

Crystallinity Changes during PVC Processing

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Synopsis

Thermal analysis, solvent sorption, density measurement, and X-ray diffraction techniques were used to investigate structural changes in a variety of PVC compounds which were extruded or compression-molded at temperatures in the range 150–220°C. In all cases processing at lower temperatures in this range resulted in a disappearance of primary crystallinity and a concomitant development of secondary crystallinity, of lower order. In many cases processing above 190–200°C caused a small increase in crystallinity. It is believed that this is more ordered secondary crystallinity, which is therefore detectable by X-ray diffraction and also capable of influencing density and solvent sorption behavior. The observed structural behavior depends on shear as well as temperature. Primary crystallinity is higher in compression moldings, which have experienced lower shear levels, and the increase in crystallinity at higher temperatures is also greater. Equilibrium solvent sorption depends on the presence of primary and ordered secondary crystallinity. Diffusion is, however, unaffected as it occurs through amorphous and disordered crystalline regions only.

INTRODUCTION

It is well known that PVC undergoes morphological changes during processing, and that the nature of these changes depends on both temperature and the level of shear.^{1,2} Furthermore, rheological studies have shown that there is change in melt flow behavior at 190–200°C.³ Below this temperature observed melt viscosity is attributed to the flow of 1 μm primary particles.⁴ An additional transition has been detected at 220°C, and attributed to the crystalline melting temperature, so that true melt flow is only observed above this temperature. The behavior described applies to pure suspension PVC; the observed transitions are modified by additives such as lubricants and plasticizers.³

Collins³ and Sieglaff⁵ suggested that crystallinity has a role in processing that was not fully understood. The importance of crystallinity was also considered by Münstedt,⁶ and changes that occur have recently been discussed more fully.^{7,8} During processing, primary crystallinity in PVC is destroyed, while secondary crystallinity forms on subsequent cooling. This secondary crystallinity creates a network, and fusion (of the PVC particles) or gelation, to produce a coherent material with significant strength, is considered to have occurred, the extent of this depending on processing conditions.⁸

Crystallinity changes have only been reported for a limited number of compounds and processing methods. In this paper a number of techniques are used to investigate the structural order in various PVC compounds subjected

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to different processing conditions in order to understand the significance of crystallinity changes more fully and to relate them where possible to the more well-established changes in morphology.

EXPERIMENTAL

Sample Preparation

Suspension grade "Corvic" (ICI) and "Breon" (BP Chemicals) PVCs were used. Compound variables investigated were the level of lubricant, and the *K* value, i.e., molar mass of the PVC. Compounds shown in Table I were prepared using an 8-L Fielder high speed mixer. The dry blends produced were processed at temperatures from 150 to 220°C, in approximately 10°C steps, using several techniques.

An extrusion program utilized a Leistritz LD-30:34 twin screw extruder fitted with a 3 × 20 mm strip die and operated at 20 rpm (L samples). Two compounds having different lubricant levels were examined. A second program utilized a Krauss Maffei KMDL-25 twin-screw extruder fitted with a 4 × 30 mm strip die and operated under nominally similar conditions (KM samples). The effect of *K* value of the PVC was investigated using these extrudates. The samples processed using the Leistritz were found to have a more severe shear history using apparently similar extrusion conditions.

Samples were also compression-molded to produce defect free sheets approximately 4 × 200 × 200 mm, with low shear history. Lubricant levels were varied in this series, which included some samples containing very high lubricant levels so that very low shear conditions could be investigated.

TABLE I
Compound Formulations in Parts by Weight

Sample code	PVC	Dibasic lead stearate	Stanclore T135 ^a	Normal lead stearate	Calcium stearate	Wax ^b GS2311P
L66A	100 ^c	2.5	—	—	0.8	0.3
L66B	100 ^c	1.5	—	1.5	0.4	0.3
KM57	100 ^d	—	3.0	—	0.8	0.3
KM62	100 ^d	—	3.0	—	0.8	0.3
KM68	100 ^d	—	3.0	—	0.8	0.3
KM71	100 ^d	—	3.0	—	0.8	0.3
CM660	100 ^c	—	3.0	—	—	—
CM661	100 ^c	—	3.0	—	3.0	0.25
CM662	100 ^c	—	3.0	—	3.0	0.5
CM663	100 ^c	—	3.0	—	3.0	1.0
CM664	100 ^c	—	3.0	—	3.0	1.5
CM665	100 ^c	—	3.0	—	3.0	3.0

^aSupplied by Akzo Chemie.

