Structure and properties of oriented plasticized poly(vinyl chloride)

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Compression mouldings were produced from PVC compounds containing 20 phr and 50 phr DIOP. These were stretched at various temperatures to a maximum draw ratio of 2.0. Drawn samples were subjected to annealing at various temperatures between 90°C and 140°C. Tensile properties of drawn and annealed samples were measured, and wide-angle X-ray diffraction traces obtained. Drawing produced increased ultimate tensile strength in the draw direction which could be attributed to the development of structural order, which was mainly two dimensional in nature. The observed effects could be further enhanced by annealing. Samples containing 50 phr DIOP returned to their original length after stretching, but this shrinkage could be avoided by annealing in the stretched state, due to the formation of ordered structures which held the oriented chains in position.

(Keywords: poly(vinyl chloride); orientation; plasticized; X-ray diffraction; birefringence)

INTRODUCTION

A number of workers have investigated the property improvements which can be achieved in poly(vinyl chloride), (PVC) by orientation[1-4]. Attention has been concentrated on rigid PVC since drawn samples above their glass transition temperature will tend to revert to their original state. Because of the limited order along a PVC molecule (commercial suspension polymers are typically 55% syndiotactic), complex structural changes can occur. The polymer as produced contains 5–10% crystallinity. However a nematic mesomorphous phase, which involves the development of two dimensional order perpendicular to the chain direction can be produced by orientation[5-9]. It has also been shown that a similar structure can be produced by annealing[9,10]. In earlier work, Vyvoda *et al.*[9] investigated the effects of drawing and annealing on the tensile properties of rigid PVC, and explained the observed behaviour in terms of structural changes detected by X-ray diffraction. In the work reported in this paper the possibility of enhancing the properties of plasticized PVC compounds was investigated. Again, the effects produced by a variety of drawing and annealing treatments have been monitored by X-ray diffraction.

EXPERIMENTAL

Sample preparation

The compound used in this work was formulated from a commercial PVC, Corvic S71/102 supplied by ICI. Di-isooctyl phthalate (DIOP) was used as plasticizer. The samples were stabilized by a liquid cadmium/barium stabilizer Lankromark LC68. The two formulations used are given in *Table 1*.

The PVC resin was agitated in an 8 litre high speed Fielder mixer to a temperature of 50°C, then the plasticizer and the liquid stabilizer were added. Mixing continued until a temperature of 120°C was reached and the compound discharged into the cooling container where it was agitated and cooled to below 25°C. The mixing conditions are shown in *Table 2*. The powder blend was further mixed on a two-roll mill for 5 min at 140°C to produce a sheet approximately 1 mm in thickness. The milled PVC was compression moulded at 180°C to produce sheets 1 mm thick; these were cooled under pressure to room temperature.

The moulded PVC sheets are colourless and transparent. Glass transition temperatures, T_g were measured using a Du Pont 990 Thermal Analyser fitted with a DSC cell and a heating rate of 10°C/minute. The T_g for the sample containing 20 phr DIOP was +20°C; that for the sample containing 50 phr DIOP was −30°C.

Stretching and annealing

Dumb-bell shaped PVC samples as used previously, and shown in *Figure 1* were uniaxially stretched to different draw ratios using an Instron testing machine. The straining rate for both compounds was 1 mm min^{-1}. Drawing temperatures for the PVC containing 20 phr plasticizer were 40°C and 70°C; the PVC plasticized with 50 phr plasticizer was drawn at room temperature. The stretching process was continuous without sample slippage from the grips. After stretching to the required draw ratio samples were cooled to room temperature while being restrained in the grips.

Table 1 Compound formulation

Component	Composition (phr)
PVC (Corvic S71/102)	100
Plasticizer (DIOP)	20, 50
Stabilizer (Lankromark LC68)	2

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Table 2 Mixing conditions

Batch weight	2 kg
Mixer rotor speed	3500 rpm
Mixer jacket temperature	75°C
Cooler jacket temperature	< 20°C
Cooler rotor speed	> 1000 rpm
Total mixing cycle	15 min

