Elasticity of poly(vinyl chloride) melts

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Using the available correlations between the first normal stress coefficient, θ, and the shear viscosity function, and between the first normal stress difference, N_1, and die swell (DS), it is possible to predict DS from experimental shear viscosity data. Poly(vinyl chloride) exhibits two distinct flow activation energies, corresponding to the development of a supermolecular flow and a true melt flow, respectively. As a result, in the low temperature range DS increases with temperature, whereas at higher temperatures the opposite effect is observed. It is possible to adapt the above methodology to include both behaviours. The predictions are experimentally assessed.

(Keywords: elasticity; poly(vinyl chloride); melt; die-swell; first normal stress difference; supermolecular flow; morphology; gelation)

INTRODUCTION

The good mechanical properties and unusual rheological behaviour of poly(vinyl chloride) (PVC) probably explain its extensive use in the production of pipes and profiles. However, the nature and multiplicity of the physical and rheological phenomena involved in the process make it a difficult task to design dies to produce products with accurate tolerances.

In practice, predictions of die swell (DS) – ratio of the extrudate diameter to the die diameter – are usually based on typical average percentage values for the material, or on measurements performed in the capillary rheometer. Predictions of die swell can also be developed by making use of correlations between the first normal stress coefficient, θ ($N_1/\dot{\gamma}^2$), where $\dot{\gamma}$ is the shear rate and N_1 is the first normal stress difference, and the shear viscosity function. Through the use of a formulation such as the one resulting from Tanner's theory of unconstrained elastic recovery[1]:

$$DS = [1 + \tfrac{1}{8}(N_1/\tau)^2]^{1/6} \qquad (1)$$

where τ is the shear stress, predictions of DS may then be inferred.

Among the available correlations[2–5], those developed by Gleissle and Wagner produce good results for a number of polymers and testing conditions[6]. Wagner's approach, resulting from a Bernstein, Kearsley and Zapas type of single-integral constitutive equation[7], is mathematically simple and only requires the available experimental shear viscosity data:

$$\theta(\dot{\gamma}) = -\frac{1}{n}\frac{d\eta(\dot{\gamma})}{d\dot{\gamma}} \qquad (2)$$

where n is a damping constant, describing the non-linearity of the model (with values between 0.13 and 0.20) and $\eta(\dot{\gamma})$ is the shear viscosity function.

Gleissle defines 'mirror relations', but requires the assumption of a trend for the shear viscosity function outside the experimental range. He also corrects the results by an empirical factor k, with values in the range 2 to 3.

Thus, if the shear viscosity function is described by a Munstedt-type polynomial[8] (of degree 2), if the effect of temperature is included through the introduction of a shift factor, a_T, and if Wagner and Tanner formulations are coupled, the die swell is given by:

$$DS = \left[1 + \frac{1}{8}\left(\frac{a_1 - 1 + 2a_2 \log(a_T\dot{\gamma})}{n}\right)^2\right]^{1/6} \qquad (3)$$

where a_1 and a_2 are the first- and second-order coefficients of the Munstedt polynomial.

With this methodology it is possible to predict the elastic behaviour of a melt within a continuous temperature range, provided a master shear flow curve at a reference temperature (typically obtained with a minimum of three shear flow curves at different temperatures) is available. Equation (3) assumes a true molecular flow, and hence a decrease of die swell with increasing temperature.

SUPERMOLECULAR FLOW AND DIE SWELL

Berens and Folt[9] showed that, within the usual processing temperature range, PVC develops a supermolecular flow. The development of such a flow had been previously identified while studying the rheology of elastomers[10]. The corresponding anomalous rheological behaviour has been discussed by several authors[11–14]. One of its main consequences is the increase in the elasticity of the melt with increasing temperature, i.e. die swell increases with increasing temperature. This behaviour has been frequently observed[11,13–18] and interpreted as evidence of the progressive fusion of the particles initially present. In fact, the increase in elasticity

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with temperature has been extensively used as a basis for assessing gelation of PVC[19].

The term 'gelation' is associated with the process of progressively changing the particulate morphology of the virgin material into a network of entanglements and crystallinity. Not only is the original morphology of a grain of PVC complex, several hierarchies of particles being identifiable[20], but also the final three-dimensional order may arise from both original crystallinity surviving the process and that formed upon cooling. Also, the mechanism of gelation is believed to be associated with the intensity of shear upon processing. Thus, the unit of flow probably depends on the route to gelation and the level of fusion attained[21–24]. At higher temperatures (high degree of gelation) a true melt flow may be expected[12], but this behaviour is difficult to observe owing to the intrinsic thermal instability of the material.