^bSupplied by Cornelius Co.

^cBreon S110/11.

^dCorvic PVCs with *K* value as sample code.

Sorption Measurement

Specimens measuring about $4 \times 14 \times 28$ mm were prepared and weighed. They were then immersed in excess reagent grade acetone contained in 30 cm³ stoppered glass bottles. The bottles were immersed in a water bath maintained at $23 \pm 1^\circ\text{C}$. Acetone uptake was followed gravimetrically at various intervals up to 30 h. An average of five measurements was used, although the solvent uptake could be measured to an accuracy of 1.0 mg.

Density Measurement

Sample density was measured using a density gradient column prepared from aqueous calcium nitrate solutions, and operating at 23°C . Samples were allowed 4 h to equilibrate and the average of three measurements was used. The measured density, d_c , was corrected for additives using the relationship⁹

$$d_c = \frac{100 + \sum P_i}{(100/d'_c) + \sum (P_i/d_i)} \quad (1)$$

where the P_i 's are additive weight fractions (phr), the d_i 's are densities of the additives, and d'_c is the actual density of the processed resin.

X-ray Diffraction

A Jeol DX-GE-2S generator operated at 40 kV and 30 mA was used to produce Ni-filtered Cu K $_{\alpha}$ radiation. Reflectance measurements were made in an air atmosphere at ambient temperature, using rectangular samples 40×15 mm in area. In the case of the PVC powder wooden holders approximately $30 \text{ mm} \times 20 \text{ mm}$ were employed. The scattering pattern was recorded through the angular range $10^\circ \leq 2\theta \leq 46^\circ$ at a scanning rate of $1^\circ/2\theta$ per minute.

Thermal Analysis

Details of the procedure, and the thermogram have been reported previously.¹⁰ The heat of fusion corresponding to endotherm *A*, the endotherm produced by recrystallization after processing, was determined using a Du Pont 990 Thermal Analyzer fitted with a DSC cell. Sample weight was corrected for the additives present so that the heat of fusion, ΔH_A , was expressed in J/g of PVC. The *B* onset temperature T_B , was also obtained from each thermal analysis trace.

RESULTS AND DISCUSSION

Solvent Sorption

The sorption behavior for compound L66A, extruded using the Leistritz extruder, is shown in Figure 1, where t is the sorption time. Results were corrected for sample thickness l . Similar results were obtained for the compression-molded samples, and the samples extruded using the Krauss Maffei extruder, except in these cases some of the samples disintegrated in acetone when processed at low temperatures.

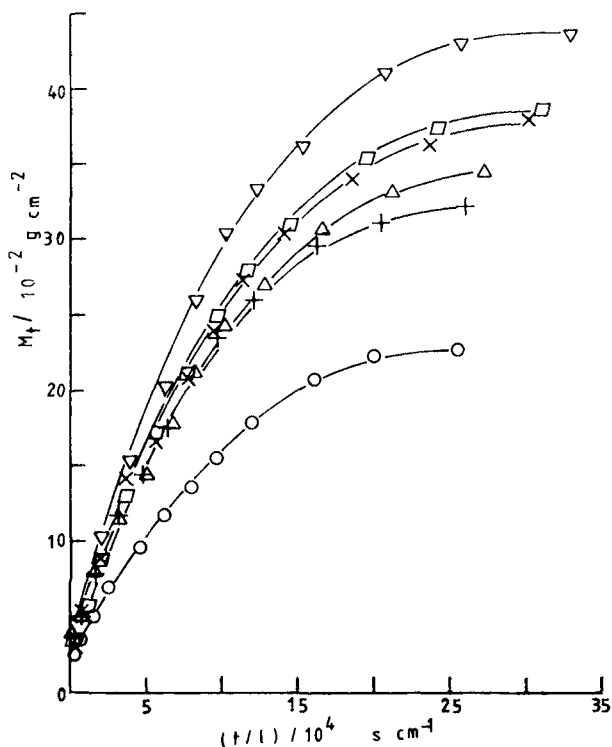


Fig. 1. Solvent sorption curves for L66A extruded at °C (○) 176; (+) 184; (Δ) 195; (×) 200; (□) 208; (▽) 220°.

