

Structure-Property Relationships in PVC Compression Moldings

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Synopsis

Compression moldings were produced from two rigid PVC compounds at a range of temperatures. The tensile and impact properties of these moldings depended primarily on the level of particle fusion as assessed by extrusion rheometry. Properties were not related to the level of primary crystallization measured by X-ray diffraction, but the particle fusion process appears to be at least partly due to recrystallization. Fusion occurred more readily in the mass PVC compound than in the suspension PVC compound. Annealing the sheet produced at 200°C caused changes in crystallinity which resulted in small property changes. The maximum annealing effect occurred at 110°C.

INTRODUCTION

It is known that the properties of rigid PVC products are controlled by a variety of structural factors, which in turn are influenced by formulation and processing conditions. PVC powder produced by mass or suspension polymerization consists of grains 100–150 μm in diameter, which are made up of agglomerated 1–2 μm primary particles.^{1–3} A smaller microdomain structure on the 10-nm scale has been shown to exist within these primary particles, and the 5–10% primary crystallinity reported for commercial grades of PVC is believed to be located within these microdomains.^{3,4} The level of particle breakdown and fusion has a major effect on final properties.^{5–7} However, these are also modified by the level of crystallinity^{8,9} and the amount of free volume within the polymer.^{8,10}

In a previous report¹¹ we considered the structural changes which could be induced by heat treatment of PVC. The effect of various heat treatments on structure and properties has also been reported by Illers.⁸ However, samples examined in these cases possessed a high level of particle fusion so that observed changes were due to changes in crystallinity and/or free volume.

The overall aim of the present program is to investigate the structural changes and resultant properties which are produced by processing. In this particular work, compression molding was used so that initially changes occurring at low shear levels could be understood.

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EXPERIMENTAL

Materials

Unless otherwise indicated, the compression moldings examined were of the following formulation (in parts by weight): PVC resin, 100; T135 thiotin stabiliser (Akzo Chemie), 3; calcium stearate, 0.5.

Two PVC resins were used: a mass-polymerized polymer, M80/50 (BP Chemicals Ltd.) and a suspension-polymerized polymer, Corvic D55/09 (ICI Plastics Division). These polymers are subsequently referred to as M-PVC and S-PVC, respectively. The ingredients were mixed in an 8-L Fielder Intensive Mixer. Compression-molded sheets, 20×20 cm², were prepared at a range of temperatures from 160 to 220°C, other conditions being constant unless otherwise stated. Cooling under pressure took 7–8 min. Molded sheets were stored before testing at –21°C to inhibit any free volume changes. For some measurements, sheets molded at 200°C were cooled under controlled conditions and subsequently annealed at temperatures from 80 to 170°C for times varying from 0.5 to 5.0 h.

Structural Investigations

Structure was investigated by thermal analysis and X-ray diffraction. Thermograms were recorded at 0–220°C using a du Pont 900 thermal analyzer fitted with a DSC cell. Sample weights were 10 ± 1 mg, and the heating rate was 20°C/min.

X-ray traces were obtained in the reflection mode at $2\theta^\circ$ 12–46 using a Jeol DX-GE-2S X-ray generator with a DX-GO-S vertical goniometer. Order factors were calculated as described in Ref. 11. The “amorphous” trace used to evaluate the amorphous component of the remaining traces was that of a sample of M-PVC quenched from 210°C into an ice–water mixture.

Property Measurement

Tensile properties were measured using an Instron Universal Testing Machine, with a crosshead speed of 10 mm/min and a dumbbell-shaped specimen of dimensions according to ASTM D638. Yield stress was obtained from the resulting load–elongation traces, and Young’s modulus was calculated by drawing a tangent from the initial linear portion of the curve.

Notched and unnotched impact tests were also carried out on some samples, using a Hounsfield Plastics Impact Testing Machine with miniature Charpy impact specimens. For notched specimens, the notch depth used was 2.5 mm, and the included angle was 45°.

Extrusion Rheometry

In order to evaluate the degree of fusion in the prepared sheets, the rheological method^{6,12,13} based on capillary entrance pressure loss was used. This pressure is due to elastic deformation of material at entry to the capillary and is correlated with the level of fusion which produces an increasingly elastic melt. Samples were extruded using a Davenport extrusion rheometer fitted with a low L/D ratio die of length 0.85 mm and diameter 2.25 mm.

