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MACROMOLECULAR DIVISION
COMMISSION ON POLYMER CHARACTERIZATION AND PROPERTIES
WORKING PARTY ON STRUCTURE AND PROPERTIES OF COMMERCIAL POLYMERS*

# THE INFLUENCE OF REPROCESSING ON THE STRUCTURE–PROPERTY CHARACTERISTICS OF A PLASTICIZED POLY(VINYL CHLORIDE) (PVC-p) COMPOUND

(Technical Report)

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# The influence of reprocessing on the structure–property characteristics of a plasticized poly(vinyl chloride) (PVC-p) compound (Technical Report)

*Abstract:* We have conducted a detailed investigation of the change in deformational structural, molecular and rheological characteristics that are attendant on a plasticized poly(vinyl chloride) (PVC-p) compound experiencing higher processing temperatures. Our study reflects an experience that occurs in the PVC industry where a loss of processing performance accompanies excursions to higher temperatures. It is apparent that, as this process continues, the material will eventually become unprocessable, unless changes are made.

The change that accompanies the material as it passes from an experience of low processing temperatures to high processing temperatures has been thoroughly mapped. However, it has been difficult to make a precise observation of the molecular and structural changes occurring. This has not been without application of a number of likely candidate methodologies, including differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), wide angle X-ray scattering (WAXS), gel permeation chromatography (GPC) and fluorescence spectroscopy. It would seem that some additional crystallization is accompanying the increase in gelation that occurs at higher processing temperatures. At the same time, the observations on the influence of annealing indicate that this is not the only consideration and that diffusion of the plasticizer into the PVC particles might also be playing a role, or even residual stresses in the materials might be important.

This study has not only been concerned with an in-depth materials characterization; it has also explored ways of alleviating the loss of processability. Two particular lines of study involving pre-shear history and blending with higher plasticized compounds have provided interesting, albeit inconclusive, results. On the other hand, there are strong implications from the DSC study that reversibility of the 'process aging' is not likely.

In conclusion, it is interesting to observe that, by conducting this study through an IUPAC Working Party, it has been helpful to pool the resources and experience of an international community of scientists which has probably given us an opportunity of conducting this study at much lower costs than might have otherwise been the case.

## INTRODUCTION

Plasticized poly(vinyl chloride) (PVC-p) compounds are used in numerous large tonnage applications, such as sheathing, electrical insulation, industrial profiles, etc. Such compounds are thermoplastic in origin and therefore products made from these materials can be reclaimed and made available for recycling.

The original compound is prepared by an extrusion compounding technique where it receives sufficient thermal and shear history so as to disperse the various ingredients of the compound and to be configured into a shape (e.g. granules) suitable for subsequent processing (often by extrusion) into a product. Each stage of processing would seem to influence the properties of the compound. These changes can be monitored by pressure through a 'zero' length die ($P_0$) as a function of processing temperature ($T$) [1]. A typical $P_0$ versus $T$ plot is shown in Fig. 1, and this enables us to define certain stages of material development. For example, Material A is the lightly compounded PVC-p; Material B might be some version of a reprocessed (at some higher temperature) form of the material and available as a regrind of the compound. As can be seen from Fig. 1, Material B will be difficult to define in terms of a specific location on the plot of $P_0$ versus $T$. Material C represents material at the extreme of this process. It has undergone either severe processing or multiprocessing. Material C would be easier to define and prepare.

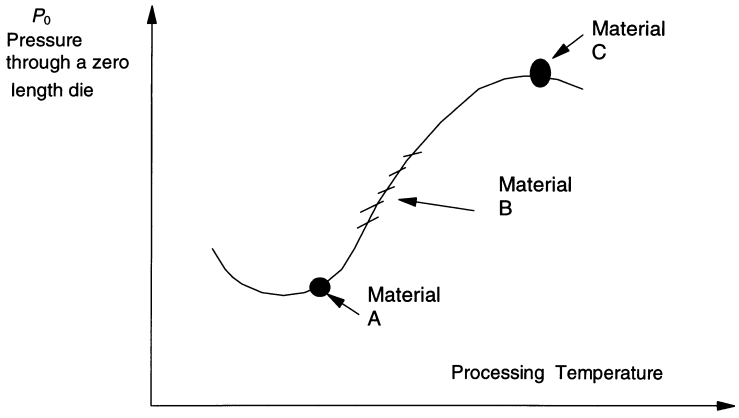


**Fig. 1** Pressure through a zero length die versus processing temperature for defining material state.

If PVC-p is to be recycled through a reprocessing route, it will be necessary eventually to cope with the properties of Material C. In a general sense, Material C is difficult to process. Therefore, the aim of this project is to determine what makes Material C a difficult material to process. In particular, we wish to describe how it differs from Material A. If this can be achieved, then it will be easier to explore whether Material C can be modified in any way so as to make its reprocessing easier. With the immense worldwide usage of PVC-p, this would provide significant energy, cost and efficiency savings.

This research project has been conducted by an international team of scientists participating through one of the International Union of Pure and Applied Chemistry (IUPAC) Working Parties, namely Working Party IV.2.1 concerned with the Structure and Properties of Commercial Plastics. The list of participating laboratories is summarized in Table 1.

**Table 1** Participants in the research study

| Laboratory number | Laboratory institution | Laboratory participants |
|---|---|---|
| 1 | ICI plc, UK | D. M. Stocks, R. S. Bailey, D. R. Moore, R. C. Stephenson (for European Vinyl Corporation) |
| 2 | Solvay SA, Belgium | E. Gandin, C. Dehennau |
| 3 | Chalmers University, Sweden | F. Maurer |
| 4 | Instytut Przemyslu Tworzyw i. Farb, Poland | P. Szewczyk |
| 5 | University of Minho, Portugal | J. A. Covas, A. V. Machado, M. J. Oliveira |
| 6 | Shell Research SA, Belgium | L. Glas, M. Lecomte, K. Neelen, K. Vaes, M. Weverbergh |
| 7 | Technical University of Budapest, Hungary | B. Pukanszky |
| 8 | Technical University Hamburg-Harburg, Germany | V. Altstadt |
| 9 | Danmarks Tekniske Universitet, Denmark | P. F. Pind, J. Lyngaae-Jorgensen |

## MATERIALS AND SAMPLE PREPARATION

Laboratories 1 and 2 prepared the samples for the study. An experimental formulation was selected that would minimize the material complications which are often attendant on PVC formulations. The formulation was based on ISO K70 suspension homopolymer of poly(vinyl chloride) (PVC) (see Table 2).