Throughout this paper, the processing temperature will be represented by the B onset temperature, T_B , obtained by thermal analysis, since this has been shown to be a good indicator of the actual temperature reached by the PVC.¹¹

Figure 1 shows that the mass of solvent absorbed after a given time increases with increase in T_B and that the differences in mass uptake became greater after extended sorption time. Also, samples prepared at higher temperatures appear to have longer equilibration times. It has been shown previously^{12,13} that equilibrium sorption decreased, and sorption half-time increased with increased crystallinity, so that these results suggest a loss of crystallinity with increased T_B .

In Figure 2, M_t/M_∞ (where M_t is the mass of solvent absorbed per unit area of sample at time t and M_∞ is the same value at equilibrium) is plotted against $t^{1/2}$. Superposition of the data suggest that the nature of the polymer into which sorption occurs is the same irrespective of T_B . In other words, it is not affected by the presence of secondary crystallinity, which is known to be produced on processing.^{7,8,11} This supports the earlier suggestion of Juijn et al.¹⁴ and subsequent thermal analysis measurements that recrystallization from a PVC melt produces a less ordered structure than the primary crystallinity present in the virgin polymer.

Other features are demonstrated by Figure 2. It is apparent that, due to the thickness of the samples used, equilibrium has not been reached during the

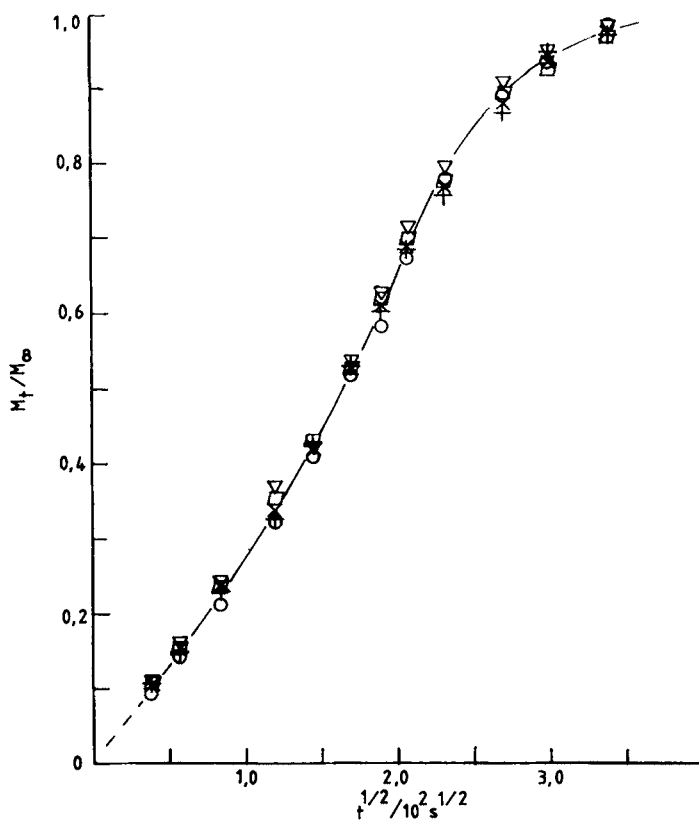


Fig. 2. Plot of M_t/M_∞ vs. $t^{1/2}$ using the data of Figure 1.

timescale of the experiment, so that M_∞ will be slightly underestimated. The type of sorption occurring may also be assessed from Figure 2. In earlier work involving toluene sorption¹³ Fickian sorption was observed only for a PVC copolymer, and for quenched samples of a suspension homopolymer. Case II sorption¹⁵ was observed for annealed samples of the same homopolymer. However, acetone is a better solvent for PVC, and comparison of Figures 1 and 2 suggest an intermediate behavior, more nearly Fickian as evidenced by the initial linear region in Figure 2.

A generalized diffusion equation which takes account of both Fickian and Case II behavior has been developed by Kwei et al.¹⁶ Kinetics parameters for acetone diffusion in PVC have been obtained by the use of the following equation:

$$M_t = C_0(D/v + vt) \quad (2)$$

where D is the average diffusion coefficient and v is the velocity of the solvent front. We have

$$C_0 = M_\infty/V_0 \quad (3)$$

where V_0 is the initial volume of the immersed sample.