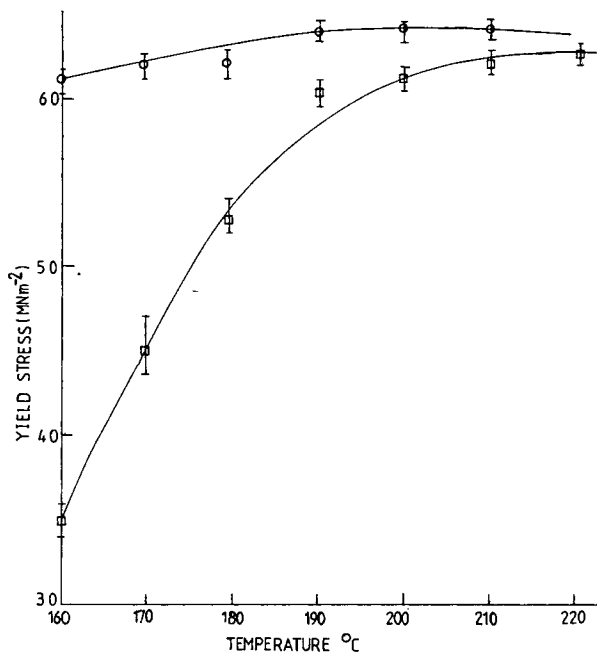


Fig. 1. Yield stress as function of mold temperature. (○) M-PVC, (□) S-PVC.

RESULTS

Molded Samples

Yield stresses for molded specimens are shown in Figure 1 for the two types of polymer investigated. It is apparent that reasonable strengths are developed in M-PVC at much lower molding temperatures than for S-PVC. This is not unexpected, since it is well known² that suspension PVC grains are surrounded by a pericellular membrane. This inhibits particle breakdown in the absence of shear, so that higher temperatures are required to achieve fusion. Stress-strain curves for the two polymer types also differ (Fig. 2), with the M-PVC demonstrating greater ductility. Young's moduli and impact strengths for the samples are shown in Table I. It is apparent that impact strengths are also considerably higher for M-PVC samples and that the effect is significant even at a molding temperature of 200°C. Modulus values increase gradually with

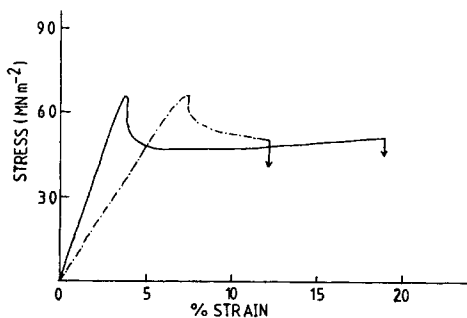


Fig. 2. Stress-strain curves for 200°C compression moldings. (—) M-PVC, (---) S-PVC.

TABLE I
Mechanical Properties of Compression Moldings

Moulding temperature, °C	M-PVC			S-PVC		
	Young's modulus, MN/m ²	Impact strength, MN/m × 10 ²		Young's modulus, MN/m ²	Impact strength, MN/m × 10 ²	
		Unnotched	Notched		Unnotched	Notched
160	762	1.7	0.37	660	0.64	0.11
170	826			692		
180	849	— ^a	1.11	706	0.88	0.17
190	914			835		
200	914	— ^a	1.56	885	4.40	0.43
210	927			898		
220				913		

^a Sample did not break.

molding temperature for both samples, and values for M-PVC are again higher.

Extrusion rheometry results for the suspension polymer are shown in Figure 3. As measured by this method, significant fusion does not commence until 180°C; maximum fusion is achieved at 210°C.

Figure 4 shows thermograms obtained for the M-PVC powder blend and the series of compression moldings produced from M-PVC. The endothermic shift at 78°C is due to the glass transition of the polymer. A broad melting endotherm B commencing about 155°C is observed for the powder blend. On compression molding at 160°C, this endotherm decreases in area and shifts to a higher temperature. This behavior is attributed to two effects: the melting of smaller or less perfect crystallites and the annealing of the remainder, leading to an overall higher melting temperature. Endotherm B continues to decrease in area and shifts to higher temperatures as molding temperature increases. Additionally, a lower-temperature endotherm A appears at a molding temperature of 170°C and increases in area as molding temperature increases. A similar series of thermograms was obtained for S-PVC. It was also observed for another PVC compound that the ratio of peak A to peak B could be increased to some extent by increasing molding time or molding pressure.