A dry blend was first prepared from this formulation and then a compound, designated Compound A, was prepared to be equivalent to Material A of Fig. 1 by compounding in a Buss Kneader PR 100 machine to a measured processing temperature of 126 °C. Compound A was then available in granule form. Compound A was then reprocessed in a single screw 45 mm Bandera extruder to achieve a processing temperature of 185 °C. The extrudate was then granulated to provide Compound C in order to be

**Table 2** PVC formulation

| Ingredient | Mass fraction of resin |
|---|---|
| K70 suspension homopolymer | 100% |
| Dioctyl phthalate (DOP) plasticizer | 50% |
| Tribasic lead sulfate (TBLS) stabilizer | 4% |
| Calcium stearate lubricant | 1% |

representative of Material C of Fig. 1. As shown later, the effective melt temperature attained upon preparing these samples can be different from the set values, due to a balance between heat transfer and viscous dissipation. Using a differential scanning calorimetry (DSC) technique on traces of samples A and C, Laboratory 5 suggested that sample A reached about 150 °C, whereas sample C was prepared at 184 °C. This is corroborated by the well 'melted' appearance of both types of pellets.

Many of the rheological measurements were made on granules of Compounds A and C, but the mechanical property and structural measurements required flat sheets of the materials. Therefore, we attempted to convert Compounds A and C from granular to sheet form. This required further processing, and both compression moulding and sheet extrusion techniques were employed. The aim was to conduct this processing with minimum change to the structure and morphology of the materials.

Compression moulded plaques were made by a two-stage process; mixing on a two-roll mill, followed by consolidation on the hydraulic press. This produced samples of nominal thickness 1.8 mm. Sheet samples were prepared by extrusion on a Troester UP 30 single screw machine with an accompanying three-roll calender stack. This produced sheet of nominal thickness 3.2 mm. Table 3 summarizes the processing histories for the four samples, namely compression moulded plaques of Compounds A and C and extruded sheet samples of Compounds A and C. It is noticeable that the barrel temperature for the preparation of the extruded sheet for compound C was 180 °C which is lower than the compounding temperature.

**Table 3** Summary of processing temperatures for the two types of sheet

| | Compound A: compression moulded plaques | Compound C: compression moulded plaques | Compound A: extruded sheet strips | Compound C: extruded sheet strips |
|---|---|---|---|---|
| Designated sample name | Compound A plaque | Compound C plaque | Compound A sheet | Compound C sheet |
| Processing temperature (°C) | 140 | 175 | Barrel 148<br>Die 144 | Barrel 180<br>Die 155 |

All the laboratories in the programme therefore had granules and two types of sheet for Compounds A and C available for their measurements. It was not assumed that the structural and morphological states for the compounds remained the same, and so their characterization formed part of the experimental study.

## EXPERIMENTAL STUDY AND DISCUSSION OF RESULTS

### Characterization of moulded and extruded sheet and comparison with granular samples

Laboratory 2 conducted tensile deformational tests at 23 °C on an Instron model 4302 at a test speed of 50 mm/min using ISO 2 type specimens. The results are shown in Table 4.

Laboratory 4 also conducted a similar set of tensile experiments, albeit with slightly different conditioning of the samples. Their results are similar to those summarized in Table 4, which show that

**Table 4** Tensile properties at 23 °C for the two types of sheet sample

| | Compound A plaque | Compound A sheet | Compound C plaque | Compound C sheet |
|---|---|---|---|---|
| Fracture stress (MPa) | 15.9 | 16.2 | 20.8 | 21.2 |
| | [0.6] | [0.3] | [0.5] | [0.5] |
| Fracture strain (%) | 207 | 214 | 304 | 310 |
| | [12] | [6] | [12] | [4] |

Values in square brackets are the standard deviations from five specimens.

there are no significant differences between the two forms of sheet for either Compound A or C. However, there are significant differences between the properties for Compound A and C. Compound C exhibits a much higher energy to fracture than Compound A because it is stronger and more ductile. This provides evidence that the difference between A and C is not simply a loss of plasticizer.

Rheological characterization was conducted in the temperature range 126–200 °C on an Instron capillary rheometer on a die of length to radius (*l/r*) ratio of 1 and an entry angle of 90°. Although measurements were taken over a shear rate range of 1.8–600/s, Table 5 shows results for a mid-range value of 60/s. A similar trend would be observed at the other shear rates.

**Table 5** Total pressure drop (kPa) through an *l/r* die of 1 at a shear rate of 60/s

| Temperature for test (°C) | Compound A plaque | Compound A sheet | Compound C plaque | Compound C sheet |
|---|---|---|---|---|
| 126 | 580 | 680 | 1150 | 1040 |
| 146 | 290 | 300 | 490 | 470 |
| 166 | 210 | 200 | 240 | 240 |
| 185 | 140 | 150 | 110 | 120 |
| 200 | 39 | 35 | 35 | 36 |

With reference to Table 5 it is clear that no rheological difference can be detected between the plaque or sheet properties for either Compound A or C. However, the pressure drops are higher for Compound C than for Compound A for all temperatures between 126 and 184 °C. However, these differences disappear at temperatures of 200 °C where the pressure drops can be taken to be the same within experimental significance.

These results suggest that there are only limited differences between the samples in the form of sheet and plaques.

Laboratory 2 also made this comparison in rheological behaviour between granules, plaque and sheet for both compounds using the same capillary rheometer conditions mentioned above. Table 6 shows the results, again at the mid-range shear rate of 60/s at a test temperature of 126 °C, where differences will be maximized.

**Table 6** Total pressure (kPa) through a die of *l/r* of 1 at 126 °C and a shear rate of 60/s

| | Granules | Plaque | Sheet |
|---|---|---|---|
| Compound A | 270 | 580 | 680 |
| Compound C | 1010 | 1150 | 1050 |

It is apparent from the data in Table 6 that, whilst there are only small differences in the rheological characteristics of Compound C in any of the three forms, the original granules of Compound A are different from the plaque and sheet. We expected such results because higher processing temperatures

needed to be used over the original compounding temperature in preparing sheet samples from Compound A.

## Mechanical and structural comparisons between Compounds A and C

The results shown in Table 4 from Laboratory 2 and others from Laboratory 4 have introduced the differences between Compounds A and C in a tensile deformational test at 23 °C where considerably higher fracture toughness (as the integral of the stress versus strain curve) is associated with Compound C. Laboratory 2 accounts for this difference in terms of the higher levels of gelation expected with this sample. We shall quantify this effect in due course. Laboratory 2 also conducted dynamical mechanical analysis (DMA) on Compounds A and C from the plaque samples using a DuPont 983 analyser operating at 1 Hz with a displacement amplitude of 0.5 mm. Although they detected little difference in the storage modulus in the temperature range −100 °C to +100 °C, it was noticeable that the modulus for Compound C was larger than that for Compound A. In addition, they observed a small but significant difference in the glass transition temperatures ($T_g$). Compound A showed a $T_g$ at −15.1 °C, whilst Compound C showed a $T_g$ at −12.9 °C and, although this is a small difference, it is believed to be real.

