Thermomechanical History Effects on Rigid PVC Microstructure and Impact Properties

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ABSTRACT: Rigid PVC microstructure strongly depends on processing conditions: under both shear and heat influence, gelation process occurs, and the resulting morphology can be characterized by the so-called gelation level parameter. But thermomechanical history also affects several other features of the microstructure. In this work, two different aspects mainly related to (i) orientation and (ii) molecular mobility are pointed out, and their respective effects on poly(vinyl chloride) (PVC) impact properties are described. Charpy impact tests have been carried out on a typical extruded window profile formulation, evidencing a strong anisotropy effect in those extrudates. It turned out that modulated differential scanning calorimetry was able to evidence macromolecular orientation. Then, the effects of heat treatments on impact properties were investigated.

Below the glassy transition temperature (T_g) of PVC, physical ageing results in a decrease of the impact performance, without affecting PVC anisotropy. The reason of this performance loss is the reduction of the molecular mobility, as evidenced by dynamical mechanical analysis experiments. After performing a heat treatment above T_g, another important decrease of the impact performance was observed. This decrease was attributed to (i) partial disorientation of the PVC macromolecular chains and (ii) reduction of the molecular mobility. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 2009–2017, 2007

Key words: polyvinyl chloride; annealing; orientation; impact resistance; modulated differential scanning calorimetry

INTRODUCTION

Commonly used in many applications, poly(vinyl chloride) (PVC) differs from other thermoplastics by two main specificities. The first one concerns its formulation, which contains a lot of different additives, allowing PVC to cover a wide range of physical and mechanical behaviors. The second one is the large dependence of its microstructure on processing conditions: during processing, PVC microstructure is fragmented into micronic particles, and under the influence of shear and heat, the interfaces of these micronic domains, known as ''primary particles,'' progressively disappear.[1–3] At a smaller scale, this process is combined with a partial melting of the PVC crystallinity.[4] The resulting morphology is usually characterized by the so-called gelation level parameter, gelation being fully achieved when primary particles structure has completely disappeared. Gelation level assessment is very important because gela-

tion state deeply affects both physical and mechanical properties of PVC.[5–8] Several different gelation assessment methods are well described in the literature,[4,9–13] and in a previous work,[14] the gelation levels of a PVC formulation subjected to different thermomechanical histories were characterized. It emerged from this work that gelation process is mainly governed by a thermal component that can be accurately measured by DSC: this thermal component is related to the highest temperature ''seen'' by PVC crystallites, and in the following part, it will be referred to as ''DSC real melt temperature.'' Thanks to DSC technique, in the case of PVC extrudates having different mechanical behaviors, it is possible to assess whether or not the gelation state is at the origin of the observed difference. However, to evaluate the intrinsic performance of additives such as impact modifiers, one can wonder whether the comparison at same gelation level is the only requirement. In other words, do other thermomechanical history effects exist that are not taken into account by gelation level measurements? Orientation effects and molecular mobility are pointed out.

Indeed, during a typical PVC extrusion process, shear stresses and drawing loads are expected to generate a certain orientation level of PVC macromo-

lecular chains. The benefits of molecular orientation on mechanical properties are well known since the eighties, leading for instance to the development of oriented PVC pipes.[15,16] To study the effects of such orientation phenomena, Hitt and Gilbert[17,18] developed a specific stretching device, and were able to evidence an increase in the falling weight impact performance with the draw ratio. However, the effects of orientation in more conventional processes (extrusion, injection, milling) are not well described in the literature. For extrusion process, if an orientation of macromolecular chains along the extrusion direction is generally assumed, neither the importance of this orientation, nor its effect on impact properties is discussed. Nevertheless, a study of Yarahmadi[19] revealed an anisotropy in extruded sheets tested in low speed tension.

In addition, mechanical properties of polymers are known to be dependant on molecular mobility.[20] This molecular mobility, often associated with "free volume," influences both viscoelastic behavior and yield stress. As the impact performance of a polymer depends on its yielding ability, a significant influence of the molecular mobility on impact properties is expected. At room temperature, PVC is in the glassy state, which is known to be an "out of equilibrium" state: indeed, in nearly all the cases, cooling rate is too fast to allow macromolecules rearrangements in a thermodynamical equilibrium configuration. Nevertheless, further rearrangements occur upon time, and the closer to T_g the temperature, the faster the rearrangements. This process called "physical ageing" leads to a reduction of the molecular mobility. For rigid PVC, the influence of physical ageing on the impact performance has been reported in the literature,[8,21,22] highlighting a decrease of the impact performance after physical ageing heat treatments at 60–70°C during a few dozen of hours. Molecular mobility also depends on the cooling rate that determines the macromolecules' glassy state configuration. However, the cooling rate influence on rigid PVC microstructure and impact properties is poorly documented.

