

# The use of differential scanning calorimetry to study the reprocessing of poly(vinyl chloride)

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The effect of reprocessing on the structural order of a poly(vinyl chloride) compound is studied using differential scanning calorimetry (d.s.c.). Reprocessing was simulated in the d.s.c. instrument by subjecting the polymer to multiple heating sequences leading to various maximum temperatures. The traces of the processed material contain information about its previous processing history. The development of a network of entanglements and of primary and more recent order re-formed in each of the cooling sequences is postulated.

(Keywords: poly(vinyl chloride); reprocessing; differential scanning calorimetry; structure; development)

## INTRODUCTION

Poly(vinyl chloride) (PVC) grains exhibit a complex morphology, with several hierarchies of particles and a small degree of crystallinity<sup>1</sup>. Unlike conventional semicrystalline polymers such as high-density polyethylene (HDPE) or polypropylene (PP), which form homogeneous amorphous melts during flow, the processing of PVC compounds takes place at temperatures (180–200°C) below those reported for the fusion of the crystalline part (160–230°C)<sup>2</sup>. As a consequence, when processing PVC the original morphology is progressively changed into a network of entanglements and of three-dimensional order, which may arise both from original crystallinity surviving processing and from that formed upon cooling. This process is known as the 'gelation mechanism'. It can involve major changes in particle size, with smaller particles constituting the unit of flow. Conversely, breakdown may play a minor role, with the original grain structure, albeit deformed and internally fused, surviving most of the process. The extent of this process or 'gelation level', depends on the intensity of the temperature and shear levels induced by processing. Also, it correlates well with the mechanical and physical properties of PVC products<sup>3,4</sup>.

It is difficult to conceive the gelation mechanism as being reversible. This would mean that the material upon reprocessing at a certain temperature would forget its previous heat history and would show a performance and a structural order similar to those corresponding to processing at that same temperature. Instead, one would probably anticipate that, when reprocessing PVC at a lower temperature, the degree of gelation equivalent to the initial processing would be retained, probably without any further progression towards total gelation. However, some authors<sup>5–8</sup> have indeed reported experimental evidence of such reversibility, but without developing a sound theoretical foundation.

Therefore, it is the purpose of this work to gain a better understanding of the effect of reprocessing on the structural order of PVC. The problems associated with reprocessing are currently of great practical relevance, owing to the increasing social and political pressure for recycling. During the complex process of recovering municipal solid waste or off-specification products, several steps must be accomplished, among them reprocessing of PVC compounds.

## GELATION AND REPROCESSING

A number of techniques for assessing gelation are currently available and have been reviewed in the literature<sup>9</sup>. Two relatively new methods — capillary rheometry and thermal analysis — produce quantitative results and have proved to be suitable to distinguish between small variations in the level of fusion. Thermal analysis in particular uses small samples and produces direct information on the structural order of the material.

A d.t.a. trace of a rigid PVC sample processed above 160°C shows a broad endotherm (usually denoted as A), from about 110°C to the onset of a narrower endotherm (B). While B is due to the annealing of crystallites that did not melt during processing, A results from the recrystallization upon cooling of melted material. The enthalpy of B decreases with increasing processing temperatures (as more ordered material is melted), whereas that of A has the opposite behaviour. Either  $\Delta H_A$  or  $\Delta H_B$  can be used to assess quantitatively the degree of gelation. Usually  $\Delta H_A$  is adopted for this purpose, owing to its higher energy in the usual processing range and ease of identification. Endothermic peaks below  $T_g$  have been observed<sup>10,11</sup> and attributed to enthalpy relaxations. A peak near 100°C may also appear; it develops on room-temperature storage of rigid PVC due to a slow reduction in free volume<sup>10</sup>. From an ample

amount of data, it has been shown that the onset of the B peak correlates well with the (maximum) processing temperature of the compound<sup>3</sup>.