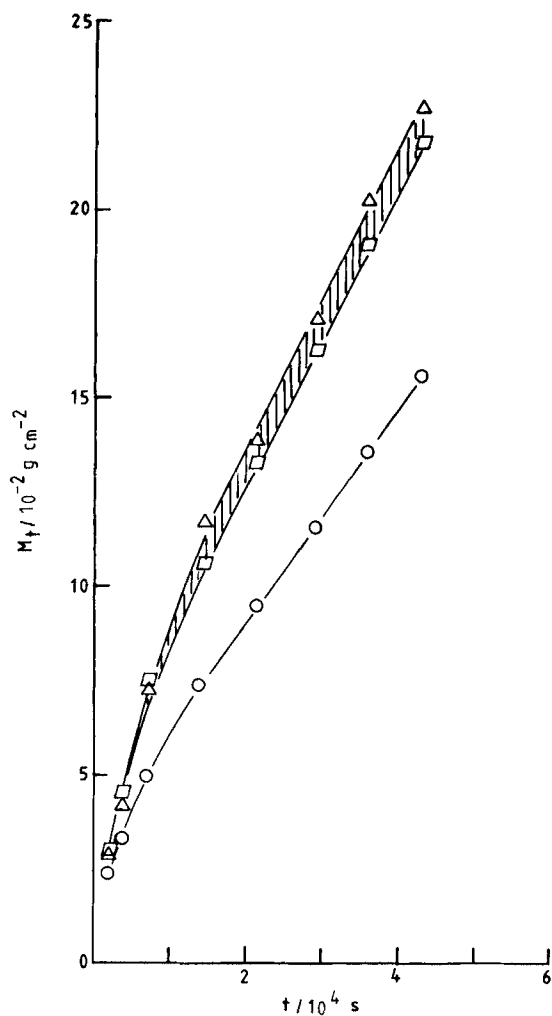


Fig. 3. Initial diffusion data from Figure 1, plotted according to eq. 2.

TABLE II
Acetone Diffusion Parameters for L66A at 23°C

<i>B</i> onset temperature (°C)	$D \times 10^{-8}$ (cm ² s ⁻¹)	$v \times 10^{-6}$ (cm s ⁻¹)
176	2.66	1.38
184	3.40	1.58
195	3.40	1.58
200	3.42	1.58
208	3.42	1.58
220	3.42	1.58

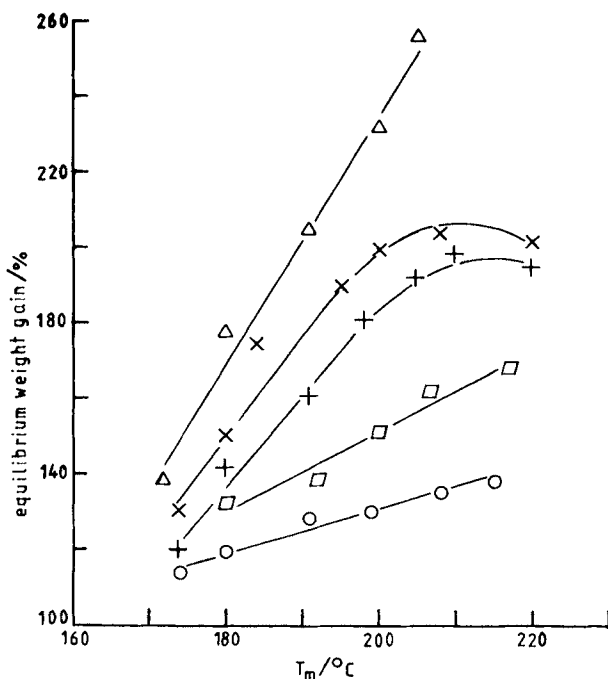


Fig. 4. Dependence of equilibrium solvent uptake on B onset temperature for: (x) L66A; (+) L66B; (Δ) KM62; (\square) KM68; (\circ) KM71.

Figure 3 shows the data from Figure 1 plotted according to eq. (2). After initial curvature straight line plots are obtained, and values of v and D calculated from the slope and intercept of the straight line region are listed in Table II. Both parameters are low for the sample processed at 176°C , and then remain essentially constant. Values are lower than those reported by Kwei et al. ($v = 1.82 \times 10^{-5} \text{ cm s}^{-1}$; $D = 7.05 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$), but his sheets were pressed at only 170°C and so would be expected to be poorly fused, which would give high values of both D and v . (Our sample processed at 176°C was extruded and so has experienced more shear, which will eliminate grain boundaries).