During extrusion process, molecular mobility is affected by the cooling rate implied at the end of the process (calibration section), and later, it can be reduced if PVC is stored a long time or used at high temperature. Sometimes, PVC is also subjected to various heat treatments devoted to prevent shrinkage or to relax "internal stresses." In this context, it appears fundamental to determine to what extent orientation, heat treatments, and cooling can affect PVC impact properties. This was the aim of the current work. Moreover, the signatures of the microstructural features involved were investigated so as to propose (at the end) appropriate tools capable of explaining the origin of a given impact performance.

TABLE I
Window Profile Formulation (Quantities Given in phr)

PVC Lacovyl® S110P (K = 67)	100
Lead one pack (lead-based stabilizer + lubricants + process aid)	5.45
Durastrength® 320 (acrylic impact modifier)	7.5
Titanium dioxide	5
Coated calcium carbonate	6

EXPERIMENTAL

Materials

The PVC formulation used in this study was a standard lead-stabilized window profile recipe detailed in Table I. All ingredients were mixed together up to 110°C using a high speed mixing station (Papenmeier 75/150). The resulting dryblend was extruded at five different melt temperatures ranging from 180 to 200°C using a conical twin-screw extruder (Krauss Maffei KMDL 25), the size of the die being 70 × 2.5 mm^2 and the screw speed set at 30 rpm. After extrusion, PVC sheets were cooled through a calibration section regulated at 5°C by water and air circulation.

The major part of this work was performed on extruded PVC sheets whose formulation is given in Table I. This PVC formulation was also milled, injection molded, and extruded at low temperature and low shear, to assess the thermomechanical history effects on the orientation state. To produce the low shear/low temperature extrudate, the dryblend was extruded using a granulating device (Andouart monovis extruder 40.20) set at 160°C. Part of these granules was injection molded using a Demag D85 NCIIIK equipment set at 195°C. Finally, the dryblend was processed at 190°C, using a two-mill system (Collin) having 15 cm diameter rolls, the relative speed of the two rolls being $V_1/V_2 = 1.1$ and the gap between the rolls set at 0.35 mm.

An annealing heat treatment was performed on extruded sheets, consisting of a-1 h isothermal holding at 130°C (i.e., above glass transition temperature (T_g) $\approx$ 85°C). The cooling condition effects were also studied: after the above-mentioned annealing heat treatment, samples were cooled in icy water (iw), in air (air), or in the closed oven (ov), coming back slowly to ambient temperature (return to ambient temperature was achieved in about 2 h). Physical ageing was performed on extruded sheets by holding the samples at 70°C (i.e., below T_g) for 23 h, followed by a cooling step performed under air. The references of the different materials and their description are summarized in Table II.

Measurements

An accurate measurement of the real maximum melt temperature reached during the processing stage can

TABLE II
References (in Bold) and Descriptions of the Different Materials

G	Granulated sample—low shear/low temperature
INJ	Injection molded sample
M	Milled sample
EXT	Samples extruded at five different temperatures: T1, T2, T3, T4, T5
EXT	Without heat-treatment
Ag-EXT	Physical ageing heat treatment $<T_g$
An-EXT	Annealing heat treatment $>T_g$
An(iw)-EXT	Cooled in icy water
An(air)-EXT	Cooled in air
An(ov)-EXT	Cooled in oven

be successfully assessed by DSC[10,23]: this temperature referred to as "DSC real melt temperature" will be used to characterize the gelation state of each sample. The assessment of the "real melt temperature" as well as the characterization of PVC after various heat treatments were performed on a Q1000 differential scanning calorimeter from TA Instruments. Twenty-milligram samples were subjected to a temperature scan from 50 to 245°C at a constant heating rate of 25°C/min (optimized conditions to limit PVC degradation). The real melt temperatures of the five extruded sheets are given in Table III.

The same apparatus (Q1000 from TA instruments) was used in its modulated mode (MDSC) to separate the reversible part from the nonreversible part of the total heat flow, the reversible part being associated to heat capacity changes, and the nonreversible part to fusion/crystallization phenomena or enthalpic relaxations. The mean heating rate in modulated mode was 2°C/min, the modulation amplitude being set at 0.21°C during a period of 40 s.

Mechanical behavior at small strains was characterized with a mechanical spectrometer consisting of a forced oscillation torsion pendulum, working in the temperature range of −170°C to 430°C and frequency range of 5×10^{-5} to 5 Hz. The storage (G') and loss (G'') moduli of the complex shear modulus (G^*) and the loss factor (tan $\Phi = G''/G'$) were measured as a function of temperature, between −120°C and 150°C, for a fixed frequency of 0.1 Hz. The dimensions of the samples were about 30 mm × 7 mm × 2.5 mm.