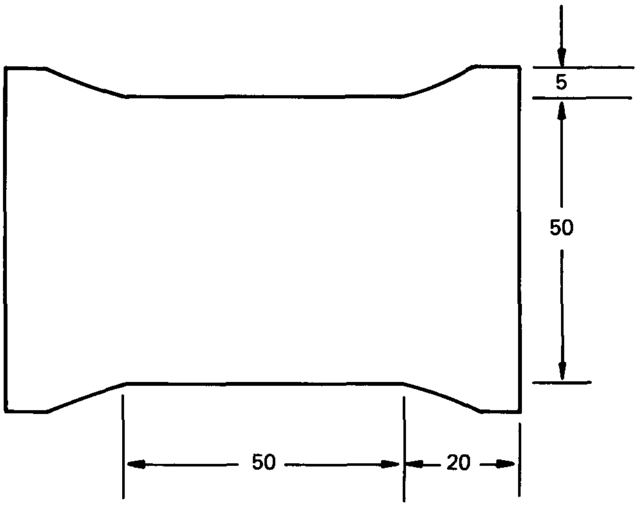

Figure 1 PVC dumb-bell used for stretching (dimensions in mm)

The Instron environmental chamber was used for annealing restrained samples. Annealing was carried out for 90 min at various temperatures between 90°C and 140°C.

X-ray diffraction measurements

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 flat rectangular samples (20 × 14 mm) and the diffraction intensity in arbitrary units was obtained over the range 11°–46° 2θ. No correction was made for air scattering; variation of scattering intensity with 2θ was recorded.

Order factors for the drawn and annealed samples were calculated as described in ref. 11. The significance of these values will be discussed later. Initially an 'amorphous' trace was prepared by heating a sample taken from the compression moulding containing 20 phr PVC at 200°C for 8 minutes, then quenching in ice-water. Templates were prepared from the trace, and fitted to X-ray traces for the drawn and annealed samples as shown in *Figure 8*.

Tensile properties

Type 2 test samples (BS903: Part A2: 1971) were cut from the compression moulded sheet and from drawn PVC in directions both parallel and perpendicular to the draw direction. Tensile tests were carried out at room temperature using a J. J. Lloyd tensile tester at 5 mm min^{-1} grip separation speed. Ultimate tensile strength was calculated using the area of the initial cross-section, and elongation at break was calculated from initial and final grip separations.

Birefringence measurements

In order to investigate further the effects of orientation, in plane birefringence measurements were made on selected samples. These measurements were made using a polarising light microscope with a monochromatic source, and fitted with an Ehringhaus compensator. Measurements were made by observing the movement of fringes up a cut wedge on the side of the specimens.

RESULTS

Tensile properties

Effect of draw ratio on tensile properties. Figure 2 shows the effect of draw ratio on ultimate tensile strength (UTS) and elongation at break for PVC samples containing 20 phr DIOP. (MD is the draw or machine direction; TD is the transverse direction.) Samples were drawn at 40°C, since it had been shown previously[2,3] that drawing just above T_g would be expected to give significant changes in orientation properties. Results show, that as for unplasticized PVC[9], there is a significant increase in UTS parallel to the direction of stretch, and a decrease in the transverse direction. Elongation at break, however, decreases substantially in the parallel direction, and also shows a small decrease in the perpendicular direction. These changes are accompanied by changes in the shape of the load–extension curves, as shown in *Figure 3*. A pronounced yield, evident for the undrawn sample, gradually disappears as draw ratio increases. A similar but lesser effect is observed for samples tested in the transverse direction.