We have shown previously¹⁷ for L66 samples processed using the Leistritz extruder that the equilibrium value of solvent uptake increases linearly with increasing processing temperature, leveling off above 200°C . However, a wider variation of processing conditions and formulations has revealed that the relationship between equilibrium solvent uptake and T_B is strongly influenced by shear history, as illustrated in Figures 4 and 5. For samples extruded using the Krauss Maffei, which have been shown to experience lower shear levels, only the linear dependence is observed. The equilibrium sorption increases as the K value of the polymer decreases, as might be expected. Compression molding produces quite different results as seen in Figure 5. The amount of sorption depends on the amount of lubricant present, reaching a maximum at an intermediate lubricant level.

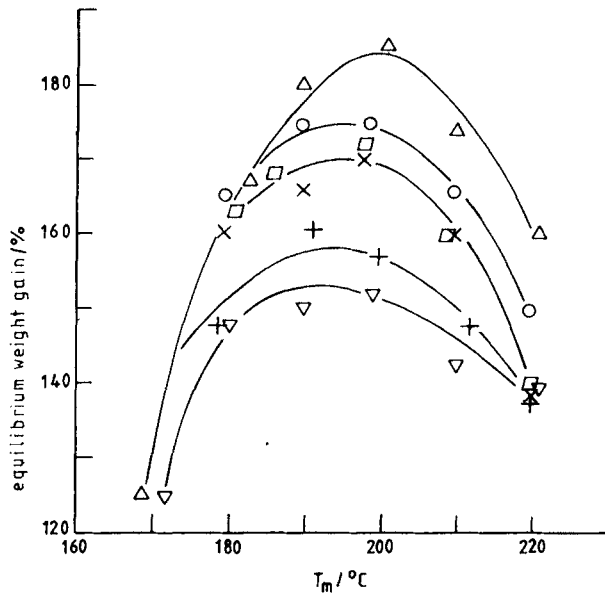


Fig. 5. Dependence of equilibrium solvent uptake on B onset temperature for: (\square) CM660; (\times) CM661; (\circ) CM662; (Δ) CM663; ($+$) CM664; (∇) CM665.

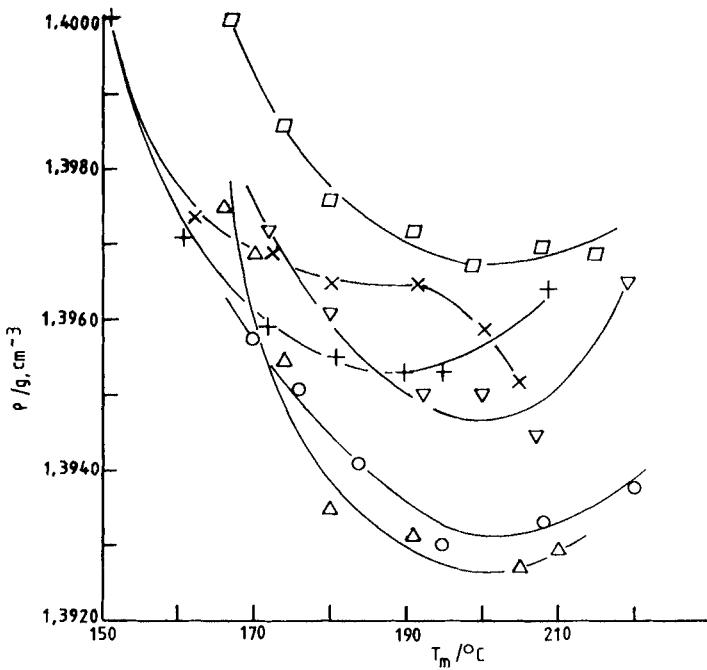


Fig. 6. Dependence of density on B onset temperature for extrudates; ($+$) KM57; (\times) KM62; (\square) KM68; (∇) KM71; (\circ) L66A; (Δ) L66B.