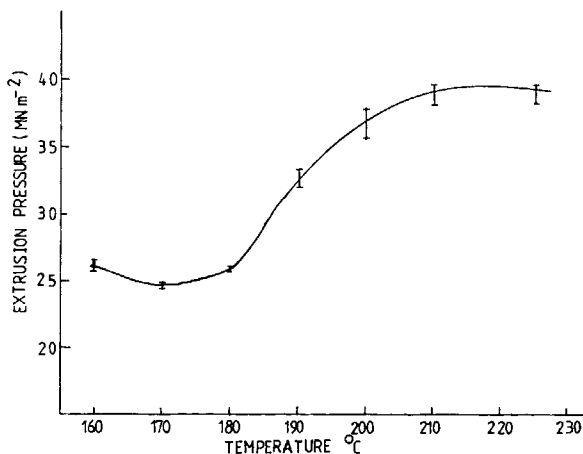


Fig. 3. Capillary rheometer extrusion pressure vs. molding temperature.

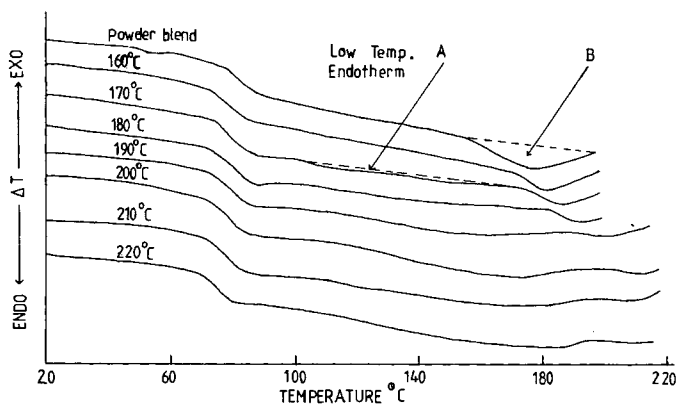


Fig. 4. Thermograms for M-PVC molded at different temperatures.

X-ray order factors for the molded samples are listed in Table II. Changes are small, but there is an overall decrease in order factor with compression molding temperature for the two series of samples.

Annealed Samples

The 200°C molded sample was selected for annealing experiments since it possessed a reasonable level of fusion but did not appear degraded. Yield stresses obtained for samples of both compounds annealed for 5 h are plotted as a function of annealing temperature in Figure 5. Also shown in this figure are results for samples quenched from 210°C into an ice-water mixture prior to annealing. The yield stress value for the quenched material before annealing was 41 MN/m². All quenched samples were brittle, having an elongation at break of only about 5%.

Thermograms of annealed samples of M-PVC are shown in Figure 6. As has been observed previously,^{8,11,14} sharp endotherms (labeled C) were produced, peaking approximately 20°C above the annealing temperature. Energies corresponding to these endotherms and their peak onset temperatures for samples annealed for 5 h are listed in Table III. A maximum area is observed at 110°C. Additionally, a broad endotherm corresponding to endotherm A in the molded samples is present.

TABLE II
X-Ray Order Factors for Compression Moldings

Moulding temperature, °C	Order factor	
	M-PVC	S-PVC
160	10.3	11.5
170	9.6	10.4
180	8.9	10.3
190	7.9	10.2
200	7.4	9.5
210	7.0	8.8
220	6.3	8.5