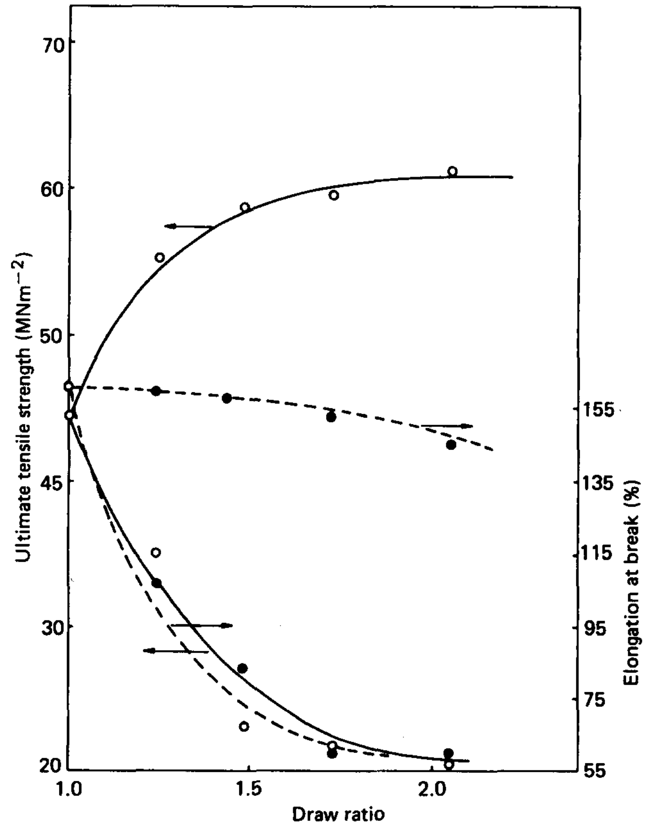

Figure 2 Tensile properties *versus* draw ratio for samples containing 20 phr DIOP: (○) in the MD; (●) in the TD

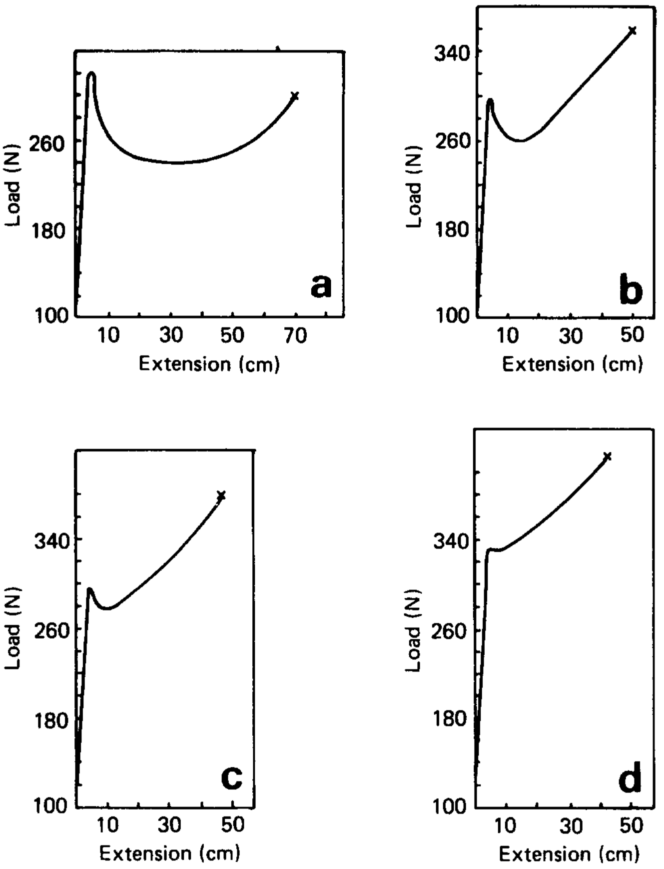

Figure 3 Load/extension curves for undrawn and drawn samples. (a) Undrawn; (b) draw ratio 1.5; (c) draw ratio 1.7; (d) draw ratio 2.0

Effect of drawing temperature on tensile properties. The effects of drawing the sample containing 20 phr DIOP at 40° ($T_g+20°C$) and 70°C ($T_g+50°C$) were compared, and results are shown in *Table 3*. The draw ratio used was 1.95–2.00; properties appear to be levelling off at this value. It is observed that drawing at 70°C has more effect on both increase in UTS and decrease in elongation at break in the MD, suggesting that greater orientation was produced at this temperature. The high elongation observed in the transverse direction for the sample drawn at 70°C is consistent with this, although the UTS in the TD is higher for the sample drawn at 70°C. This experiment suggested that reasonable results should be obtained for the sample containing 50 phr DIOP by stretching at room temperature, a much more convenient process than low temperature stretching.

Effect of annealing on tensile properties. Both plasticized samples were annealed at a range of temperatures between 90° and 140°C after drawing. (Draw ratio for the compound containing 20 phr DIOP was 1.80–1.85; that for the compound containing 50 phr was 1.90–1.95.) Tensile properties after annealing are shown in *Figures 4* and *5*. Properties for the samples before drawing are shown in *Tables 3* and *4*. The sample containing 20 phr DIOP did not shrink after drawing and cooling, so it was possible to measure tensile properties of the drawn sample. Due to its low T_g, the sample containing 50 phr DIOP reverted almost to its original length after drawing, cooling, and removal from the grips. Tensile properties were measured immediately, but were found to be very similar to those of the undrawn sample. Therefore annealing treatments for this sample were carried out immediately after drawing, before release of stress. After annealing, shrinkage was not observed except for the sample annealed at 90°C which did show considerable shrinkage. Annealing at temperatures of 100°C and above therefore had the effect of 'setting' the orientation produced by drawing.