Laboratory 4 conducted DMA measurements on a Polymer Laboratories instrument operating at 1 Hz with a heating rate of 3 °C/min. They observed a higher storage modulus for Compound C in the temperature range −30 °C to +100 °C and a lower $T_g$ for Compound C by about 4 °C. They also measured the Shore A hardness on the plaque samples (according to ISO 868) and recorded plaque A at 85.5 and plaque C at 87.5. They showed that this was due to lower volatiles in plaque C, probably associated with its lower content of plasticizer, as a consequence of further processing.

Laboratory 8 also conducted DMA measurements in shear on a Rheometrics RDA II analyser at 1 Hz and a heating rate of 4 K/min, and in tension on a Rheometrics RSA-SL solid analyser at a frequency of 6.28 rad/s with a strain of 0.1% and the same heating rate as for the shear measurements. They prepared test specimens from the sheet for the shear measurements and from the plaques for the tensile measurements. In addition to testing as-received samples, they also annealed their specimens for 10 h and 60 h at 70 °C.

In general, their results agreed with those from Laboratory 2 and 4 and they made a number of observations.

(i) The storage modulus for Compound C was higher over the entire temperature range compared with that for Compound A, although the differences were quite small.

(ii) The $T_g$ of Compound C was lower than that for Compound A by about 1 °C.

(iii) The onset of 'melting', as seen by a drop in modulus well above 100 °C, was about 10 °C higher for Compound C than that for Compound A.

(iv) Annealing influences the DMA curves, as shown in Fig. 2 for Compound A and Fig. 3 for Compound C, for the shear experiments. In both cases, as expected, annealing increases the storage modulus, although to a larger extent for Compound A compared with the relative change for Compound C.

Laboratory 8 also conducted some cyclic fatigue experiments on a computer-controlled servo-hydraulic fatigue testing machine (Schenck model S56) at a frequency of 2 Hz with a sinusoidal applied waveform. The signal was controlled by ensuring that, during the loading phase, the displacement was kept constant at 10 mm and, during the unloading phase, the minimum load did not become smaller than 4 MPa. The specimens were of a dog-bone type S1 according to DIN 53504. The hysteresis loop of stress versus strain during fatigue was monitored as a function of the number of fatigue cycles up to 100 000 cycles. The area of the hysteresis curve is the lost energy during the test [2], and this was recorded as a function of the number of cycles for as-received and annealed plaque samples. Figure 4 shows the lost energy versus the number of cycles for both as-received compounds, where it is clear that more energy is lost for Compound C, although the change with the number of cycles is not too dissimilar for either. Annealing the samples reduces the lost energy for both compounds; the more severe the annealing, the less the lost energy.

Laboratory 7 reviewed the possible importance of processing history on behaviour, in particular, the

