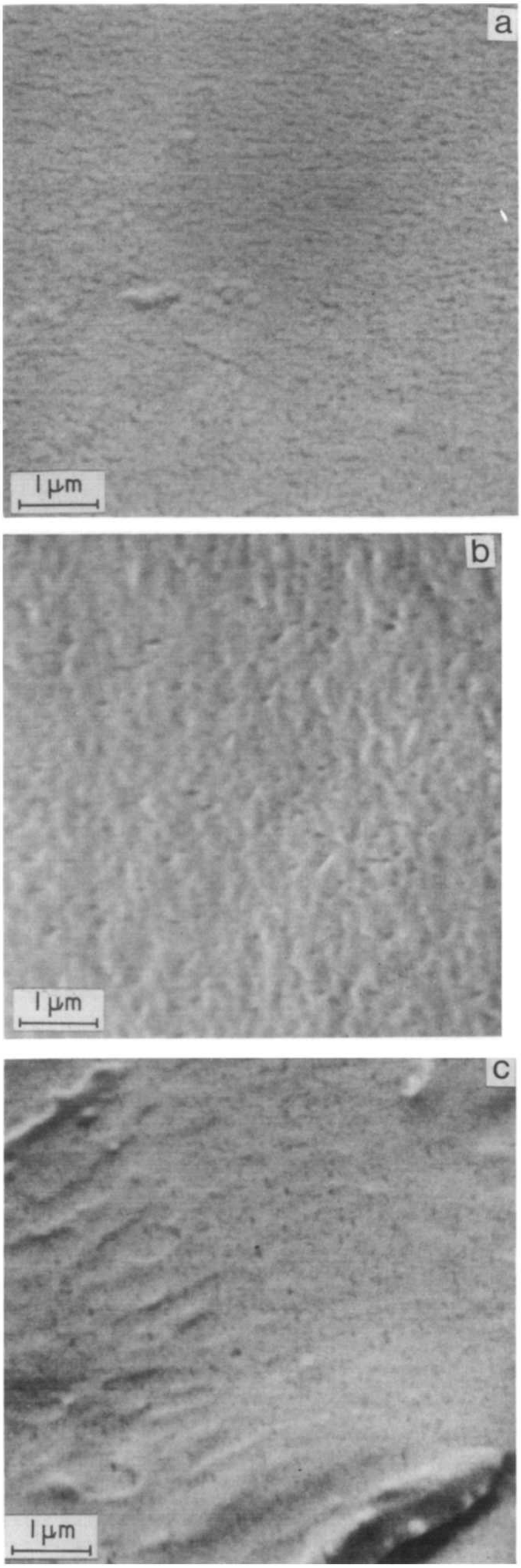

Figure 10 Fracture surface of compression-moulded PVC. (a) Drawn to λ = 2.37, annealed; (b) Drawn to λ = 1.35, annealed; (c) Undrawn and unannealed

a fine nodular structure of about 200 Å in unplasticized compression-moulded PVC.

CONCLUSIONS

A comparison of *Figures 3* and *4* show that cold-drawing of compression-moulded material leads to a reduction in 3-dimensional order in the mouldings (decrease in height of the 24° 2θ peak) and an increase in oriented 2-dimensional order (an increase in the 17°–19° 2θ peak). As might be expected this gives rise to anisotropy of mechanical properties as shown in *Figure 9*. The drawn–annealed compression-mouldings show decreased mechanical anisotropy. Although one might attribute this loss or reduction in amorphous orientation the shrinkage results of *Table 1* and X-ray diffraction data of *Figures 4* and *8* suggest that the change in anisotropy cannot be entirely explained in this way.

At low draw ratios, annealing results in the development of an X-ray diffraction pattern typical of that for non-oriented local 3-dimensional order. The anisotropy of yield stress is negligible (*Figure 9*). However, at high draw ratios the intensity in the 17° 2θ region increases and anisotropy rapidly develops. This may be attributed to a conversion of 3-dimensional order to 2-dimensional order on drawing as shown in *Figure 8*.

The annealing of undrawn compression-mouldings produces no changes in the X-ray diffraction patterns suggesting that the crystallinity produced at low draw ratios is strain-induced.