Table 3 Tensile properties of PVC plasticized with 20 phr DIOP

		Drawing temperature (°C)		Undrawn sample
		40	70	
Ultimate tensile strength (MN m^{-2})	MD	64.0	72.2	38.4
	TD	22.3	26.1	
Elongation at break (%)	MD	68	44	131
	TD	130	220	

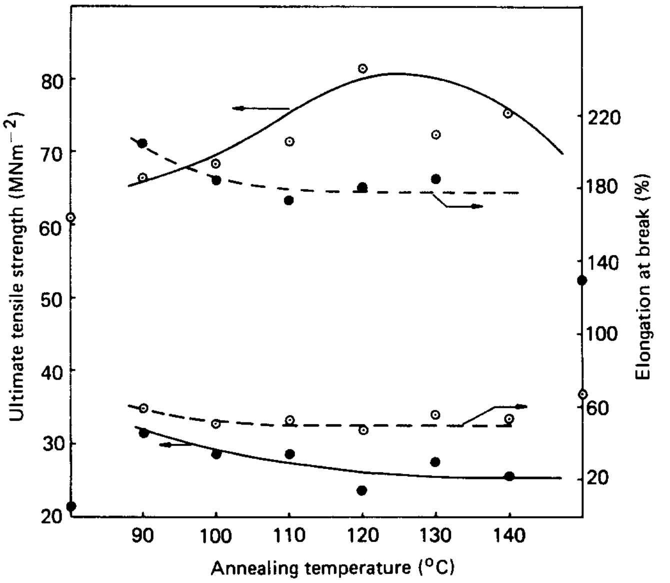

Figure 4 Tensile properties for drawn PVC containing 20 phr DIOP *versus* annealing temperature: (○) in the MD; (●) in the TD. Points on axes refer to drawn sample before annealing

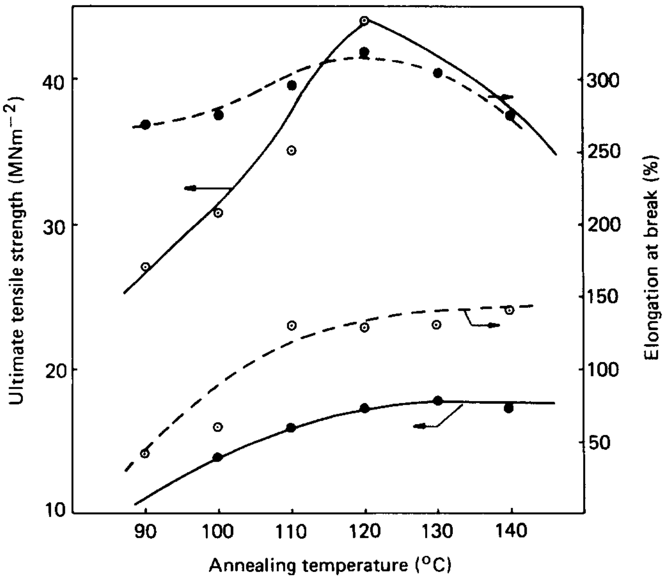

Figure 5 Tensile properties for drawn PVC containing 50 phr DIOP *versus* annealing temperature: (○) in the MD; (●) in the TD

Results show that drawing produces increased UTS and decreased elongation at break in the MD for the sample having a T_g of 20°C; for the sample with lower T_g the effect could not be observed. Annealing however produced enhancement of UTS in the MD for both samples; in both cases the maximum strength was observed after annealing at 120°C, the effect being particularly noticeable for the sample containing 50 phr DIOP. Elongation at break was still lower in the MD than the TD. For the sample containing 20 phr DIOP changes in elongation at break in the MD as a function of annealing temperature were small, but did tend to reflect changes in UTS in that higher values of UTS corresponded with lower values of elongation at break. For the sample containing 50 phr DIOP elongation at break in the MD direction tended to increase with annealing temperature to a limiting value. (It should be noted that all results obtained for samples annealed at 90°C are open to question due to the observed shrinkage after annealing.)