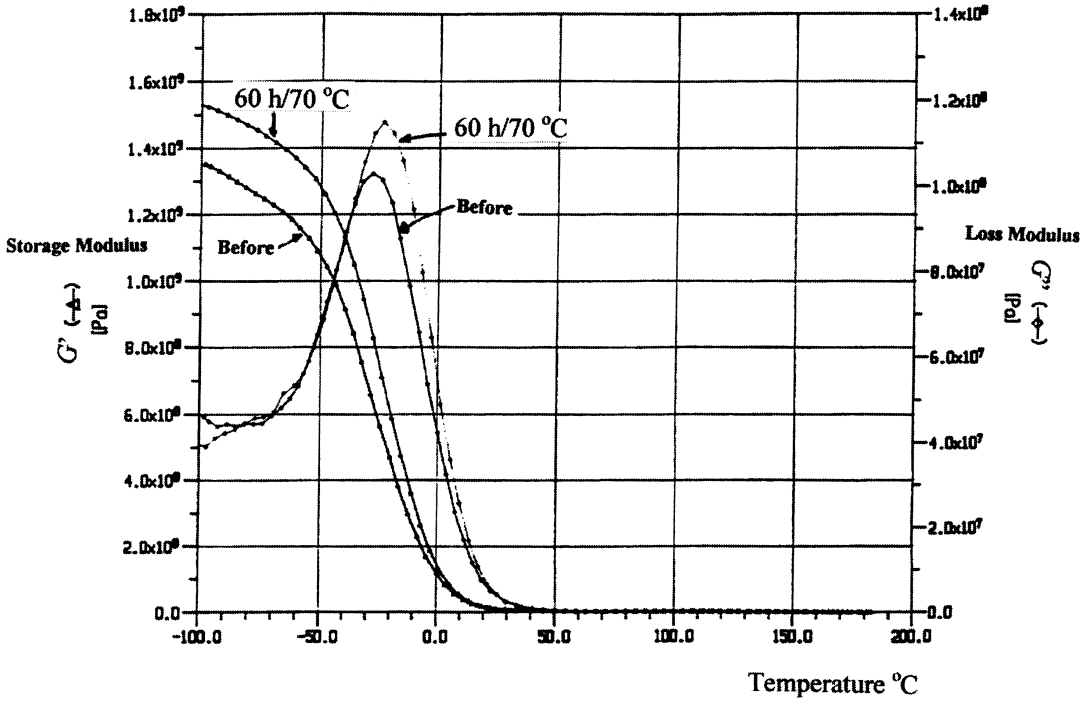


**Fig. 2** DMA measurements under shear loading for Compound A sheet before and after annealing for 60 h at 70 °C.

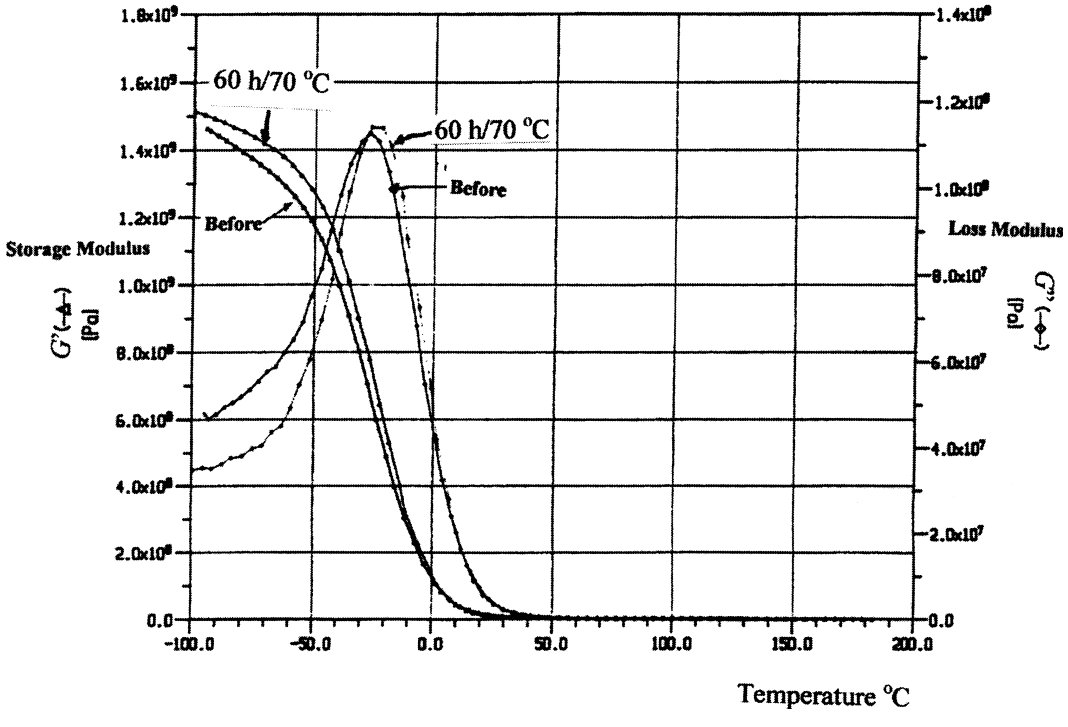


**Fig. 3** DMA measurements under shear loading for Compound C sheet before and after annealing for 60 h at 70 °C.

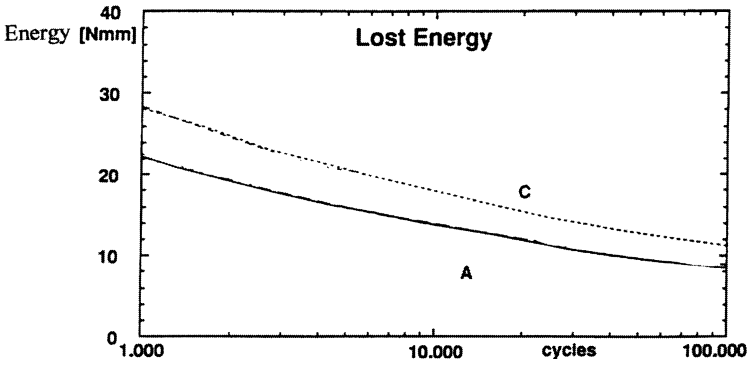


**Fig. 4** Effect of reprocessing on the hysteresis parameter lost energy as plotted against the number of fatigue cycles.

balancing effects of diffusion of the additives (particularly plasticizer in this work) and the influence of gelation. The process of mixing the additives with the PVC and establishing a state of gelation during processing will likely be incomplete. This implies that the process of annealing of the samples can influence the mixing or diffusion of the additives. Consequently, the influence of annealing on the DMA and fatigue results implies that the state of mixing (and certainly gelation) is different for Compounds A and C.

On the other hand, we have observed that the annealing effect is more important for sample A than for sample C (as presented by Laboratory 8 on the DMA curve). Also, the $T_g$ values of the two compounds are practically the same after annealing (Figs. 2 and 3). Therefore, there is an implication that the state of internal stress for the two samples might be different, bearing in mind that sample A is prepared at a lower temperature than that for sample C. These possible differences in internal stress can also influence the fatigue behaviour.

Such considerations will influence the morphology of the samples. Therefore, Laboratory 8 attempted to distinguish between the levels of crystallinity and crystal perfection of the samples by conducting some wide angle X-ray scattering (WAXS) measurements. Although they were able to estimate a level of crystallinity at about 10%, they observed no differences in crystallinity between the two compounds.

## Rheological, structural and molecular comparisons between Compounds A and C

Laboratory 2 conducted an extensive capillary rheometry investigation. A number of their results are summarized in the data given in Tables 5 and 6 where, in general terms, it is clear that the viscosity of Compound C is larger than that for Compound A. Their measurements also incorporated the influence of the die total entry angle, which they altered from 20° to 180°. In addition, they conducted a qualitative investigation of melt fracture behaviour by observing the quality of the rod extrudate in their capillary rheometer tests. In all, four conclusions emerged from their studies.

(i) The biggest differences in rheological behaviour between Compounds A and C are observed at the lowest test temperatures (126 °C in their experiments).

(ii) The influence of the total entry angle on the pressure drop data seems to be a function of the gelation level and the temperature.

(iii) The extrudates from Compound A always have a good appearance (low melt fracture), except at 185 °C where the same level of poor quality as with Compound C is found.

(iv) The extrudates from Compound C show a very poor appearance at the lowest temperatures used. For example, at 126 °C, a powder type extrudate was obtained. Laboratory 6 used both rheological and DSC methods in order to quantify the level of gelation in the samples. A Rosand twin bore capillary rheometer was used to measure entrance pressure losses at a temperature of 125 °C with a die with $l/r = 2$ and an entry angle of 180 °C. A Perkin Elmer DSC 7 instrument was used to conduct the thermal analysis using specimens of 10 mg which were heated from 23 °C to 215 °C at a rate of 20 °C/min.

They started with Compounds A and C in granule form, but created other samples by additional

processing of both materials on a Collin roll mill at temperatures of 146 °C and 166 °C. Therefore six samples were available for the study: Compound A as-received (i.e. processed at 126 °C) and Compound A processed at 146 °C and 166 °C, as well as Compound C as-received (i.e. processed at 185 °C) and Compound C processed at 146 °C and 166 °C. These six samples are designated: A[126], A[146], A[166], C[146], C[166] and C[185].

Figure 5 shows the plot of the pressure drop ($P$) versus processing temperature and indicates which points on the plot relate to which samples. This is similar to the schematic diagram of Fig. 1. The level of gelation ($G_{\text{rheol}}$) can then be determined from these pressures [3,4]:

$$G_{\text{rheol}} = \frac{(P - P_{\min})}{(P_{\max} - P_{\min})} \times 100 \tag{1}$$

where $P_{\min}$ and $P_{\max}$ are the minimum and maximum values of the pressure drop which can readily be seen in Fig. 1. However, these values are not so easily defined in Fig. 5, so it was assumed that A[126] was both the minimum and zero level of gelation and this provided a point of correlation for the other samples.