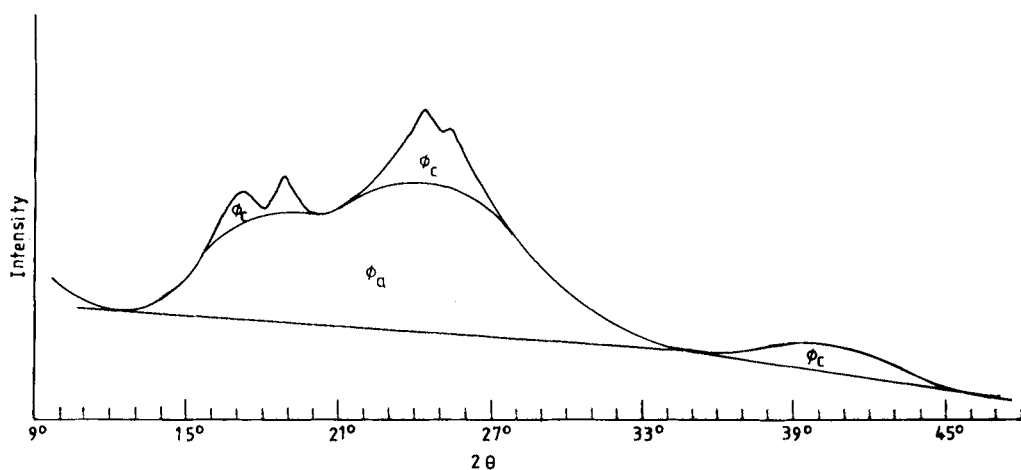


Fig. 7. Wide angle X-ray diffraction pattern of Breon S110/11 powder.

Density Measurement

Other work has shown that sample density decreases with processing temperatures.^{8,17} Similar trends are observed here (Fig. 6). However, in this work a density increase is also detected at the higher processing temperatures in some cases.

X-ray Diffraction

A typical side angle X-ray diffraction trace for an unprocessed powder sample is shown in Figure 7. The "double hump" amorphous curve¹⁸ was fitted to experimental curves as shown in Figure 7 by consistently drawing smooth curves of $12^\circ \leq 2\theta \leq 21^\circ$ and of $21^\circ \leq 2\theta \leq 28^\circ$. Baselines were drawn between $12^\circ \leq 2\theta \leq 35^\circ$ and $35^\circ \leq 2\theta \leq 46^\circ$. This method was adopted because it proved difficult to produce amorphous templates which satisfactorily "fitted" experimental traces for the range of compounds examined. While the values obtained by this approach are not necessarily absolute, they do enable different samples to be compared.

The diffraction patterns were analyzed by the Hermans-Weidinger method. By assuming that the areas ϕ_c and ϕ_a , as defined in Figure 7, are proportional to the weight fraction of the crystalline and amorphous polymer, respectively, Weidinger and Hermans¹⁹ obtained the relationship

$$\phi_c = -(C/A)\phi_a + C \quad (4)$$

where C and A are the values of ϕ_c and ϕ_a for 100% crystalline and 100% amorphous PVC, respectively.

Figure 8 shows a selection of results for both extruded and compression molded samples, and a variety of compounds plotted according to eq. (4). The regression line gives a value of $C/A = 1.51$, of a similar order to the reported¹⁸ value of 1.35, hence supporting the method used to analyze the traces. The value of C/A was used to calculate the crystallinity index, X_r , for

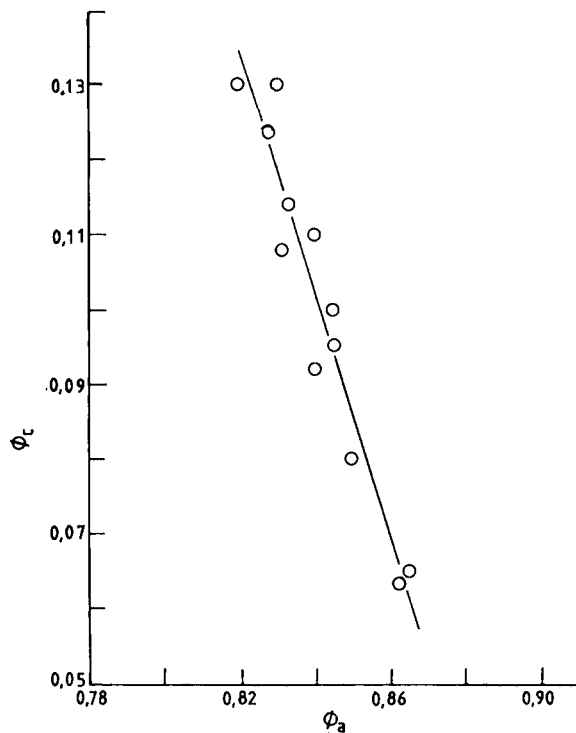


Fig. 8. Plot of X-ray diffraction results according to eq. (4).

processed samples, using the following equation¹⁹:

$$X_r = 1 / [(C/A)(\phi_a/\phi_c) + 1] \quad (5)$$

Values so calculated are illustrated in Figure 9. In all cases X-ray crystallinity decreases as T_B increases. A minimum at approximately 200°C is observed for compression moldings and for Krauss-Maffei extruded samples, but is not obvious for the Leistritz extrudates. The X-ray crystallinity is noticeably higher for the compression-molded samples, which have experienced least shear, and lowest for the least lubricated Leistritz extrudate, which has experienced the most shear.