Therefore, equation (3) can only be used to predict the die swell of PVC compounds at temperatures above the onset of true melt flow (denoted T_x). However, since n (see equation (2)) is a material parameter associated with the maximum recoverable shear strain, one can speculate that below T_x the effect of temperature on viscosity and n will be similar. Thus, in this case, in equation (3) n is replaced by $(n'a_T)$, where n' is Wagner's coefficient at the reference temperature (i.e. temperature used to represent the master shear flow curve). Die swell will now increase with temperature:

$$DS = \left[1 + \frac{1}{8}\left(\frac{a_1 - 1 + 2a_2 \log(a_T\dot{\gamma})}{n'a_T}\right)^2\right]^{1/6} \qquad T < T_x \tag{4}$$

The onset of the true melt flow T_x can be detected by adopting the technique previously presented by Collins and Krier[25], who showed that PVC melts exhibit two distinct flow activation energies, a low ΔE at low temperatures and a high activation energy at high temperatures. This suggests a different rheological behaviour in the low and high temperature ranges. The transition occurred at approximately 200°C, where gelation is usually reported as reaching significant values[23,24]. However, it should be remembered that the melting point of the crystalline material is frequently reported to be in the range 200–260°C[11,12,21]. This seems to indicate that, although the contribution of crystallinity to the anomalous rheological behaviour of PVC compounds should be recognized, the particulate nature of the flow is probably predominant[12]. Hence, it should be possible to switch from one flow behaviour to another below a certain degree of crystallinity.

Collins and Krier also showed that changes in the rheological behaviour are more easily detected when ΔE is computed at constant shear rate, especially at low values of $\dot{\gamma}$, than at constant shear stress.

The rheological anomalies detected by capillary rheometry may be induced not only by the development of a supermolecular flow, but also due to slip of the melt at the wall caused by the presence of certain additives (e.g. external lubricants) in the compound. The existence of supermolecular entities due to structural order can be detected via differential scanning calorimetry (d.s.c.). It has been shown[23,24] that d.s.c. detects the crystallinity present upon processing, as well as that developed upon cooling. Since the method can be used to assess the degree of fusion[23], it also provides indirect information on the nature of the morphology probably present at the different stages of the process, provided a model for gelation is available.

In the remaining sections of this paper equations (3) and (4) will be experimentally assessed by comparing their predictions with the experimental values available for a range of materials and processing conditions.

Some degree of error can be anticipated in the predictions, as the result of the possible interactions between several factors:

(i) The Tanner and Wagner models may carry some inaccuracy. Tanner's formulation cannot cope with dies with different L/D ratios.

(ii) The shift factor may not completely superimpose the shear flow curves at different temperatures.

(iii) Any variations of the residence time of the material inside the capillary rheometer may well affect both the shear and the elastic characteristics. Thermal degradation may also develop.

(iv) There are practical difficulties in measuring the die swell due to distortions of the extrudate, draw-down and shrinkage upon cooling.

Anyway, given the practical relevance of this subject, it is believed that if only small errors are observed the adequacy of the technique will be implicitly proved.

EXPERIMENTAL

A number of commercial rigid and plasticized compounds, manufactured by independent companies, were selected for this study. *Table 1* identifies them and indicates the temperature range over which they were tested.

Master flow curves were obtained in a Daventest Capillary Rheometer, using a computer program developed for monitoring and processing the experimental data[26]. A set of dies with L/D ratios of 1, 7.5 and 10 was used, the extrudates from the latter being collected for measuring the die swell. For each temperature and compound, small lengths of extrudate were cut and dropped into cold water, to avoid subsequent shrinkage. The cross-sections of the extrudates were measured from photographs taken from a stereomicroscope using a × 16

Table 1 The commercial plasticized and rigid PVC compounds used[a]

Material	Temperature range (°C)	n'
Dorlyl GPC650 (blow moulding)	190–210	0.145
Gaplas T04/23 (piping)	190–210	0.258
Norsk Hydro VH647 (medical tubing)	150–180	0.388
Rio Rodano Plastirex 5219 (blow moulding)	170–210 $T_x = 200$	0.221
BF Goodrich[15] Geon 8700A (profiles)	180	0.230
BP Chemicals[24] Breon S110/11 (profiles)	190	0.193
Atochem Lucalor (piping)	205	0.233

[a]Norsk Hydro VH647 is a plasticized PVC (PPVC). Others are rigid unplasticized PVC (UPVC); Lucalor is a chlorinated PVC (CPVC)

magnification. Even in the absence of flow defects, the extrudates were frequently distorted. Thus, the method used, although time-consuming, proved to be adequate.