TABLE III
Real Melt Temperature (°C ± 0.1°C) of Extruded Sheets Measured by Conventional DSC

EXT-T1	186.8
EXT-T2	189.5
EXT-T3	190.9
EXT-T4	196.3
EXT-T5	203.5

Impact performances were determined according to a "modified" version of the "Charpy BS 0.1" standard. The only modification concerned the notch radius that was either 0.25 mm or 1 mm instead of 0.1 mm. This increase of the notch radius shifts the "brittle/ductile" transition and it allows the discrimination of samples that would appear "brittle" in BS 0.1. Impact performances were evaluated at 23°C with a noninstrumented Charpy pendulum, the pendulum energy being 4 J and the corresponding impact speed close to 2.9 m/s. The dimensions of the sample were 50 mm × 6 mm × 2.5 mm. Samples were notched with a pneumatic device (Notchvis from Ceast), the depth of the notch being 1.8 mm and its radius either 0.25 or 1 mm. The energy dissipated during impact solicitation was recorded, and at least 10 samples were tested for each reference. Fracture was arbitrarily considered to be "brittle" when the sample was broken into two pieces, and "ductile" (hinge break) otherwise. Afterwards, the "impact performance" was calculated as the mean value of both "brittle" and "ductile" breaks strengths.

RESULTS AND DISCUSSION

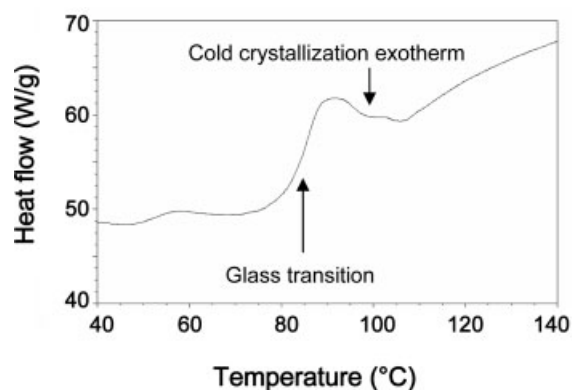### Evidence of the PVC anisotropy

To evidence the magnitude of the anisotropy existing in extruded sheets, charpy samples were taken in two different directions: samples whose length was parallel to the extrusion direction were denominated "a," and samples whose length was perpendicular to the extrusion direction "b." Both series were taken from the extrudates (EXT T1–T5 series). After samples notching (with $r = 0.25$ mm), impact performance was evaluated with the charpy pendulum and results are presented in Figure 1.
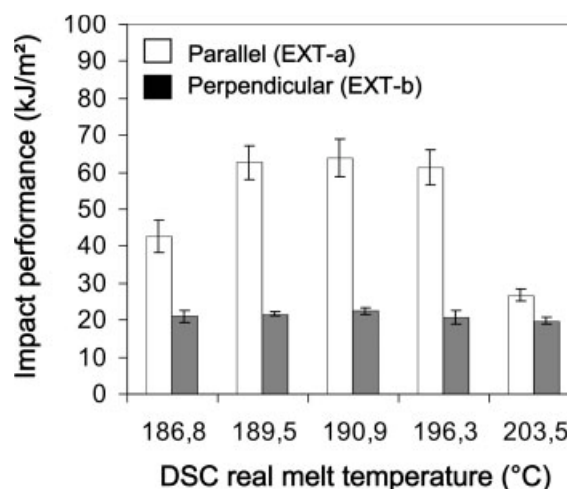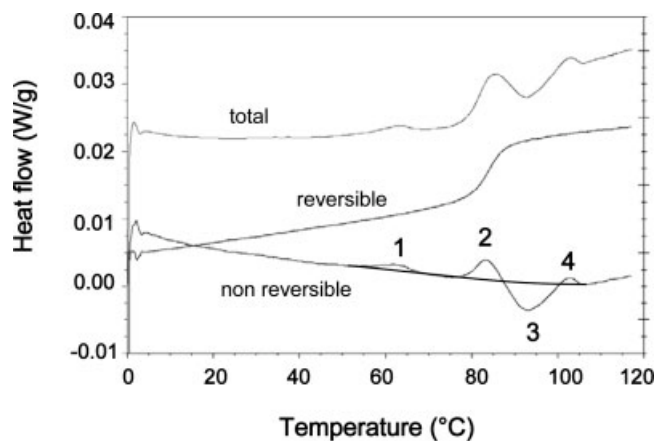

Figure 1 Charpy impact performances (notch radius = 0.25 mm) of extruded series as a function of the gelation level—specimens taken parallel or perpendicular to the extrusion direction.

The charpy impact performance exhibits a maximum at intermediate DSC real melt temperature (i.e., at intermediate gelation level), which is in accordance with many results reported in the literature.[6,7,8,24] Concerning the comparison of the samples taken parallel or perpendicular to the extrusion direction, a great difference is noticed. At intermediate gelation level, 100% of the breaks of the "parallel" series (a) are "ductile," whereas for the "perpendicular" series (b), 100% of the breaks are "brittle," whatever the gelation level. This result reveals a strong anisotropy in extruded sheets, and the effect of orientation on impact performance seems to manifest even to a greater extent to that of gelation.