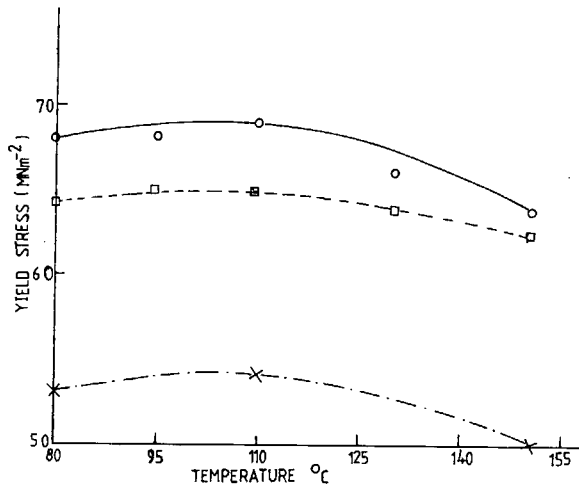


Fig. 5. Yield stress as function of annealing temperature. (O) M-PVC, (□) S-PVC, (x) quenched M-PVC.

X-ray order factors for the annealed samples are listed in Table IV. These are all higher than those for the corresponding 200°C molded samples. Again, a maximum value is observed at 110°C.

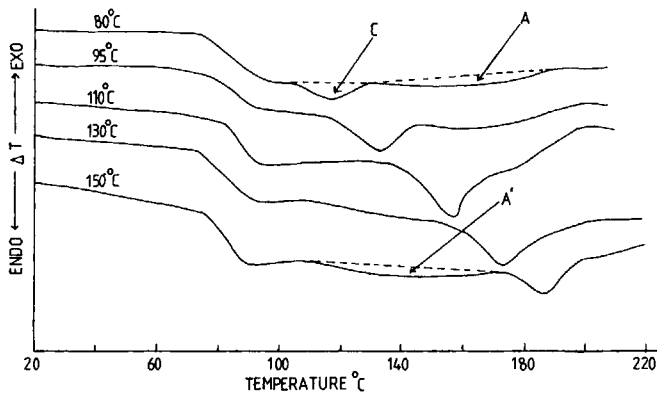


Fig. 6. Thermograms for annealed samples of M-PVC.

TABLE III
Thermal Analysis Data for Annealed Moldings

Annealing temperature, °C	M-PVC		S-PVC	
	"C" Endothermic energy, J/g	"C" Onset temperature, °C	"C" Endothermic energy, J/g	"C" Onset temperature, °C
80	1.26	96	0.54	95
95	2.36	113	1.10	114
110	3.32	132	2.91	130
130	2.62	149	2.32	146
150	2.22	170	2.32	169

TABLE IV
X-Ray Order Factors for Annealed Moldings

Annealing temperature, °C	M-PVC	S-PVC
80	10.3	10.1
95	10.9	10.3
110	13.3	12.0
130	9.4	9.4
150	8.3	8.1

DISCUSSION

For the series of compression moldings produced at a range of temperatures, the main factor affecting properties is the level of particle fusion. Figure 3 shows that the S-PVC compound, as measured by the extrusion rheometry method, is fully fused above 200°C; maximum yield strength is also achieved for the series at this temperature, as shown in Figure 1. The difference in properties between the M-PVC and S-PVC compounds also confirms the predominating effect of particle fusion. Modulus is measured at lower extension, so that the level of entanglement between particles is less important than it is for yield stress and impact strength measurements. Hence the difference in modulus between the two compounds is less significant.

X-ray diffraction and thermal analysis measurements do show that samples molded at different temperatures possess different types and levels of crystallinity. While it is appreciated that there are problems in using X-ray diffraction to measure percent crystallinity in PVC¹⁵ so that order factors do not necessarily represent absolute values of crystallinity, it is still considered that the data are useful for purposes of sample comparison. Results in Table II show a decrease in crystallinity with increasing molding temperature and suggest that the S-PVC is overall slightly more crystalline. The X-ray traces themselves are typical of the normal orthorhombic crystal structure observed in PVC.¹⁶ The loss in crystallinity observed by X-ray is considered to be due to loss in the primary crystallinity discussed by Juijn.¹⁴ As this is thought to be located within the microdomains of PVC,³ it would not be expected to affect tensile yield stress and impact strength. It is likely that the disappearance of X-ray crystallinity corresponds to the decrease in endotherm B observed by thermal analysis for samples prepared at increasing molding temperatures, but the equipment used was not sufficiently sensitive to make accurate measurements of the small B peak to confirm this.