Small samples of the compounds were scanned from room temperature up to 240°C at 20°C min^{-1} in a Perkin–Elmer DSC7 differential scanning calorimeter coupled to a 3700 Data Station. Processing under different conditions was simulated in the d.s.c. by performing a previous heating programme up to a set temperature, followed by fast cooling. With this technique it became possible to detect the structural order present and to infer, from the degree of gelation defined by the corresponding gelation curve, the morphology developed.

The degree of gelation was computed from[23]:

$$\text{gelation level} = \frac{\Delta H_{\mathrm{A}} - \Delta H_{\mathrm{A,min}}}{\Delta H_{\mathrm{A,max}} - \Delta H_{\mathrm{A,min}}} \times 100 \qquad (5)$$

where ΔH_{A} is the enthalpy of the sample, and $\Delta H_{\mathrm{A,max}}$ and $\Delta H_{\mathrm{A,min}}$ are the maximum and minimum values observed, respectively. Normalized gelation curves were obtained by plotting gelation levels against the processing temperature.

The full characterization of the gelation mechanism of a PVC compound would require heat treatment to relatively high temperatures. However, the use of the capillary rheometer above the experimental range defined in *Table 1* would induce degradation of the compounds, hence affecting the validity of the results obtained.

It was therefore decided to characterize the degree of gelation of the extruded samples (in the rheometer) using the data obtained with the d.s.c. for the same heating temperature. This procedure should be reasonably valid, since the capillary rheometer was used with limited levels and time of shear. Applying these results to practical extrusion implies detecting the real melt temperature (which results from the combined effect of conduction and shear), which can be done using the d.s.c.[23].