Structural order in polymers is classically studied by X-ray scattering,[25] but it should be pointed out that this technique only focuses on the crystalline part of the material. To evidence both amorphous and crystalline oriented parts, birefringence measurements should be preferred.[26] However, this technique can only be applied on transparent formulations, i.e., it does not cover applications such as PVC window profiles or pipes. Another technique that could evidence orientation in rigid PVC is DSC. Illers[27] and Gray and Gilbert[28] reported the existence of an exotherm immediately above the glass transition. According to Illers, this exotherm, referred to as "cold crystallization peak" (CCP), emerges if PVC has been quenched from the molten state, generating a quasi-amorphous glassy state that tends to crystallize if a sufficient amount of heat is brought. More recently, Yarahmadi[19] observed a similar peak on DSC thermograms of rigid extruded PVC. In that case, the peak was attributed to the crystallization of amorphous parts oriented during the process. Thus, CCP could be considered as a signature of orientation, but as the peak emerges close to the glass transition region (Fig. 2), the analysis of the thermo-
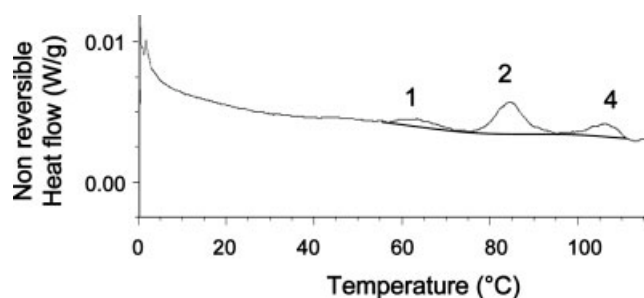

Figure 3 MDSC thermogram of processed PVC (EXT-T3), the total heat flow being the sum of the reversible and the nonreversible parts (Exo down).

grams is difficult. The advantage of modulated DSC (MDSC) is precisely to separate the glass transition from other phenomena. Therefore, MDSC could be advantageously used to investigate CCP. The MDSC thermogram of an extruded sheet (EXT-T3) is reported in Figure 3, MDSC thermograms being similar whatever the gelation level.

It can be noticed that the signal of Figure 3 associated with the total heat flow is rather different from the signal of Figure 2 obtained in conventional DSC. This can be explained by the very low heating rate used in MDSC (2°C/min), which leads to higher resolution. On the reversible part of the MDSC signal, a clear glass transition is evidenced close to 85°C. On the nonreversible part, four peaks (three endotherms and one exotherm) are observed. To identify their origin, the formulation was also evaluated in its powder state (dryblend). The nonreversible part of the signal is given in Figure 4.

The three endotherms are present in both processed and unprocessed PVC, whereas the exotherm only exists in processed PVC. Hence, the three endotherms can be attributed to the components of the formulation, and after further investigations, it turned out that they were attributed to the fusion of

Figure 2 Thermogram of processed PVC (EXT-T3) obtained by conventional DSC at a heating rate of 25°C/min (Exo down).

Figure 4 MDSC thermogram (nonreversible part of the signal) of unprocessed PVC (Exo down).
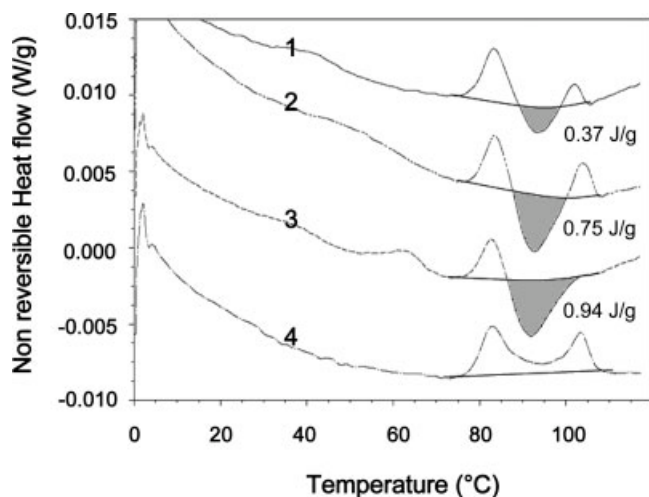
Figure 5 MDSC thermograms (nonreversible part) of (1) milled, (2) extruded, (3) injected, and (4) granulated samples (Exo down).

ingredients of the one pack (stabilizers + lubricants). As the exotherm only appears on the thermogram of processed PVC, it is consistent to attribute it to the CCP mentioned in the literature. As MDSC provides a clear separation of the glass transition from the other phenomena, a precise analysis of the enthalpy value of the CCP is allowed. At this stage, one can wonder whether the value of this enthalpy could reflect a quantitative orientation level. To check this assumption, samples of same formulation obtained by different processing routes were characterized. The nonreversible part of the heat flow is given in Figure 5. In this figure, it can be noticed that the granulated sample (processed at very low temperature with low shear) does not exhibit any CCP, suggesting that this kind of soft process does not generate any significant orientation of the macromolecules. On the contrary, for the three other processing routes, CCPs are observed and enthalpy values can be calculated. The observed trend is that the stronger the assumed orientation, the higher the enthalpy value. Indeed, the strongest orientation was assumed for the injection molded sample and the lowest for milled sheets.