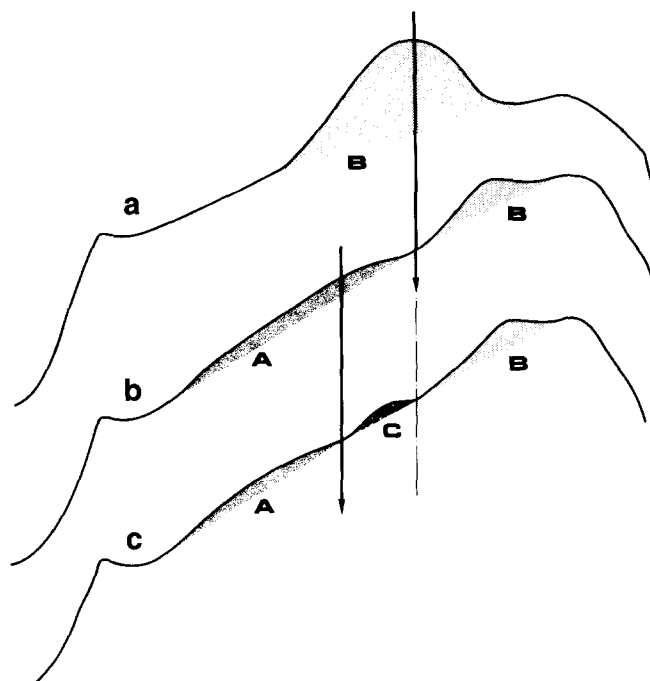
The apparent inversion of gelation has been previously observed using capillary rheometry<sup>5-7</sup>, thermal analysis<sup>7,8</sup>, or the measurement of mechanical properties<sup>8</sup>. Portingell<sup>6</sup> processed unplasticized PVC samples in a Brabender at temperatures up to 180°C and then reprocessed some of the latter at 135 and 180°C. The extrusion pressure showed similar readings for the samples produced at 180°C, but lower entry pressures for the sample reprocessed at 135°C. Since no significant changes in molecular-weight distribution could be obtained, the author attributed this behaviour to a 'combing out' effect on the molecular network. Patel<sup>7</sup> compounded samples in a Banbury at several temperatures and later extruded the material at lower temperature (134°C). The extrusion pressure and the A endothermic energy of all the samples reprocessed reduced to the values of that compounded at 134°C. Patel explained these findings through the breaking down of the secondary crystalline crosslink sites at various points, under the high shearing forces.

Thus, reprocessing seems to affect the material at the molecular level. Since d.s.c. is a convenient tool to monitor such changes, it may be worth giving some consideration to the features of the conventional PVC traces. As described above, when PVC is processed at sufficiently high temperatures, part of the crystalline material is melted, whereas the higher-melting material is annealed. Some of the melted material will reorganize upon cooling. Thus, peaks A and B are formed. The same principles can be used to predict the effects of reprocessing at lower temperatures. While B will remain unaffected, A should now behave as B during processing. Therefore, A will produce a smaller endotherm, corresponding to material recrystallizing upon the second cooling, and a third endotherm (which will be denoted as C), corresponding to the annealing of the surviving A. This hypothesis is schematized in *Figure 1*, which shows, from top to bottom, the typical d.s.c. of a PVC powder, the d.s.c. of a sample processed above 160°C and the predicted trace of a sample reprocessed at a temperature lower than that attained during the previous processing. The vertical arrows represent the temperatures of processing and reprocessing. Thus, upon reprocessing at lower temperature, one would anticipate the following:

- The energy of peak B is not affected.
- If the difference between the temperatures of processing and reprocessing is sufficiently high, a new endotherm (C) appears.
- A is decreased, probably down to values similar to those attained for the same processing temperature.
- The onset temperatures of peaks B and C correspond to the processing and reprocessing temperatures of the compound, respectively.

When reprocessing at temperatures above the initial processing, the degree of gelation will probably be increased to values similar to those corresponding to processing at those temperatures.

According to these arguments, there is no real inversion of gelation when reprocessing at lower temperatures, despite the possible similarity of the mechanical and physical properties of samples produced under those conditions. Instead, a network of entanglements of primary, secondary and tertiary structural order will be formed.



**Figure 1** Typical and predicted d.s.c. traces for a sequence of heat treatments: (a) PVC powder; (b) material processed above 160°C; (c) compound reprocessed at lower temperature. The vertical arrows represent processing and reprocessing

**Table 1** Formulation used

	phr
S-PVC ( $K=61.5$ )	100
Tribasic lead sulfate	3
Calcium stearate	0.4
Stearic acid	0.3

## EXPERIMENTAL

The hypothesis put forward above was evaluated by processing and reprocessing a simple formulation, based on a suspension PVC resin (*Table 1*), under different temperatures and subsequently examining its behaviour in a dual-furnace, power-compensated, d.s.c. (Perkin-Elmer DSC7).