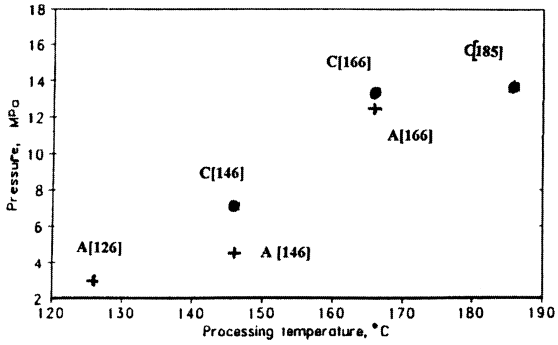


**Fig. 5** Pressure drop through a capillary die as a function of the processing temperature.

The DSC traces can also provide a means of quantifying the level of gelation [4,5]. The salient features for this analysis are shown in Figs. 6, 7 and 8. Figures 6 and 7 show the DSC traces of Compounds A and C (i.e. A[126] and C[185]). Up to 125 °C, the traces of both materials are similar: an endotherm between 50 °C and 90 °C relating to the glass transition of PVC and two endotherms between 90 °C and 125 °C (of unknown origin, but unlikely to be related to a form of crystallinity in PVC). Above 125 °C, the DSC trace of A[126] shows one endotherm which is related to primary crystallinity. The DSC trace of material C[185] shows two endotherms above 125 °C, one above 185 °C for the remainder of the primary crystallinity and one between 125 °C and 185 °C representing the secondary crystallinity. The gelation level ($G_{\text{DSC}}^{\text{PS}}$) can be defined from these curves as:

$$G_{\text{DSC}}^{\text{PS}} = \frac{H_{\text{S}}}{(H_{\text{S}} + H_{\text{P}})} \times 100 \tag{2}$$

where $H_{\text{S}}$ and $H_{\text{P}}$ are the enthalpies of secondary and primary crystallization, respectively. This does not always lead to the best definition of the level of gelation [3], because no account is taken of tertiary crystallization. This is shown in Fig. 8 for C[146] and C[166], where three endotherms are observed between 125 °C and 215 °C. The endotherm between 125 °C and the processing temperature is due to tertiary crystallization for which we designate the term Peak B for later discussion. (The next two are again secondary and primary crystallization, respectively.) In order to accommodate the tertiary crystallization, a modified definition of gelation ($G_{\text{DSC}}^{\text{PST}}$) is used [3]:

$$G_{\text{DSC}}^{\text{PST}} = \frac{H_{\text{L}}}{H_{\text{TOT}}} \times 100 \tag{3}$$

where $H_{\text{L}}$ is the enthalpy of the tertiary crystallites and $H_{\text{TOT}}$ is the total enthalpy of the PVC crystals.

Using these definitions of gelation in Eqns (1) and (3), it is then possible to construct a plot of the two measures of gelation for the samples derived from Compounds A and C, as shown in Fig. 9. This shows a

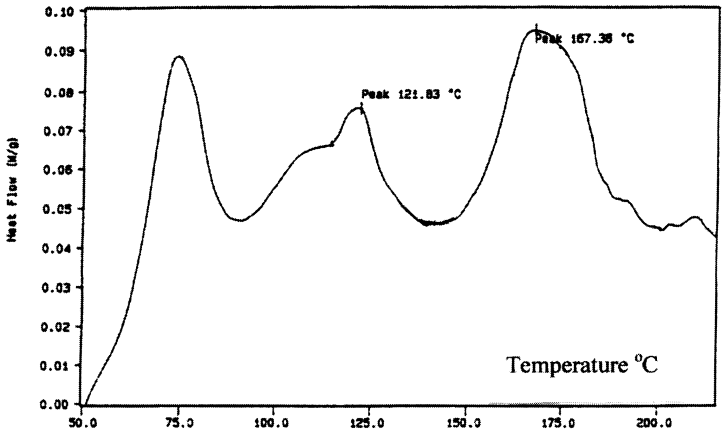


**Fig. 6** DSC trace for Compound A ([A126]) at a heating rate of 40 °C/min.

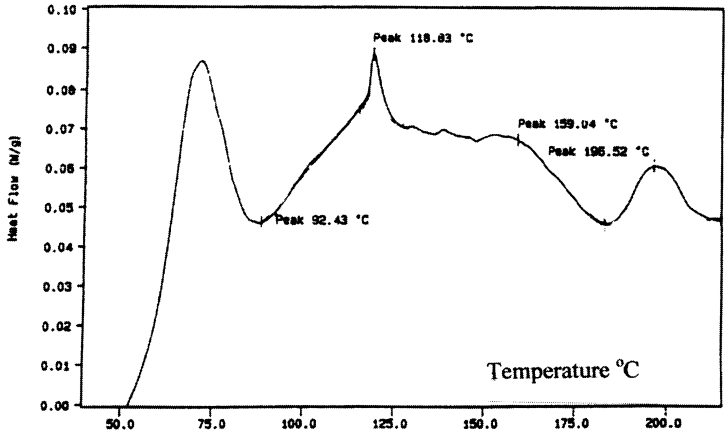


**Fig. 7** DSC trace for Compound C ([C185]) at a heating rate of 40 °C/min.

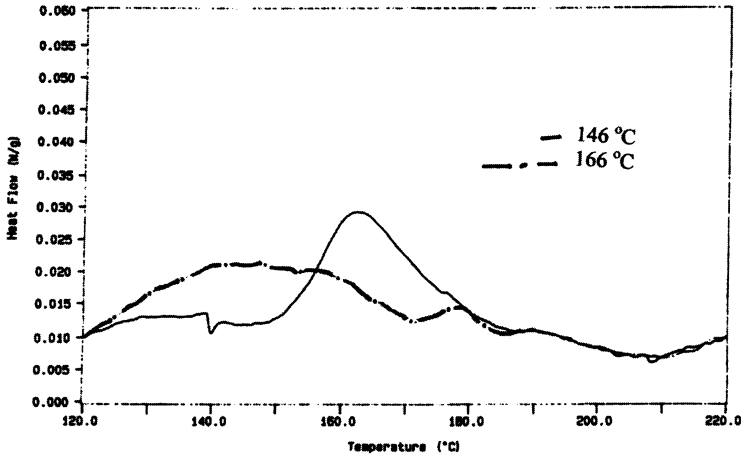


**Fig. 8** DSC trace for Compound C reprocessed in the roll mill at 146 °C and 166 °C.

good link between these two definitions of gelation and enables us to quantify the higher gelation level in as-received Compound C.