Thermal Analysis

As previously reported, S-shaped curves were obtained when the heat of fusion corresponding to the *A* endotherm was plotted against *B* onset temperature. Examples of these results are shown in Figure 10, and represent the development of secondary crystallinity.¹¹

COMPARISON OF RESULTS

X-ray diffraction measurements, solvent uptake, and density measurements all suggest that processing results in an initial loss of crystallinity. Thermal

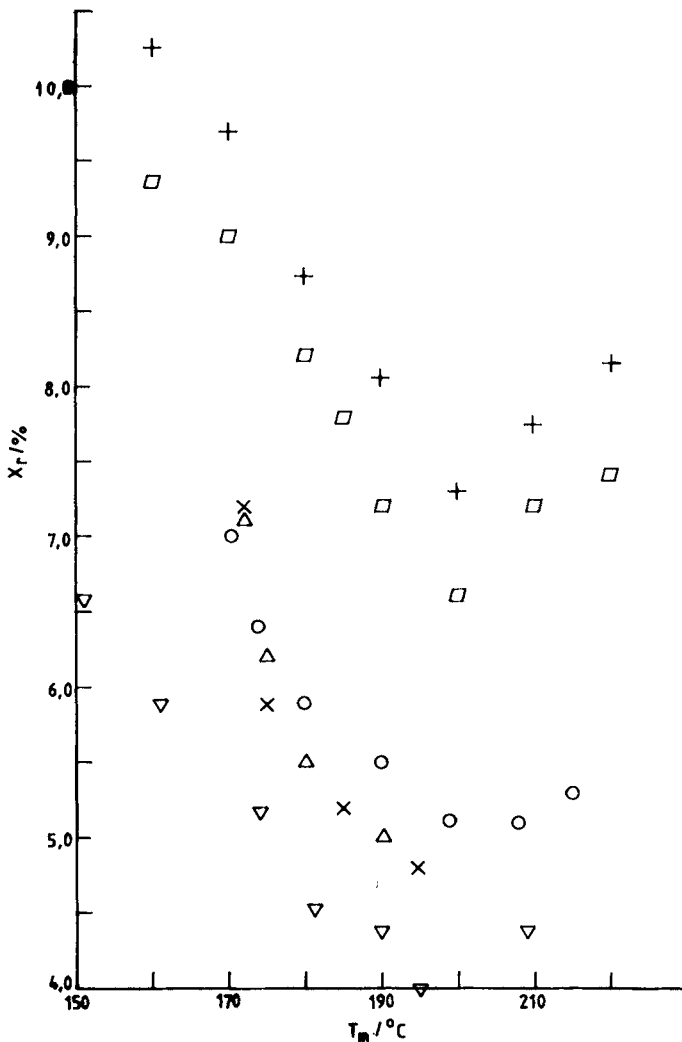


Fig. 9. Dependence of X-ray crystallinity index on B onset temperature for: (\square) CM660; (+) CM663; (\circ) KM57; (\times) KM68; (Δ) L66A; (∇) L66B.

analysis demonstrates that this loss of the primary crystallinity originally present in the PVC powder is accompanied by development of secondary crystallinity (Fig. 10). Covas et al.⁸ also showed that the density decrease observed for twin screw extruded samples could be related to the disappearance of the B endotherm detected by thermal analysis. In the present work it appears that under some conditions a subsequent increase in crystallinity can be observed at high temperatures.

Information about the effect of processing conditions on crystallinity is shown by Figures 4, 5, 6, and 9.