Samples were initially processed at 160, 170, 180, 190, 200, 210 and 215°C. Some of the samples originally processed at 190, 200 and 210°C were also reprocessed at lower and, eventually, higher temperatures, whenever visible degradation would not occur. Processing and reprocessing were carried out in the d.s.c. instrument, according to the sequence shown in *Figure 2*, thus in the total absence of shear and under close temperature control.

The d.s.c. traces were obtained after heating 8–12 mg of sample in a pure nitrogen atmosphere from room temperature to 240°C at a heating rate of 20°C min<sup>-1</sup>.

## RESULTS AND DISCUSSION

The d.s.c. traces of the various samples were examined in detail and the enthalpies of peaks A, B and C were computed. *Figure 3* shows the variation of the energy of peak A with temperature for both processing and reprocessing. As expected, A increases with increasing

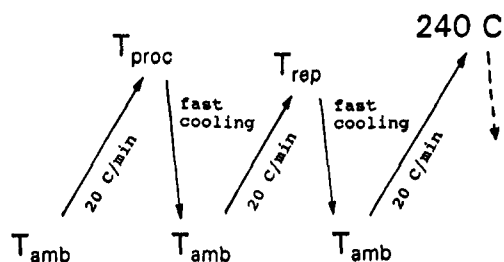


Figure 2 Processing and reprocessing sequence in the d.s.c.

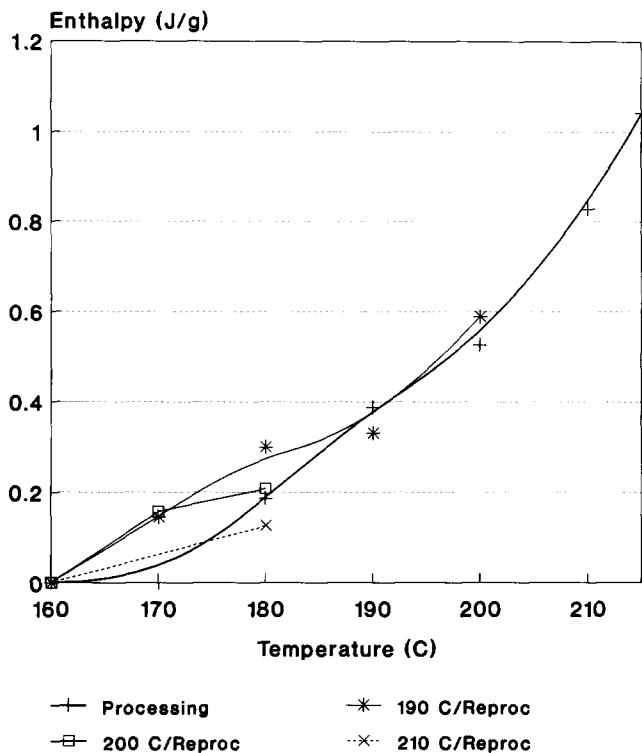


Figure 3 Effect of reprocessing on the variation of the enthalpy of peak A with temperature

processing temperature, i.e. the degree of gelation increases with increasing temperature<sup>3</sup>. Considering the errors in measuring the energies, it can be concluded that the enthalpy of A of a particular sample is not significantly affected by its previous heat history. This correlates well with previous experiments<sup>7,8</sup> and confirms the prediction that upon reprocessing at lower temperatures the energy of peak A would be decreased to values equivalent to those for processing at the same temperature. When reprocessing at higher temperatures, A follows the expected trend, i.e. gelation progresses observing the same pattern.

Figure 4 exhibits similar data, but for the B endotherm. The energies are often difficult to compute, because the peaks are very small at high temperatures, their ends being difficult to identify. The conventional dependence of B on the processing temperature is again confirmed<sup>3</sup>. Since the difference between the horizontal lines, which correspond to the values of B at 190, 200 and 210°C, and the experimental points is small, it can be concluded that B is not affected by reprocessing at temperatures lower than or equal to those induced upon processing. This has also been reported by Patel<sup>7</sup>. When reprocessing at the above temperatures, the energy of the B peak corresponds to the value observed for processing.