Electron microscopy of the fracture surfaces of drawn and annealed compression-mouldings has shown structure which appears to be related to the drawing and annealing processes. *Figure 10c* shows a smooth surface at a magnification of X12 000, although normal fracture morphology is evident on the larger scale. This type of image was consistently obtained in the case of undrawn material. *Figure 10b* illustrates the fracture surface of material drawn to λ = 1.35, corresponding to the situation described above where X-ray diffraction indicates non-oriented 3-dimensional order. The texture displayed is on a scale of about 0.2–0.3 μm and is only slightly aligned. However at λ = 2.37, which we tentatively believe gives rise to a substantial shift towards 2-dimensional order, the fracture surface texture becomes finer (0.1–0.2 μm)and highly aligned. Although it is tempting to over-interpret these images in terms of microstructure, the texture seen is believed to reflect some modification to the fine scale morphology of the material over and above amorphous orientation. Also, sharper X-ray patterns were observed for the samples in which structure was detectable. These sharper peaks could arise from larger crystallites.

On annealing injection-mouldings a variety of effects are observed. The diffraction intensities increase between 80° and 110°C then fall. As the annealing temperature is raised there is also an increase in the X-ray diffraction intensity in the 17° 2θ region relative to the 24° 2θ peak up to 110°C. Thereafter this ratio falls. Before 90°C is reached there is evidence for the splitting of the 17° 2θ peak so that peaks corresponding to (200) and (110) planes can be discriminated. Mammi and Nardi[10] have published diffraction patterns for a non-oriented PVC sample having a crystallinity of 20–30% and an oriented sample which they interpret as resulting from a nematic mesophase. Our diffraction patterns for samples annealed between 90° and 130°C are intermediate between these two and suggest the development of 2- and 3-dimensional order. Relative peak height measurements show that a maximum in 2-dimensional order occurs at 110°C. It is difficult to separate the X-ray data relating to crystallinity and the nematic phase, but above 130°C 2-dimensional order appears to break down and there is clear evidence of the presence of 3-dimensional order.

Regardless of temperature the effects produced occur very rapidly.

Injection-mouldings of PVC can have a skin and core structure and this is true of the mouldings used in this work[16]. Furthermore we have shown that in the absence of restraint structural changes on annealing do not occur. To explain the data obtained from injection-mouldings it must be assumed that the core is at least partly effective in restraining the relaxation of the skin.

If external restraint is applied to an injection-moulded specimen while annealing at 110°C, the amount of order developed is increased (*Figure 7*).

ACKNOWLEDGEMENTS

The authors wish to acknowledge the Science Research Council for the provision of a grant to support the programme of which this work forms a part.

REFERENCES

1 Wenig, W. *J. Polym. Sci. (Polym. Phys. Edn)* 1978, **16**, 1635
2 Gray, A. and Gilbert, M. *Polymer* 1976, **17**, 44
3 Illers, K. H. *Makromol. Chem.* 1969, **127**, 1
4 Ohta, S., Kajiyama, T. and Takayanagi, M. *Polym. Eng. Sci.* 1976, July, No. 7, **16**, 465
5 Gouinlock, E. V. *J. Polym. Sci. (Polym. Phys. Edn)* 1975, **13**, 961
6 Baker, C., Maddams, W. F. and Preedy, J. E. *J. Polym. Sci. (Polym. Phys. Edn)* 1977, **15**, 1041
7 Lemstra, P. J., Keller, A. and Cudby, M. *J. Polym. Sci. (Polym. Phys. Edn)* 1978, **16**, 1507
8 Brady, T. E. and Jabarin, S. A. *Polym. Eng. Sci.* 1977, **17**, 686
9 Gilbert, M. and Vyvoda, J. C. *Polymer* 1978, **19**, 862
10 Mammi, M. and Nardi, V. *Nature* 1963, **199**, 247
11 Yeh, G. S. Y. and Lambert, S. L. *J. Appl. Phys.* 1971, **42** (No. 12), 4614
12 Yeh, G. S. Y. and Geil, P. H. *J. Macromol. Sci. (Phys)* 1967, **1**, 251
13 Yeh, G. S. Y. *Polym. Eng. Sci.* 1976, **16**, 145
14 Challa, G., Hermans, P. H. and Weidinger, A. *Macromol. Chem.* 1962, **56**, 169
15 Natta, G. and Corradini, P. *J. Polym. Sci.* 1956, **20**, 251
16 Copsey, C. J. and Gooding, V. J. C. *Inst. Phys. Conf. Processing, Structure Properties and Performance of Polymers, University of Nottingham,* July 1977
17 Rayner, L. S. and Small, P. A. (to Imperial Chemical Industries Ltd.), *Br. Pat.* 847 676, 1951, October 30
18 Gezovich, D. M. and Geil, P. H. *Int. J. Polym. Mater.* 1971, **1**, 3