By quantifying the cold crystallization phenomenon, MDSC appears as a promising technique to characterize orientation. However, it was earlier underlined that CCP can also emerge on quenched PVC samples. In the current work, the samples processed by the different routes were not quenched from the molten state, but they were cooled slowly from a partially molten state. Moreover, their crystallinity degrees were found to be very similar, as assessed in a previous work[14] by DSC and X-ray measurements. Thus, the differences observed between the CCP enthalpies associated to different

processing routes can be mainly attributed to orientation effects. To correlate MDSC results to those given by another experimental technique, an interesting perspective may be to study the birefringence properties of a transparent PVC formulation.

### Effects of a heat treatment below T_g (physical ageing)

To simulate the effects of long storage periods of PVC products, accelerated physical ageing can be performed by heat-treating PVC extrudates just below the T_g. In the current work, extruded sheets were aged at 70°C for 23 h. Charpy impact performances of samples taken parallel or perpendicular to the extrusion direction were evaluated before and after physical ageing. Results are given in Figure 6. The influence of physical ageing on the nonreversible part of the heat-flow measured by MDSC is illustrated in the case of EXT-T3 in Figure 7.

After physical ageing, a significant decrease in the impact performances occurs, but results still exhibit a strong anisotropy. Moreover, the fact that CCP still exists on MDSC thermogram after physical ageing suggests that heat treatment below T_g does not bring enough mobility to macromolecules to disorientate. In addition, physical ageing is highlighted on MDSC thermogram by the typical physical ageing endotherm.[29] It appears, in the present case, superimposed on one of the endotherms associated to the fusion of the one-pack ingredients.

The effects of physical ageing on molecular mobility are often investigated by dynamical mechanical analysis (DMA). The loss factor (tan Φ) of one of the
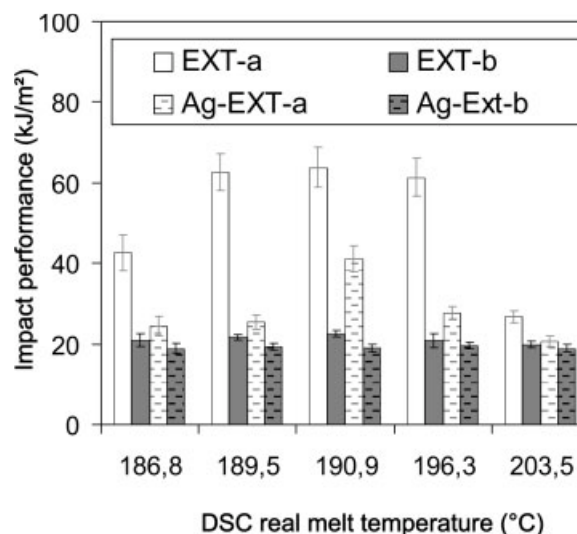

Figure 6 Charpy impact performances (notch radius = 0.25 mm) of extruded series (a) parallel or (b) perpendicular to the extrusion direction as a function of the gelation level, before and after physical ageing.
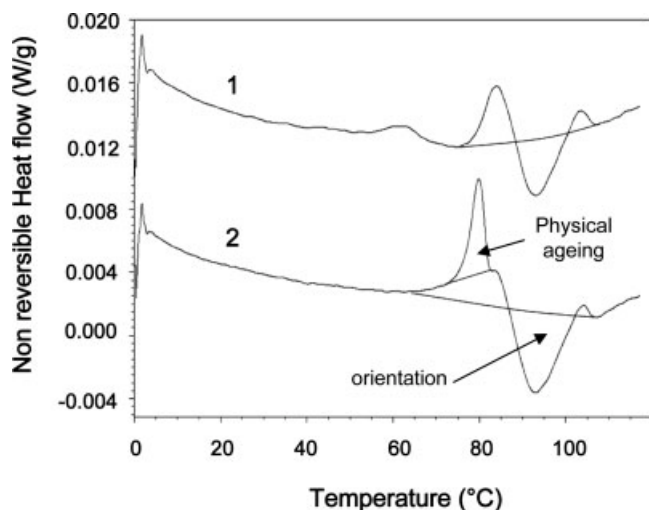
Figure 7 MDSC thermograms (nonreversible part) of processed PVC (EXT-T3) (1) before and (2) after physical ageing (Exo down).

extrudates (EXT-T3) was determined before and after physical ageing. Results are given in Figure 8. Between −120°C and 30°C, a broad peak associated to the β relaxation of PVC is observed, and it is not significantly affected by the physical ageing heat treatment. On the contrary, the low temperature part of the second peak, related to the α relaxation and observed between 30°C and 120°C, is deeply affected by physical ageing. The loss factor decrease corresponds to a reduction of the mobility of PVC macromolecules, explaining the impact performance loss observed in Figure 6.