The appearance of a third fusion peak when reprocessing at lower temperatures is confirmed in Figure 5. This figure shows the normalized traces (i.e. the energy of the traces was divided by the weight of the samples, so that the areas of the peaks are directly proportional to their enthalpy) of a sample processed at 200°C, and of samples also heated up to 200°C and subsequently reprocessed at 160, 170 and 180°C, respectively. The simultaneous representation of the four traces altered the optimum scale for the individual curves, hence the peaks appear to be less intense. Nevertheless, the following features can be detected:

- (a) Upon processing to 200°C, a broad peak A and a narrower peak B can be detected.
- (b) The onset of B is unaffected by reprocessing.
- (c) The area and broadness of peak A increase with increasing reprocessing temperature.
- (d) Upon reprocessing, a third peak, C, developing

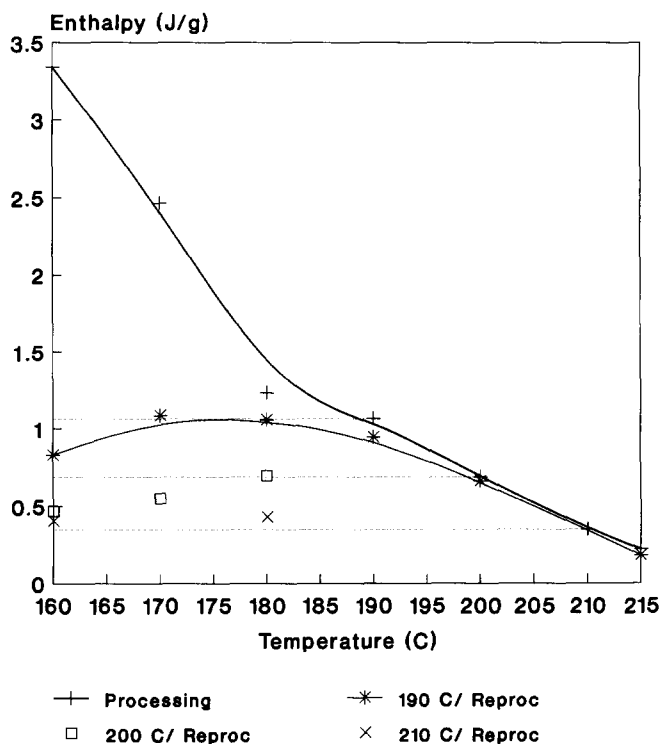


Figure 4 Effect of reprocessing on the variation of the enthalpy of peak B with temperature

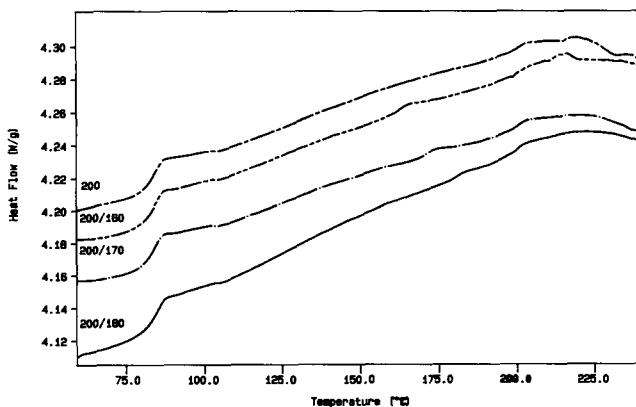


Figure 5 Normalized d.s.c. traces of samples heated to 200°C, and reprocessed to 160, 170 and 180°C after being previously heated to 200°C

between peaks A and B, can be identified. Its area decreases with increasing reprocessing temperature.

(e) The onset of C increases with increasing reprocessing temperature and seems to be near to the reprocessing temperature. The onset of B takes place around 200°C.

Thus, if a sequence of reprocessing temperatures is considered as in Figure 6, where the data presented correspond to reprocessing at several temperatures after