Laboratory 5 also conducted some DSC measurements and, in particular, tried to ascertain how material A is different from material C. As discussed for Laboratory 6, they started with Compounds A and C in granule form, but created other samples by additional 'processing' of both materials in the

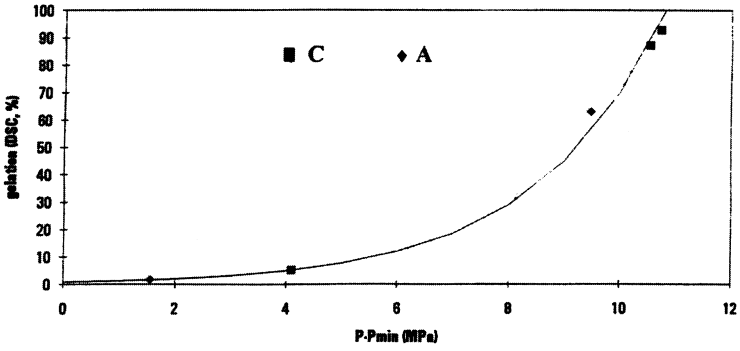


**Fig. 9** Gelation from DSC plotted against gelation from capillary data.

furnace of the DSC, under well-controlled heating histories. Hence, pellets A were heated to 150 °C, 160 °C, 170 °C, 180 °C, 190 °C, 200 °C and 210 °C, thus creating seven samples. Identically, pellets of material C were subjected to lower and higher temperatures than that attained upon processing, thus producing a further seven samples. Figure 10 represents the onset of tertiary (Peak B) crystallization, as defined earlier, plotted against the process temperature attained in the DSC. There is a good correlation between the results obtained by processing in a 'production' type machine and the DSC. Therefore, by observing the Peak B onset temperature of the DSC traces of samples A and C, one can estimate that they were produced at processing temperatures that approximate to 152 °C and 184 °C, respectively.

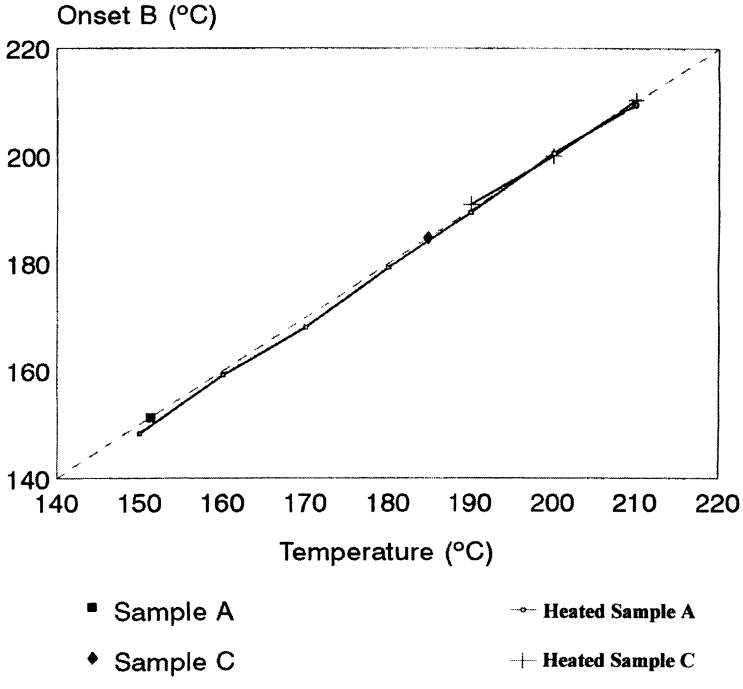


**Fig. 10** DSC results for the onset temperature for 'process B' versus processing temperature.

The gelation level of all the samples can be defined as in Eqn (2), which would produce a curve similar to that shown in Fig. 9. This means that heating sample A at progressively higher temperatures produces characteristics (primary and secondary crystallinities) closer to those of sample C. As shown in Fig. 5, at constant processing temperatures, the gelation of samples produced from C is higher than that of samples obtained from A, given the original role of shear upon their preparation. The features of the various DSC traces observed when reprocessing samples are depicted in Fig. 11. Figure 11 shows DSC traces of sample A heated to 184 °C (similar to the temperature reached when preparing sample C) and subsequently heated to 150 °C, 160 °C, 170 °C and 180 °C (i.e. A/184/160 designates a sample heated to

184 °C and then subsequently reheated to 160 °C). The appearance of peaks corresponding to primary, secondary and tertiary crystallinity are easily perceived [5]. This seems to demonstrate that, at the structural level, gelation is not reversible, i.e. sample A can be transformed into sample C with adequate heat and shear, but sample C cannot be converted into sample A, since it retains some 'memory' of previous processing cycles. Nevertheless, one should bear in mind that differences in the macroscopic behaviour (rheology and mechanical properties) between samples A and C are not only explicable in structural terms, but also in morphological features (e.g. destruction of grains, primary particles, etc).

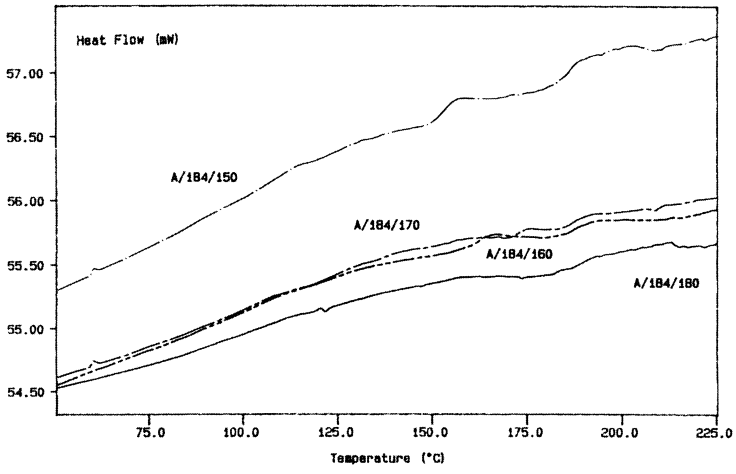


**Fig. 11** DSC results for sample A heated to 184 °C and subsequently reheated to other temperatures in the range 150–180 °C.

Laboratory 8 also conducted some DSC measurements and, in particular, explored the influence of annealing on the DSC traces. They employed the same annealing conditions as already discussed and, of particular note, they observed for material A that the $T_g$ of the compound was reduced from −14 °C to 18 °C after 10 h at 70 °C and then to −24 °C after 60 h at 70 °C. This is more dramatic a change in $T_g$ than that reported earlier for the influence of reprocessing, i.e. when comparing the $T_g$ values of Compounds A and C.

Laboratories 3, 5 and 9 conducted some molecular characterization of the two compounds. Laboratory 3 used a gel permeation chromatography (GPC) technique (Waters 150CV on-line with a Wyatt dawn F[LS]), and concluded that there were no observable differences between Compounds A and C in terms of their molecular weight distribution and no long chain branching was observed. Laboratories 5 and 9 confirmed this conclusion with their size exclusion chromatographic (SEC) technique, again based on an apparatus from Waters Associates, model 200.