Moreover, the existence of a shoulder on the low temperature part of the α relaxation of the nonaged PVC can be noticed. In the PVC literature, the presence of a shoulder close to 50°C is sometimes mentioned but not really discussed.[30] However, Diaz-
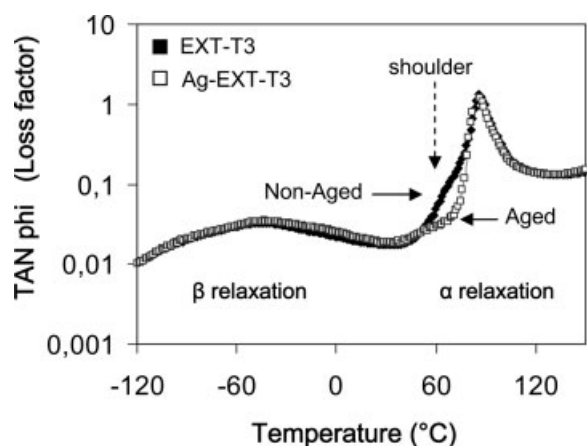

Figure 8 Evolution of the loss factor (tan Φ) with the temperature of processed PVC (EXT-T3) before and after physical ageing.

Calleja[31] reported, in the case of quenched samples, the existence of a "relaxation" occurring between the α- and β relaxation of PVC. According to the author, this process is not a true relaxation but the result of a quenched state that exhibits higher molecular mobility. This aspect will be discussed in the following part, the effects of a heat treatment above T_g as well as the influence of the cooling rate being investigated.

Effects of a heat treatment above T_g

Extruded sheets presenting different gelation levels were annealed at 130°C for 1 h, and after this heat treatment, samples were cooled in icy water (iw), in air (air), or in oven, coming back slowly to ambient temperature (ov). The charpy impact performances of the series cooled in air were first evaluated, samples being taken either parallel or perpendicular to the extrusion direction. Results before and after annealing are reported in Figure 9, as a function of the gelation level.

After annealing above T_g, charpy impact performances decrease drastically. For instance, when Figures 6 and 9 are compared, it can be noticed that the performance decrease is more pronounced for annealing than for physical ageing. A first explanation of the performance decrease after annealing at 130°C could be related to the disorientation of the polymer chains. Indeed, after the annealing heat treatment, a shrinkage of about 2% along the extrusion direction was measured. This shrinkage is a direct consequence of the macromolecular chains reorganization allowed by the mobility increase provided by heat-
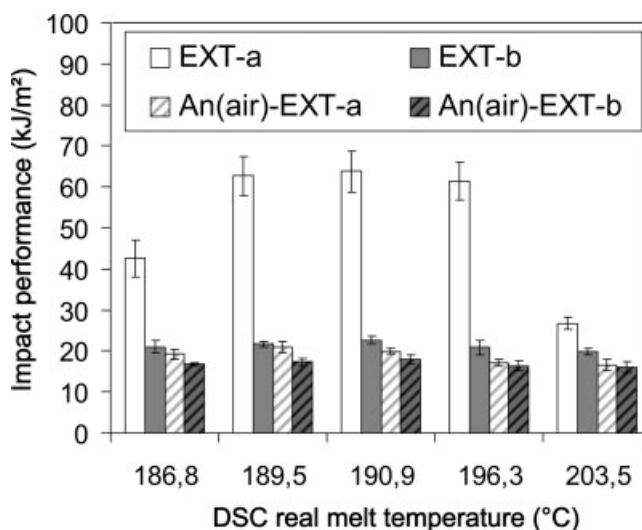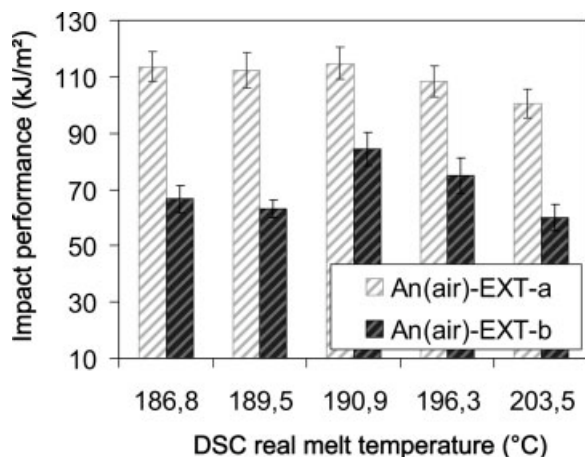

Figure 9 Charpy impact performances (notch radius = 0.25 mm) of extruded series (a) parallel or (b) perpendicular to the extrusion direction as a function of the gelation level, before and after annealing and cooling in air.
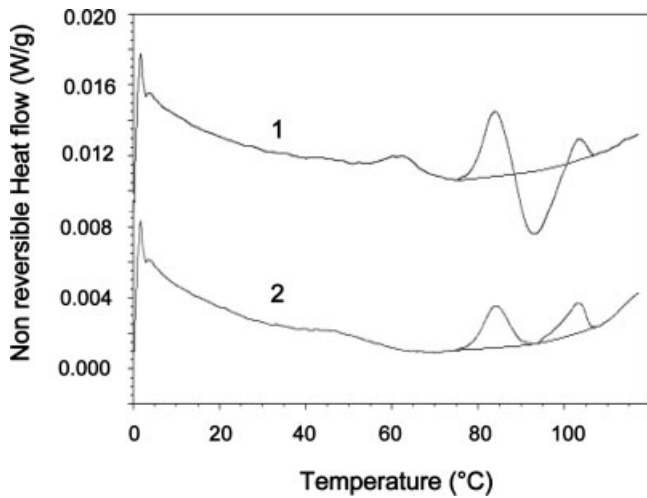
Figure 10 MDSC thermograms (nonreversible part) of processed PVC (EXT-T4) (1) before and (2) after annealing and cooling in air (Exo down).

ing above T_g. As MDSC yields information about the orientation state, annealed PVC was also characterized by MDSC. The thermograms before and after annealing are given in Figure 10.