The sample containing 20 phr DIOP UTS in the TD showed only small variation, but as expected, a minimum value was observed at 120°C. Elongation at break in the TD decreased slightly with annealing temperature to reach a limiting value. For the sample containing 50 phr DIOP, elongation at break in the TD reached a maximum at 120°C, but UTS increased to a limiting value.

X-ray diffraction results

Effect of drawing. As observed previously[5–9] for rigid PVC samples, drawing produced relatively high diffraction intensity in the region of 17° 2θ. *Figure 6* shows that the intensity in this region also increases with draw temperature.

Order factors were calculated as described previously[11]. It was not considered necessary to use the rigorous methods recommended in ref. 10, in view of the relatively low order present in our samples, and also the nature of the order present. *Figure 7* shows that order factor increases with draw ratio, sharply at first, and then appear to reach a limiting value.

Effect of annealing. X-ray traces for the plasticized PVC containing 50 phr DIOP, annealed at different temperatures are shown in *Figure 8*. Similar traces were obtained for the more lightly plasticized PVC. It is observed that order increases with annealing temperature, and calculated order factors are plotted for the sample containing 50 phr in *Figure 9*, and are shown to increase with annealing temperature, rapidly at first, and then more slowly. Limited results are available for the sample containing 20 phr, and drawn at 40°C, and these are also shown in *Figure 9*. (The order factor for this sample after drawing but before annealing was 19.5%.) Higher order factors are observed for this sample, and these also appear to increase to a plateau. The intensity increase in both cases is largely due to increased intensity in the 16°–18° 2θ region.

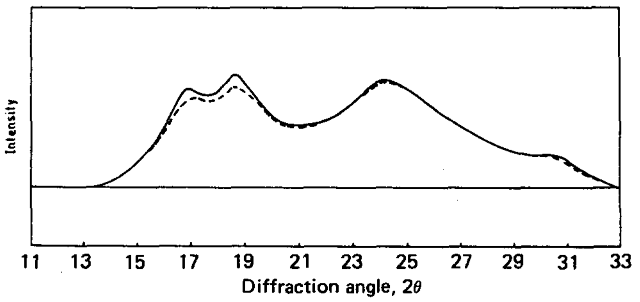

Figure 6 X-ray diffraction traces for samples of PVC containing 20 phr DIOP drawn at (- - -) 40°C and (——) 70°C