Laboratory 1 attempted the measurement of the entanglement densities of Compounds A and C in the form of plaque and sheet mouldings in order to explore subtle differences in molecular structure. According to the procedures of Wu [6,7], it is possible to determine entanglement densities from a measurement of 'plateau modulus' ($G_N^0$), which is obtained by oscillatory shear on a torsional rheometer. In practice, a plateau modulus is not observed but, instead, by careful measurement, it was possible to determine a point of inflexion at a critical test frequency. The 'plateau modulus' is then used to determine the molecular weight of entanglement ($M_e$):

$$M_e = \rho RT/G_N^0 \tag{4}$$

where $R$ is the gas constant and ρ is the melt density, which was taken to be 1200 kg/m$^3$. The entanglement density ($\nu_e$) was then derived from the relationship:

$$\nu_e = \rho_a/M_e \tag{5}$$

where the amorphous density ($\rho_a$) is taken as 1300 kg/m$^3$.

Results are summarized in Table 7 which indicate more entanglement in Compound C, although the

differences are so small that the likely conclusion is that these samples show a negligible difference in entanglement density.

**Table 7** Summary of data for the determination of entanglement density

| | Compound A plaque | Compound A sheet | Compound C plaque | Compound C sheet |
|---|---|---|---|---|
| Entanglement density (mmol/cm$^3$) | 0.25 | 0.28 | 0.28 | 0.28 |
| $G_N^0$ (Pa) | $6.8\times10^5$ | $7.7\times10^5$ | $7.6\times10^5$ | $7.7\times10^5$ |

Laboratory 5 also used thermogravimetric analysis (TGA) and fluorescence measurements to estimate whether the observed changes in the behaviour of the samples were due to changes in gelation, or whether degradation could play a role. Samples A and C were exposed to 150 °C, 160 °C and 184 °C during increasing periods of time and their weight loss was compared. The choice of the temperatures is related to the values attained upon preparing the pellets. Figure 12 compares the relative rates of degradation of samples A and C when heated to 150 °C. Despite the higher temperatures attained upon preparing sample C, it seems to be less degraded than sample A. This could be explained by the fact that higher levels of gelation promote the progressive destruction of the PVC granular morphology, hence allowing a more effective action of the stabilizer. Figure 12 also shows the rate of degradation of sample C when subjected to increasing temperatures. As expected, the higher the temperature, the higher the rate of degradation.

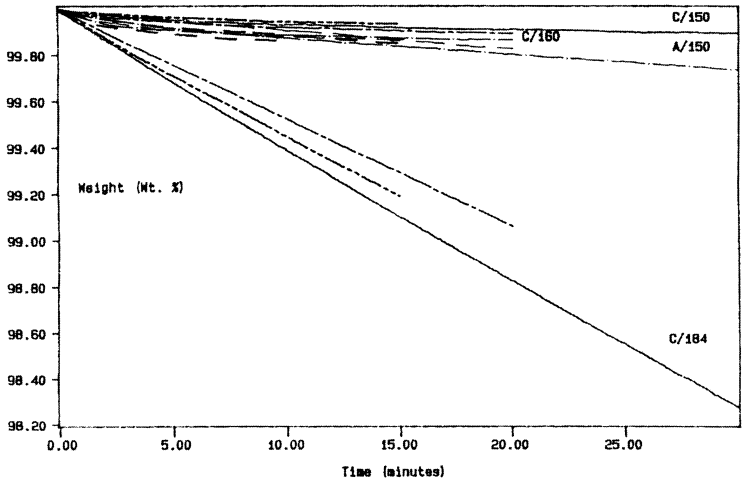


**Fig. 12** TGA results for various reheated versions of samples A and C showing weight loss versus time at the reheat temperature.

Figure 13 shows measurements of the fluorescence intensity at the same temperatures as above. It is well known that degraded PVC fluoresces in the visible region of the spectrum, where the amount of fluorescence is proportional to the degree of degradation. The measurements shown in Fig. 13 were conducted by attaching a photometer to an optical microscope in reflection mode. As the area of measurement was kept constant, the amount of light corresponds to a 'fluorescence index'. The results agree with those obtained with TGA, although the technique cannot discriminate between samples A and C exposed to 150 °C.

## Processing comparisons between samples A and C

Two laboratories attempted to impose a well-described strain history on the samples in order to explore the influence of shear dynamics on the rheological properties. Laboratory 6 attempted their experiments by using the granular feedstock to form a disc specimen, but experienced torque overloads and normal

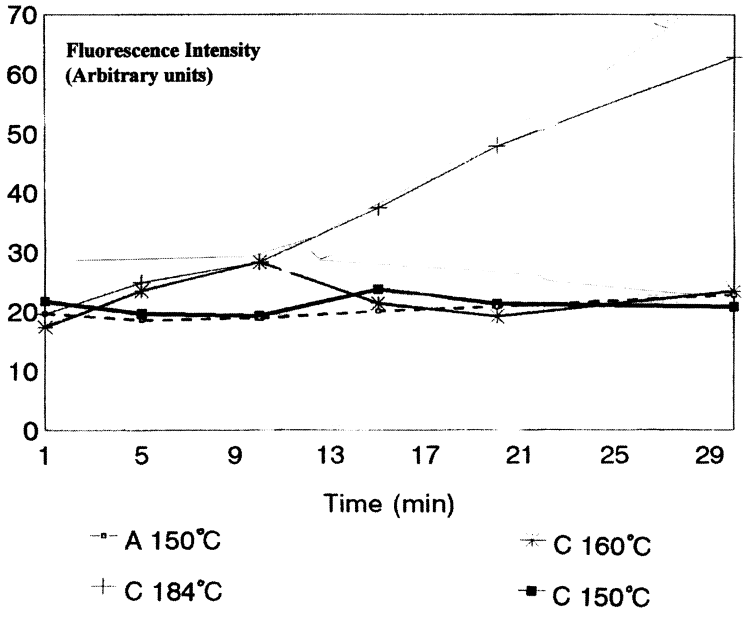


**Fig. 13** Fluorescence intensity plotted against time at the reheat temperature for various reheated samples of A and C at a specimen thickness of 0.04 mm.

force overloads as the deformations of their 'disc' specimens became too large. Consequently, they were not able to generate acceptable data.

Laboratory 1 used the extruded sheet samples in order to prepare disc specimens for their experiments. Naturally, large deformations of their specimens also occurred, but they were able to generate some data which can now be presented. Laboratory 1 conducted some processing trials on sample C by various pre-shear conditioning of the sample prior to the measurement of viscosity. Pre-shear history was influenced by the amount of shear, the time of shearing and the temperature of shear. The viscosity was measured at 190 °C by dynamic shear rheometry on a Rheometrics Mechanical Spectrometer (RMS800) with parallel plate geometry. The results are summarized in Table 8.