After the annealing heat treatment, the CCP completely disappeared. From this observation, it could be concluded that (i) PVC is totally disoriented or (ii) cold crystallization took place during the heat treatment at 130°C. In the latter case, this suppresses any further possibility of cold crystallization during the MDSC test. From Figure 9, it seems that some anisotropy still exists after annealing. But as both series ''parallel'' and ''perpendicular'' exhibit fully ''brittle'' breaks, it is difficult to conclude. To better discriminate these series, the severity of the charpy test was reduced by increasing the notch radius

from 0.25 to 1 mm. Impact performances of annealed PVC evaluated in these latter conditions are given in Figure 11.

The results highlight the subsistence of anisotropy after annealing at 130°C. This demonstrates that such thermal heat treatment does not allow a complete disorientation of the PVC chains. At this stage, one can wonder whether the dramatic impact performance loss observed after annealing can only be explained by a partial disorientation. After the heat treatment above T_g, as PVC has been cooled from the rubbery state, an influence of cooling rate on the molecular mobility is expected. To check this assumption, viscoelastic properties and impact performances of annealed PVC cooled in three different conditions were assessed. The DMA thermograms were first analyzed by focusing on the previously mentioned shoulder linked to quenching. The evolution of the loss factor (tan Φ) with the temperature is given in Figure 12 for the three different cooling conditions, the reference extruded sample before heat treatment also being reported.

In the Figure 12, it can be noticed that the faster the cooling rate, the more pronounced the shoulder. Thus, the shoulder appears as being a signature of a quenched state exhibiting a high molecular mobility. It has been shown in the previous part that the reduction of this shoulder caused by physical ageing was correlated to an impact performance decrease. As expected and shown in Figure 13, a similar behavior is also observed when the reduction of the shoulder is caused by a slower cooling rate: the faster the cooling rate, the more pronounced the shoulder, and the higher the impact performance.

Since the influence of cooling conditions on impact properties has been clearly evidenced, the cooling conditions after the 130°C heat treatment has also to be taken into account, together with the disorienta-
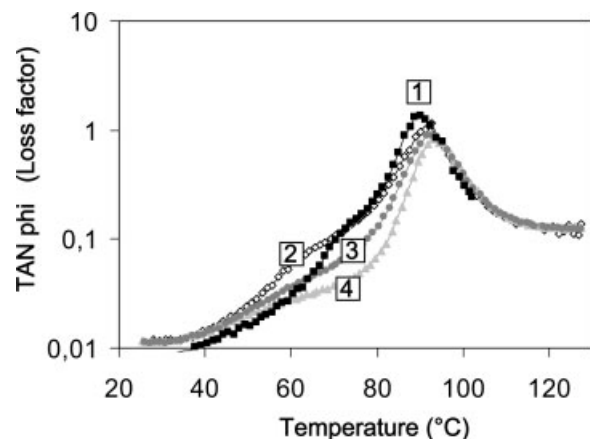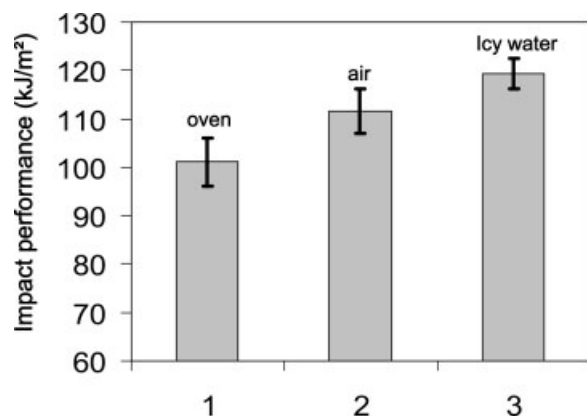

Figure 11 Charpy impact performances (notch radius = 1 mm) of annealed extruded series (a) parallel or (b) perpendicular to the extrusion direction as a function of the gelation level.

Figure 12 Evolution of the loss factor (tan Φ) with the temperature of (1) EXT-T3, (2) An(iw)-EXT-T3, (3) An(air)-EXT-T3, and (4) An(ov)-EXT-T3.