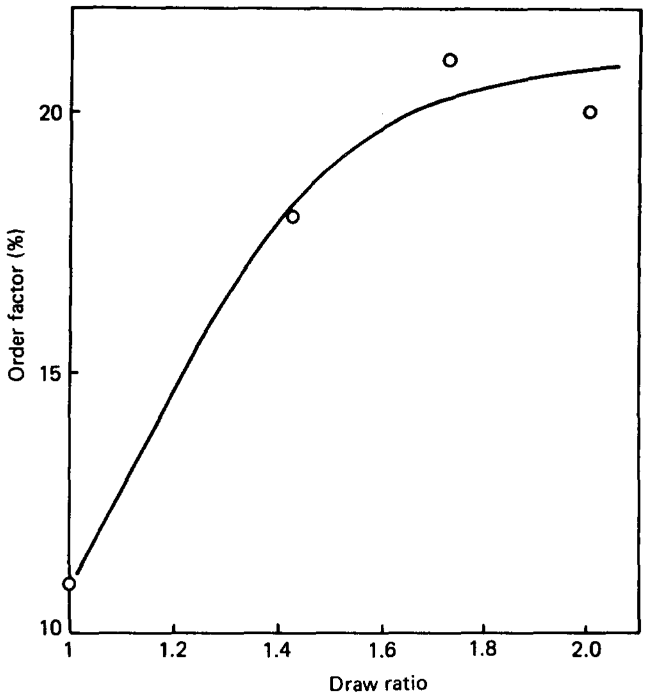

Figure 7 Effect of draw ratio on order factor for sample containing 20 phr DIOP

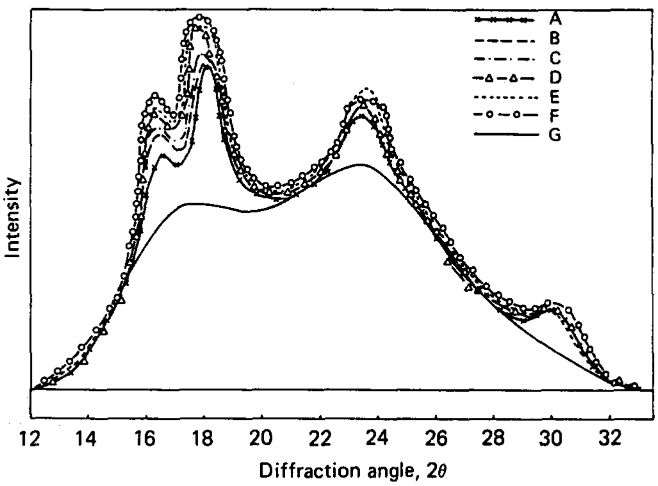

Figure 8 X-ray diffraction traces for PVC containing 50 phr DIOP annealed at (A) 90°C; (B) 100°C; (C) 110°C; (D) 120°C; (E) 130°C; (F) 140°C; (G) 'amorphous' trace

Birefringence measurements

To further investigate structural changes, birefringence measurements were made for selected samples and results are shown in *Table 4*, together with property measurements for the particular samples examined. It is observed that the compression moulded samples do possess some birefringence, so are not completely anisotropic. However, for the sample containing 20 phr DIOP, birefringence was increased by drawing, as expected. (It was not possible to make this measurement for the drawn sample containing 50 phr DIOP due to shrinkage.) Both annealed samples showed a substantial increase in birefringence.

DISCUSSION

Effect of drawing and annealing on properties

Providing that the glass transition temperature of the polymer is not significantly below room temperature, drawing can produce property anisotropy due to molecular orientation, accompanied by ordering. It was found that drawing also reduces the extent of yield on subsequent tensile testing. This is reasonable, if the observed yielding is due to some chain orientation. In the MD this will already have partly occurred during the drawing process; in the TD less chains will be available for orientation during testing.

Under the conditions used in this work for the sample containing 20 phr DIOP, an increased draw temperature produced greater orientation. Both temperatures were above the T_g of the PVC compound; increased flexibility at the higher temperature facilitated orientation under these conditions. However, the effect of temperature also depends on stretching rate[12].

The more dramatic increase in UTS observed for the more flexible sample probably arises because of need to prevent relaxation of orientation in this sample.

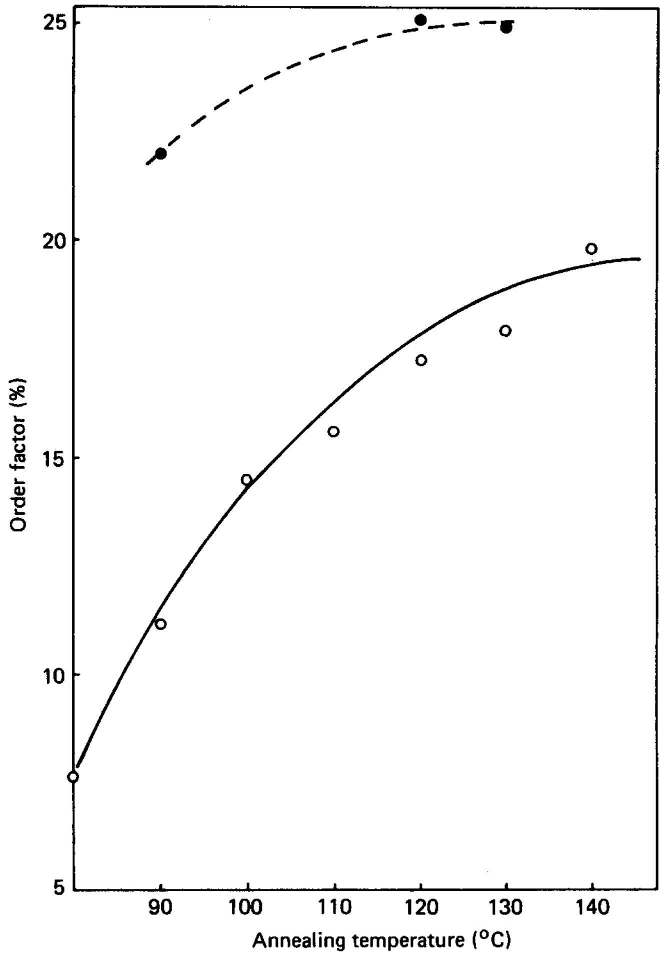

Figure 9 Effect of annealing temperature on order factor for (●) 20 phr sample; (○) 50 phr sample

Effect of drawing and annealing on structural order

In order to consider the above effects, an order factor was defined as the area of an X-ray trace excluded by a fitted 'amorphous' template as a percentage of the total area (*Figure 8*). The nature of the order is discussed later.