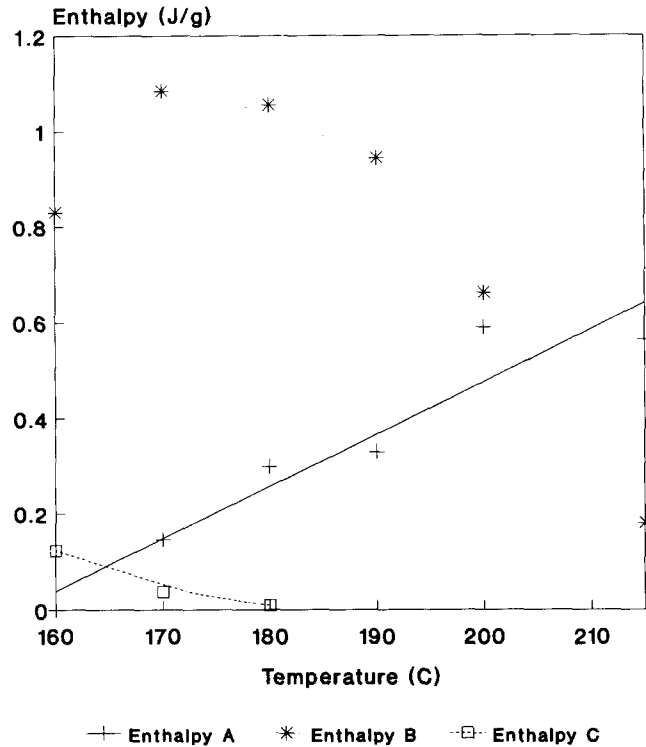


Figure 6 Variation of the enthalpies of peaks A, B and C with temperature, for samples initially processed at 190°C

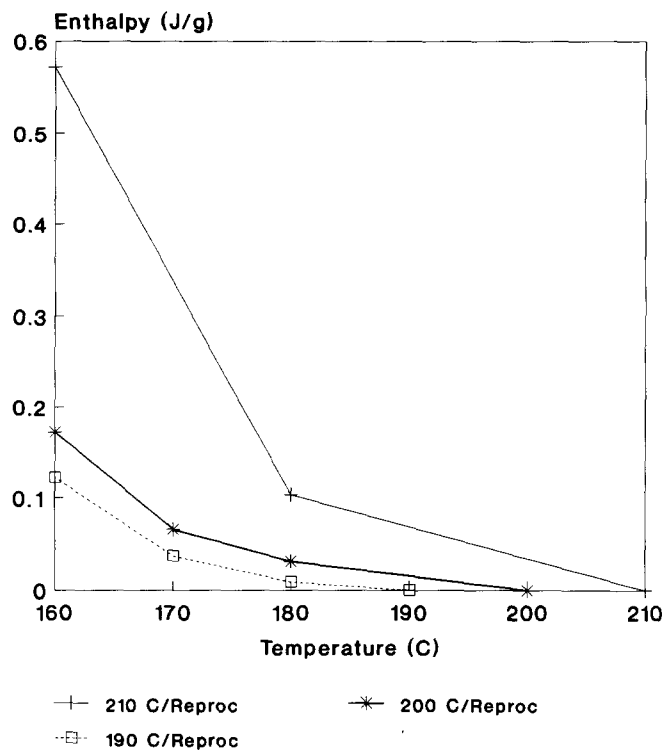


Figure 7 Variation of the enthalpy of peak C with the temperatures of processing and reprocessing

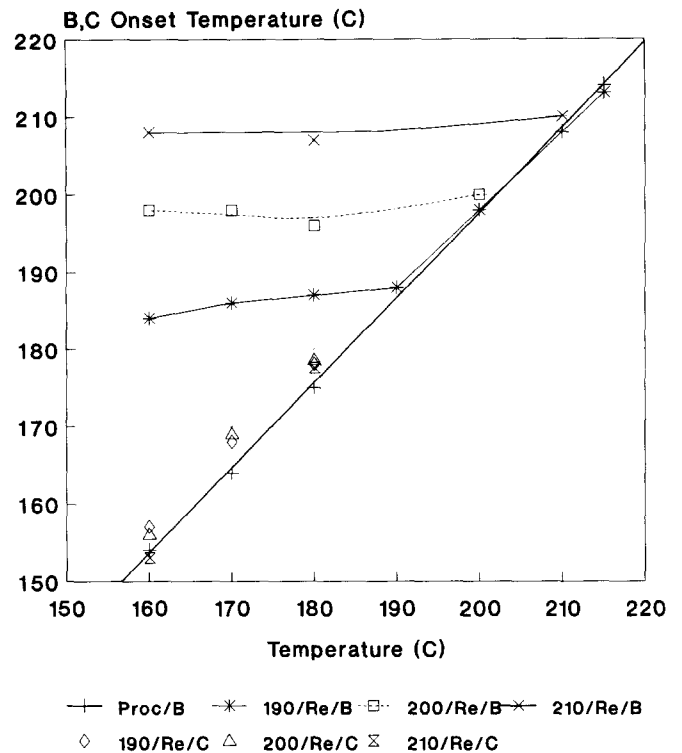


Figure 8 Comparison between the onset temperatures of peaks B and C and the processing or reprocessing temperatures