Figure 13 Charpy impact performances (notch radius = 1 mm) of (1) An(ov)-EXT-T3, (2) An(air)-EXT-T3, and (3) An(iw)-EXT-T3.

tion, to explain the impact loss observed in Figure 9. Indeed, before annealing, the molecular mobility is determined by the cooling conditions that follow the extrusion, and after annealing, molecular mobility is determined by the cooling conditions that follow the annealing heat treatment. These two cases correspond, respectively, to the DMA thermograms 1 and 3 of the Figure 12. In this figure, it can be seen that the shoulder before annealing (thermogram 1) is more pronounced than the shoulder after annealing and cooling in air (thermogram 3). This means that the cooling rate of the extrusion process is faster than standard air cooling. As a consequence, annealed samples exhibit a lower molecular mobility, and this reduced mobility could be part of the origin of the significant impact performance loss observed after annealing.

The impact performance of a PVC sample that has been heat-treated above T_g seems to be affected by (i) PVC partial disorientation and (ii) reduced molecular mobility caused by cooling conditions. But in addition to these two effects, a third one related to PVC crystallinity could be considered. Indeed, during the heat treatment above T_g, isothermal crystallization occurs, as evidenced by DSC thermograms presented in Figure 14.

In this figure, thermogram 1 corresponds to the PVC reference sample (EXT-T3) before annealing, and the two well-known endotherms related to primary and secondary crystallites of processed PVC are observed.[23] After annealing either at 110°C (thermogram 2) or at 130°C (thermogram 3), a third peak is superimposed on the endotherm related to secondary crystallites, highlighting the isothermal growth of crystallites that melt at temperatures slightly above the heat treatment temperature. This phenomenon has been reported in the literature by several authors,[25,26,32] but few studies have evidenced the influence of this crystallinity modification

on impact properties. In the work of Kim and Gilbert,[26] crystallites isothermal growth appears to affect more the ability of PVC to resist to shrinkage, than the mechanical properties. However, one can wonder whether the isothermal growth of crystallites does not affect the molecular mobility of PVC. In Figure 12, it can be seen that the height of the loss factor peak decreases after annealing. Flores-Flores[33] also evidenced in rigid PVC such a decrease after a heat treatment slightly higher than T_g, and he attributed it to crystallites isothermal growth. If this assumption looks quite consistent with the results of the present work, the decrease of the loss factor could also result from the reorganization of the amorphous polymer chains (partial disorientation). Further investigations would be needed to definitely conclude on the origin of the loss factor decrease after annealing.

CONCLUSIONS

The sensitivity of rigid PVC microstructure and impact strength to its thermomechanical history has been investigated. Whatever the gelation level, rigid PVC processed by extrusion may exhibit a strong impact strength anisotropy effect, which is related to macromolecular orientation occurring along extrusion direction. This orientation phenomenon has been successfully highlighted by MDSC experiments, since oriented PVC chains exhibit a crystallization exothermal peak upon heating (so-called cold crystallization peak). Moreover, the enthalpy of this exotherm appears as being directly correlated to the extent of macromolecular orientation. When a rigid PVC extrudate is heat-treated below its T_g, a significant impact strength loss is observed without significant modifica-
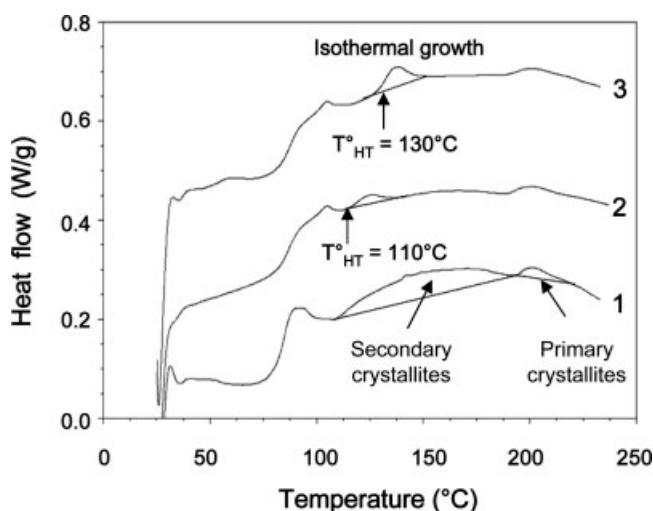
Figure 14 DSC thermograms of EXT-T3 (1) before and after annealing for 1 h at (2) 110°C and (3) 130°C (Exo down).

tion of the PVC orientation state. This performance decrease is associated to a reduction of the molecular mobility (typical physical ageing effect), as evidenced by DMA experiments in the low temperature part of the α mechanical relaxation. If rigid PVC is heat-treated above its T_g, an even more pronounced impact performance loss is observed. The annealing heat-treatment above T_g provides a complex modification of the microstructure that can be seen as a superimposition of three possible effects: (i) a partial disorientation of the PVC chains, (ii) a modification of the molecular mobility depending on the cooling rate after the heat-treatment, and (iii) a reduction of the molecular mobility induced by the isothermal growth of PVC crystallites. Disorientation as well as molecular mobility reduction contribute to the overall impact performance loss observed after having annealed PVC above its T_g. Finally, it emerges from this work that DSC could be advantageously used in its modulated mode to assess the orientation state of PVC. And from a more general point of view, this work highlights the fact that impact performance of PVC is not only governed by its gelation level, it also strongly depends on both orientation state and molecular mobility.

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