**Table 8** The influence of pre-shear history on the processing of extruded sheet C

| Complex viscosity at 190 °C at 0.1 rad/s (kPa s) | Pre-shear history, extrusion | Pre-shear history at 190 °C, frequency (rad/s) | Pre-shear history at 190 °C, time (s) |
|---|---|---|---|
| 14.0 | None | None | None |
| 14.0 | None | 0.1 | 60 |
| 10.2 | None | 1 | 60 |
| 8.9 | None | 2 | 60 |
| 4.9 | None | 5 | 60 |
| 8.2 | None | 1 | 120 |
| 12.5 | Capillary at 120 °C at 100/s | None | None |
| 8.6 | Capillary at 120 °C at 100/s | 1 | 60 |

The data in Table 8 show that, as the frequency of pre-shear is increased at 190 °C, so the viscosity of the compound decreases. In addition it can be seen that, at a fixed frequency of pre-shear, but for a longer time, the viscosity of the compound also decreases.

Experiments were also conducted in which low temperature extrusion at 120 °C was used as a pre-shear treatment. This had little influence on the measured viscosity. However, the same materials were then exposed to modest subsequent high temperature pre-shear (at 190 °C) which resulted in a large

reduction in the measured viscosity. It would seem that the higher temperature pre-shearing is either removing the tertiary crystallization discussed earlier and/or reducing the size of some 'supramolecular' flow units.

To some extent, these pre-shear results are quite surprising because other rheological results have shown that only small differences are found at relatively high temperatures in the viscoelastic response of samples A and C (which have had very different mixing and shear history). However, we have no evidence to suggest that these results from Laboratory 1 lack credibility in terms of excessive deformations during the shear experiments.

Laboratory 4 conducted some processing experiments on a single crew Goettfert extrusion machine using a rod die with an *l/r* ratio of 15 and a screw with a compression ratio of 1:4. They established extrusion conditions at a range of melt temperatures at various screw speeds. Their mass rate output results are summarized in Table 9.

**Table 9** Mass output data for single screw extrusion experiments

| | Output (g/min) | Screw speed (rpm) | Processing temperature (°C) |
|---|---|---|---|
| Compound A | 51.9 | 20 | 166 |
| Compound C | 38.3 | 20 | 166 |
| Compound A | 50.0 | 20 | 143 |
| Compound C | 32.0 | 20 | 143 |
| Compound A | 35.2 | 15 | 127 |
| Compound C | 26.1 | 15 | 127 |

These results show that, over a range of processing temperatures, Compound C provides less mass output under the same conditions as Compound A. The densities of the two samples were measured to be the same, at 1267 kg/m$^3$, and therefore these output results also reflect volume as well as mass output performance.

There is an expectation that a material that has a higher level of gelation could provide a lower extruder output because it will tend to 'melt' later in the extruder barrel and therefore modify the transportation and pumping balance. In effect, the fully filled length in the extruder will become shorter and the ability to pump material through the die will be impaired. However, there are other complicating factors. Laboratory 4 reports that Compound A has a regular cylindrical shape, whilst Compound C (after its further processing) is of irregular and different shape. It is therefore possible that the regularity and shape of the feedstock is influencing the observed differences in output, as the feed section in the extrusion process, particularly for small diameter extruders, is influenced by the shape of the granule.

Laboratory 4 also experimented with ways of restoring the performance of Compound A from Compound C. They used a commercial insulation compound of PVC-p which had a Shore A hardness of 80, i.e. a more highly plasticized compound than the formulation of our study. As it was a commercial compound, the precise formulation details are not known. They added 10% by weight of this compound to Compound C and then conducted a similar extrusion experiment with processing temperatures of 127 °C and 166 °C. The mass output rates were restored in both cases to within experimental error. At first sight, it might seem that the restoration of an apparent loss of plasticizer experienced by Compound C can rejuvenate its performance. However, other more credible explanations are also available. It is likely that the regularity and shape of the feedstock has been changed again, in the preparation of the new compound. The characteristics in the feed section of the extruder with this new compound might be influential in restoring mass output. In any case, there is no corroborating evidence for loss of plasticizer since the DMA results after annealing and the viscometry curve at high temperature provide no interpretation in terms of different plasticizer levels. We are therefore left with an interesting but inconclusive position. This can only be resolved by a further set of experiments where much more control over the shape and size of the feedstock is made, together with appropriate control over the levels of gelation. However, an expectation of being able to control all the variables necessary to prove a particular point can often become elusive.

## CONCLUDING COMMENTS

We have conducted a detailed investigation of the change in deformational, structural, molecular and rheological characteristics that are attendant on a PVC-p compound experiencing higher processing temperatures. Our study reflects an experience that occurs in the PVC industry where a loss of processing performance accompanies excursions to higher temperatures. It is apparent that as this process continues the material will eventually become unprocessable, unless changes are made.

The change that accompanies the material as it passes from an experience of low processing temperatures to high processing temperatures has been thoroughly mapped. However, it has been difficult to make a precise observation of the molecular and structural changes occurring. This has not been without application of a number of likely candidate methodologies, including DSC, TGA, WAXS, GPC and fluorescence spectroscopy. It would seem that some additional crystallization is accompanying the increase in gelation that occurs at higher processing temperatures. At the same time, the observations on the influence of annealing indicate that this is not the only consideration and that diffusion of the plasticizer into the PVC particles might also be playing a role, or even residual stresses in the materials might be important.

This study has not only been concerned with an in-depth materials characterization; it has also explored ways of alleviating the loss of processability. Two particular lines of study involving pre-shear history and blending with higher plasticized compounds have provided interesting, albeit inconclusive, results. On the other hand, there are strong implications from the DSC study that reversibility of the 'process aging' is not likely.

In conclusion, it is interesting to observe that, by conducting this study through an IUPAC Working Party, it has been helpful to pool the resources and experience of an international community of scientists which has probably given us an opportunity of conducting this study at much lower costs than might have otherwise been the case.

## APPENDIX

### Definitions

| | |
|---|---|
| DMA | dynamical mechanical analysis/analyser |
| DOP | dioctyl phthalate |
| DSC | differential scanning calorimetry/calorimeter |
| GPC | gel permeation chromatography |
| *l/r* ratio | ratio of length to diameter for an extrusion die in capillary rheometry |
| PVC-p | plasticized poly(vinyl chloride) |
| SEC | size exclusion chromatography |
| TBLS | tribasic lead sulfate |
| TGA | thermogravimetric analysis |
| $T_g$ | glass–rubber transition temperature |
| WAXS | wide angle X-ray scattering |

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