processing at 190°C, one may conclude, as initially expected, that the enthalpies of B and C decrease with increasing temperature, whereas that of A follows the opposite trend. The dependence of the enthalpy of peak C on the reprocessing temperature is illustrated in Figure 7, for various initial heat histories. The higher the difference between the temperatures of processing and reprocessing, the higher the enthalpy of C. If those temperatures are similar, the amount of A surviving will be insufficient to produce a peak. For samples obtained with the same reprocessing experience, the energy of C depends on the heat history of the processing stage. Again, this is related to the value of the initial A peak, since the higher the processing temperature, the higher the value of A.

The practical value of the onset of peaks B and C was also investigated, the results being presented in Figure 8. Here, the onset temperatures of the peaks are compared with the processing and reprocessing temperatures. The onset of the B peak produces reasonably accurate information on the processing temperature, especially above 160°C (the maximum error is 6°C), confirming earlier reports<sup>3</sup>. The data on B and C onset temperatures for reprocessing are close to the 45° slope line, thus providing a good estimate. The three almost horizontal lines correspond to the onset of the B peak when reprocessing at lower temperatures takes place. Since in this case the energy of the peak is not affected (see Figure 4), its onset provides information on the processing temperature. This means that the material contains information about both its recent and previous processing history.

The consequences of this 'memory' effect can be explored further. Applying the same argument illustrated in Figure 1, one could predict that when the material is subjected to successive reprocessing cycles at progressively lower temperatures, more fusion peaks can be generated.

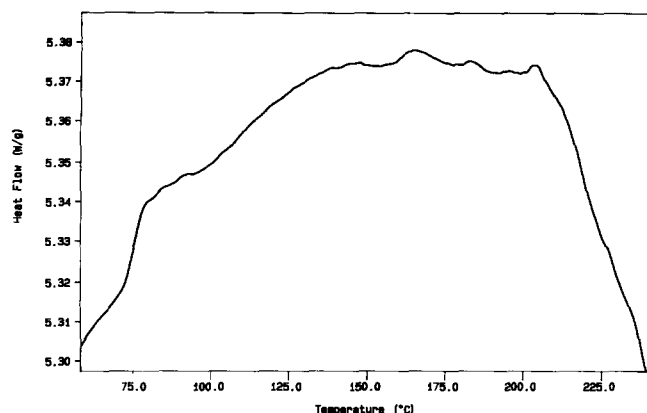


Figure 9 D.s.c. trace of a sample initially heated up to 200°C, subsequently heated to 180°C and finally heated to 160°C

This is illustrated in *Figure 9*, which shows the d.s.c. trace of a sample initially heated up to 200°C, subsequently reprocessed at 180°C and again reprocessed at 160°C. The material exhibits some degradation, as shown by the intense exothermic peak that developed at higher temperatures. This is due to the increased time of subjecting the polymer to relatively high temperatures, under the absence of shear (which would promote the action of the additives, especially the heat stabilizer). Consequently, the energies of the peaks may be meaningless. Nevertheless, four peaks are distinctly observed, extending from ca. 100 to 153°C, from 156 to 178°C, from 180 to 190°C and from 199 to possibly 213°C. According to the previous reasoning, these traces will be denoted as A, D, C and B respectively. Peak B should correspond to the remaining initial structural order, peak C to the surviving secondary crystallinity, peak D to the surviving material reorganized upon the second cooling (first reprocessing sequence) and peak A to the ordered material developed during the last reprocessing cycle. Moreover, the onset of B provides a good estimate of the processing temperature, the onset of C a good assessment of the first reprocessing temperature, and the

onset of D a reasonable evaluation of the second reprocessing temperature.

## CONCLUSIONS

Although the hypothesis proposed in this paper should be strengthened by analysing more PVC compounds and including the effect of shear, it seems to explain well the effect of reprocessing on the structural order of PVC.

The physical and mechanical properties of reprocessed PVC samples seem to prove the inversion of the gelation mechanism. However, it has been shown that the process is in fact irreversible. During processing at lower temperatures, a new network of initial and more recent three-dimensional order is developed. The closer the processing and reprocessing temperatures, the more similar the molecular networks formed upon processing and reprocessing will be. When reprocessing at higher temperatures, progression towards total gelation maintains the same trend.

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