The order factor still has a finite value for samples moulded at 220°C showing that the sample possesses some crystallinity (Fig. 7). This may either be unmelted or recrystallized material. Juijn¹⁴ has suggested that no recrystallization occurs in PVC on cooling. Present results indicate that this is not always true, since the appearance of endotherm A must be explained by some type of recrystallization process. Like the annealing effect leading to "secondary crystallinity" discussed by Juijn, the magnitude of endotherm A depends on the extent to which the primary crystallinity has been melted by prior heating. However, the total area of the two endotherms increases with molding temperature, so that the recrystallization process is not a reversal of the melting one. It is suggested that melting releases crystallizable segments in PVC which sub-

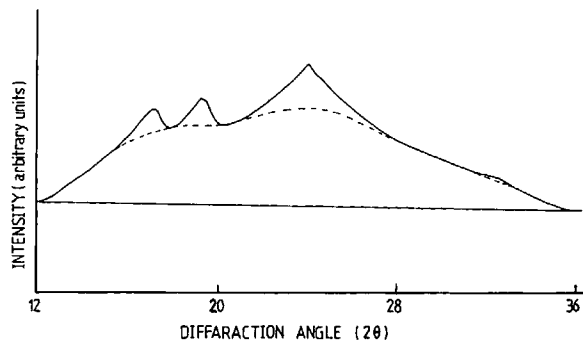


Fig. 7. X-Ray diffraction pattern of M-PVC molded at 220°C.

sequently recrystallize to produce a larger number of smaller or less perfect lower melting crystallites. These are too small or imperfect to be detected by the X-ray method. It is feasible that these crystallites are important in the linking of individual PVC grains; current investigations¹⁷ (using more sensitive thermal analysis equipment) are concerned with the possibility that the area of the A endotherm may be a useful method of evaluating the level of fusion in processed PVC.

Annealing the 200°C molded sample at temperatures above T_g resulted in a small increase in yield strength (Fig. 5). Also, the yield stress-annealing temperature plot passed through a maximum, the highest values of yield strength and minimum elongation at break being observed for samples annealed at 110°C. The property changes in this series can be attributed to changes in the level of crystallinity, since maximum order factors were observed for both blends annealed at 110°C. While order factors were similar for the two polymers after annealing, yield strengths were still higher for the mass polymer as the effect of fusion was still significant. The endothermic energy (Table III) for peak C also passed through a maximum as annealing temperature was increased.

The thermal behavior observed for annealed samples was very similar to that reported previously.¹¹ The area and temperature of endotherm C both increased with annealing time, and there was a similar relationship between annealing temperature and peak temperature. However, the broad peak A was an additional feature in the present work. This is further evidence for a recrystallization process, since previously samples had been quenched prior to annealing. For samples annealed at lower temperatures where melting temperature $T_C < T_A$, the A endotherm is presumably unchanged after the initial sample preparation. However, in the cases where $T_{A'} < T_C$, the A' endotherm must be due to a second recrystallization.

It is difficult to make accurate measurements for peak A, since peaks A and C overlap. However, it appears from the thermograms that the total area corresponding to peaks A and C together does not change very much. This suggests that peak C is mainly due to improvement of existing, rather than formation of new, crystallites. These are of sufficient size to affect properties and be detectable by X-ray diffraction. The X-ray diffraction pattern remained typical of an orthorhombic structure.

A maximum annealing effect at 110°C has been reported previously by Juijn¹⁴ and in some of our earlier work,¹⁸ although for quenched samples the maximum effect occurred at a higher temperature.¹¹

Quenching substantially reduced yield stress, as has been reported previously.⁹ Elongation at break and modulus were also lowered in quenched samples; these effects were not as expected, but were possibly due to frozen-in stresses produced by rapid cooling. Annealing above T_g again increased yield stress, although samples remained brittle. Thermal analysis showed that annealing after quenching did cause some crystallization to occur. For the sample annealed at 80°C, the crystallization exotherm normally observed after the glass transition temperature in quenched samples^{8,11,14} was reduced in area, implying that some crystallization had already occurred. For samples annealed at 110 and 150°C, the exotherm had disappeared completely, and melting endotherms were present with onset temperatures 16 and 22°C above the respective annealing temperatures. Thus, it appears that the observed property changes for quenched and annealed samples could be attributed to crystallization.

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