Figures 7 and *9* show that order is increased by both drawing and annealing, as for unplasticized PVC[9]. It is suggested that drawing produces 'strain induced crystallization' resulting from molecular alignment. The order produced can then be enhanced by annealing. Annealing causes sharpening of the peak at 24° 2θ while two distinct peaks are produced in the 16°–18° region.

As observed previously for rigid PVC, the enhanced intensity in the 16°–18° 2θ region suggests that some of the order produced by drawing and annealing treatments is two dimensional in nature. Peaks in this region arise only from (*hk*0) reflections so enhanced intensity here implies that the lateral dimensions of crystallites increase. Order along the chain direction is limited by the short syndiotactic sequences in a commercial PVC resin.

Furthermore, the intensity of the peak at approximately 18° 2θ (110) is greater than that at the peak at about 16.5° 2θ (200), a situation observed for highly crystalline experimental grades of PVC[8,13], but not normally for commercial polymers. The unusual relative intensity probably arises from the orientation of the crystallites within the plane of the film. Re-examination of results obtained earlier for drawn and annealed rigid PVC shows that similar ratios were observed for those samples[9].

The higher order observed for the 20 phr DIOP sample is believed to be a real effect, since X-ray traces are not much affected by plasticizer at the levels used, and any effect would be reduced by the curve fitting procedure.

Table 4 Birefringence measurements

phr DIOP	Draw ratio	Ultimate tensile strength (MN m^{-2})	Elongation at break	Birefringence $\times 10^3$
50	[a]	22.4	305	0.036
50[b]	1.9–1.95	44.1 (MD), 17.4 (TD)	130 (MD), 318 (TD)	1.76
20	[a]	44.6	161	0.073
20[c]	1.9	59.5 (MD), 21.2 (TD)	63 (MD), 153 (TD)	1.76
20[b]	1.95	81.0 (MD), 23.4 (TD)	48 (MD), 180 (TD)	2.56

[a] Undrawn, unannealed
[b] Annealed at 120°C
[c] Before annealing

Results are also in line with the value of 30% estimated earlier for rigid PVC[9]. Possibly the plasticizer molecules limit the amount of order which can be formed.

Structure/property relationships in drawn and annealed samples

Comparison of *Figures 2* and *7* suggests that improved tensile strength in the MD is closely related to the development of structural order. Both UTS and order increase rapidly at first, then reach a plateau. Assuming that the *c* directions of the crystallites are aligned in the MD, as are the amorphous chains in the polymer, the observed decrease in TD UTS, and MD elongation at break is as expected.

The order is further improved by annealing as is UTS in the MD, the maximum effect in the latter case being observed at 120°C. Due to the small changes observed in both cases it is not obvious whether there is a direct relationship between them. The increased birefringence observed after annealing for the compound containing 20 phr DIOP demonstrates that annealing causes improvement of ordered regions in the MD, hence the strength enhancement. This result contrasts with that observed for annealing of rigid PVC which caused reduction of yield strength.

The UTS for the 50 phr DIOP sample before drawing and annealing was 22.4 MN m^{-2}; its elongation at break was 305%. Thus, as for the 20 phr DIOP sample, properties shown in the two lower curves in *Figure 5* initially decrease as expected. The subsequent increase must be due to the presence of ordered regions in an otherwise flexible matrix. Although aligned in the MD these will still effectively hold chains together in the TD. This effect will of course be absent for the more rigid sample.

CONCLUSIONS

Drawing at 40°C produced an increase of 67% in the MD UTS; at 70°C the observed increase was 88%. However these changes were accompanied by decreases in the TD UTS of 42% and 32% respectively. Subsequent annealing caused a significant further increase in MD UTS, but the TD UTS still remained low. The most beneficial effect of annealing was for the sample with a low T_g since it had the effect of preventing shrinkage. Presumably the small crystallites produced held the oriented structure in position, as long as the annealing temperature was high enough.

The maximum annealing effect was observed at 120°C, similar behaviour to that observed for rigid PVC. In general, the structural changes seen by X-ray diffraction were very similar to those for rigid PVC.

Changes in tensile properties could be attributed to the development of structural order; most of this order appeared to be two dimensional in nature.

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