Comparison of Figures 4, 5, and 9 shows that the increase in crystallinity is most noticeable for the compression-molded samples, although this trend was

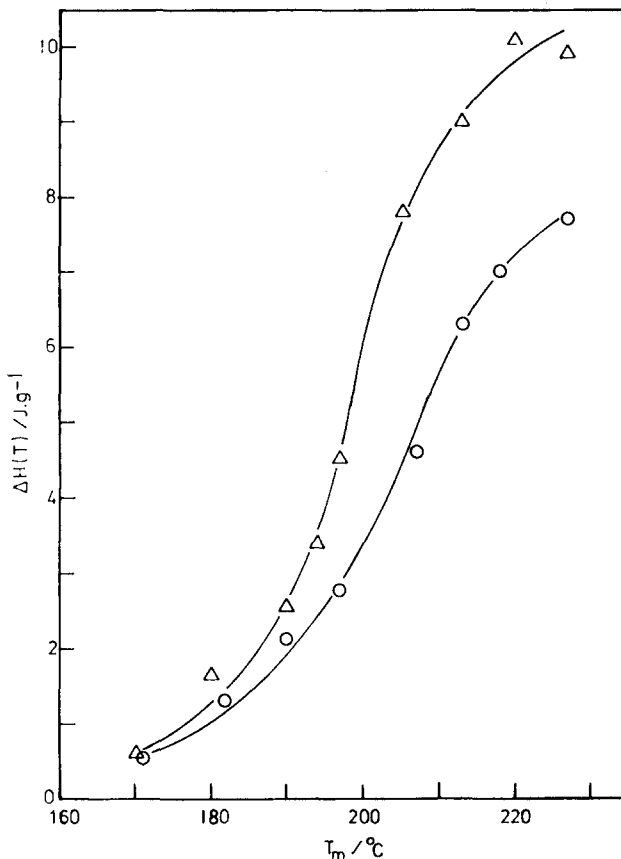


Fig. 10. ΔH_A vs. B onset temperature for L66A and L66B.

not detected earlier for such samples having a different formulation.²⁰ The decrease in solvent sorption at elevated temperatures observed in Figure 5 could have been attributed to compaction of the PVC grains, which are not completely destroyed by compression molding. However, comparison with Figure 9 does suggest that the effect is due to crystallization.

Also, results in Figure 5 show that solvent sorption increases with the level of wax, then decreases. It is known²¹ that samples CM664 and CM665 are significantly less fused than the other compression moldings investigated here, due to the presence of incompatible lubricants on the grain boundaries. However, these moldings absorb relatively low levels of solvent, presumably because less primary crystallinity has been destroyed. Moldings CM660, CM661, and CM662 are all well fused, although it is not known why the level of solvent sorption increases through this series.

Density results also suggest that an increase in crystallinity occurs at processing temperatures above about 200°C, although only extruded samples were examined using this technique. Comparison of Figures 6 and 9 shows that density measurement and X-ray diffraction show similar behavior for samples examined by the two techniques, e.g., KM62 and KM68, thus provid-

ing further evidence for an apparent crystallinity change at elevated temperature.

When secondary crystallinity is produced at low temperatures, its melting temperature is low, suggesting small and/or imperfect crystallites. This crystallinity does not possess adequate order to be detected by X-ray diffraction. Furthermore, this secondary crystallinity does not prevent a decrease in density, nor does it inhibit solvent sorption. As the processing temperature is increased, the melting range of the secondary crystallinity increases to higher temperatures (see Fig. 12 in Ref. 11). Presumably a point is reached where this secondary crystallinity is sufficiently ordered to again be detectable.

CONCLUSIONS

Crystallinity changes are shown by the various techniques to be dependent on the amount of shear. There is less destruction of primary crystallinity on compression molding than extrusion, as shown in Figure 9. Effects of shear are further demonstrated in Figure 5. Highly lubricated compression moldings show the lowest solvent sorption of any of the samples examined. The increase in crystallinity at higher processing temperatures also seems more noticeable under lower shear conditions. Presumably crystallites that have melted will be able to recrystallize with little disturbance.

When a high temperature increase in crystallinity is observed, it commences at about 200°C. It seems that at this temperature secondary crystallites are large enough to have significant effects. It may also be noted that the majority of primary crystallinity would be expected to have been destroyed at this temperature^{3,4} so that additional regions for recrystallization will be available.

The equilibrium mass uptake of acetone into the PVC samples is dependent on the amount of crystallinity of adequate order because sorption will only occur in the amorphous or disordered regions. However, acetone diffusion parameters do not appear to be affected by crystallinity because the solvent is diffusing through the disordered regions.

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