RESULTS AND DISCUSSION

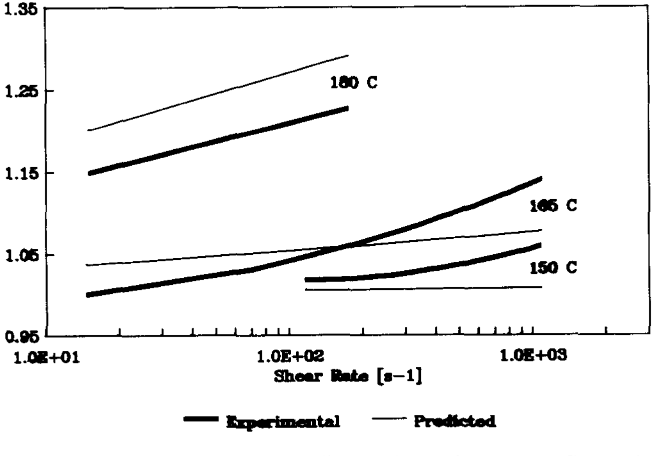

Figure 1 Experimental and predicted die swell for PPVC Norsk Hydro VH647

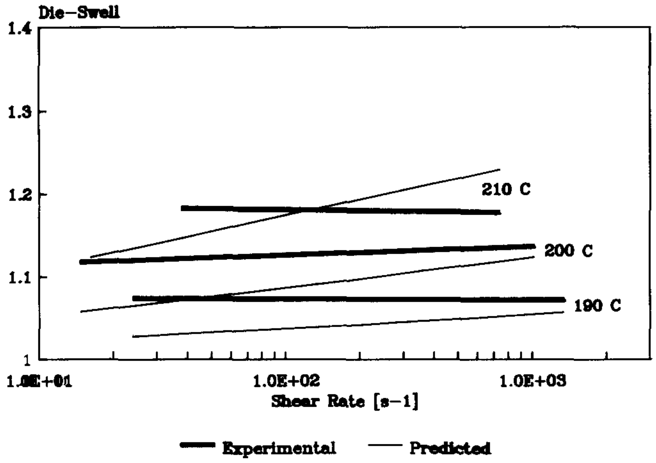

Figure 2 Experimental and predicted die swell for UPVC Gaplas T04/23

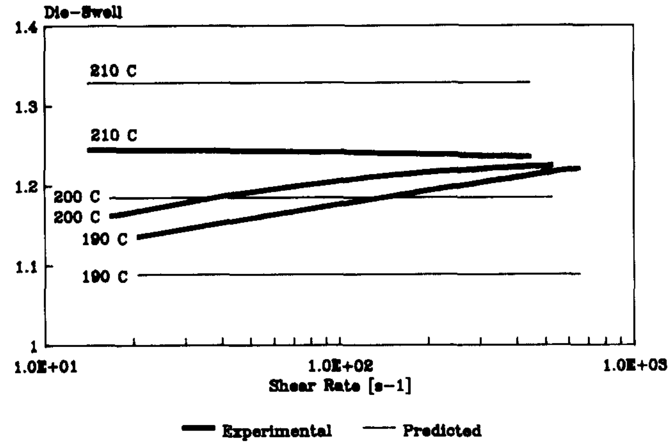

Figure 3 Experimental and predicted die swell for UPVC Dorlyl GPC650

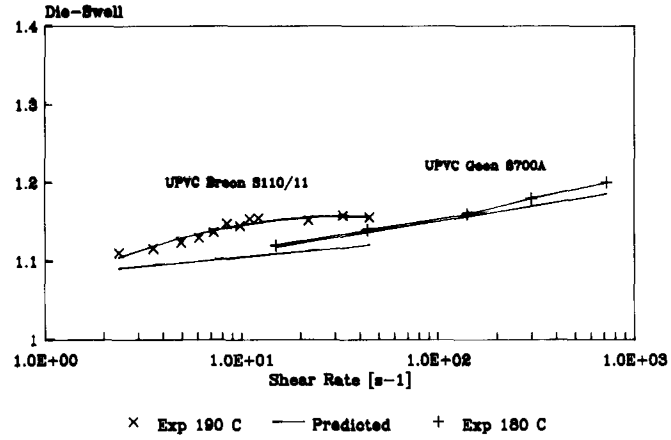

Figure 4 Experimental and predicted die swell for two UPVCs, BF Goodrich Geon 8700A and BP Chemicals Breon S110/11. Predictions were made using an average value of n' (0.235)

Figures 1 to *4* compare the experimental with the predicted values of die swell for several PVC compounds. Errors were usually below 5%. The predictions were made using equation (4) and a master shear flow curve, obtained from flow curves at three different temperatures. The value of the n' parameter at the reference temperature was numerically adjusted, using a software package.

The experimental die swell curves were obtained from polynomial regressions of the experimental values of die swell at various shear rates. The predictions were made using equation (4), which assumes a Munstedt-type polynomial of degree 2. Experience has shown that generally this degree correctly describes the rheological shear behaviour of PVC compounds. With the exception of the material depicted in *Figure 2*, the predicted die swell varies less with shear rate than the corresponding experimental values. This is due to the power 1/6 appearing in equation (4). The predictions are independent of the shear rate (see, for example, *Figure 3*) when a polynomial of degree 1 is adopted to describe the shear flow curve ($a_2 = 0$).

The experimental results shown in *Figure 4* were taken from the literature[15,27]. As they were accompanied by shear flow curves for one temperature only, the value of n' was numerically adjusted for each material. However, since these formulations and the Gaplas compound were developed for similar applications (unplasticized compounds for extrusion of pipes or profiles), an average n' was used in the predictions presented.

The comparatively poor results obtained for the compound studied in *Figure 3* are probably explained by its shear behaviour throughout the experimental range. As can be seen from *Figure 5* the activation energy is highly dependent on shear rate, hence creating difficulties in the superposition of the individual shear flow curves at different temperatures (necessary to obtain a master flow curve).

The results presented so far show, for the range of temperatures tested, an increase in die swell with increasing temperature. This should correspond to the development of a particulate flow. This hypothesis can be verified by checking eventual changes with temperature in the shape of the flow curves (they cannot be detected as shown in *Figure 5*), or by using d.s.c. to identify the presence of structural order and to assess gelation.

Figure 6 shows the variation of the enthalpies of the initial crystallinity surviving processing (denoted B) and that formed upon cooling (denoted A) with the processing temperature, for one of the compounds studied. Despite the practical difficulty in measuring the areas of the B peak (beyond 200°C they usually become smaller than 0.15 J g^{-1}), it appears that, even at the maximum temperature used in the capillary rheometer (210°C), there is still some surviving primary crystallinity.

Figure 7 shows the corresponding normalized gelation curves. Relatively small degrees of gelation (60 to 70%) are attained, probably due to the lack of shear (at normal extrusion conditions a significantly higher degree would be observed). Under these conditions, not only is some degree of crystallinity still present, but primary particles (or even remains of grains) are to be expected[22,23].

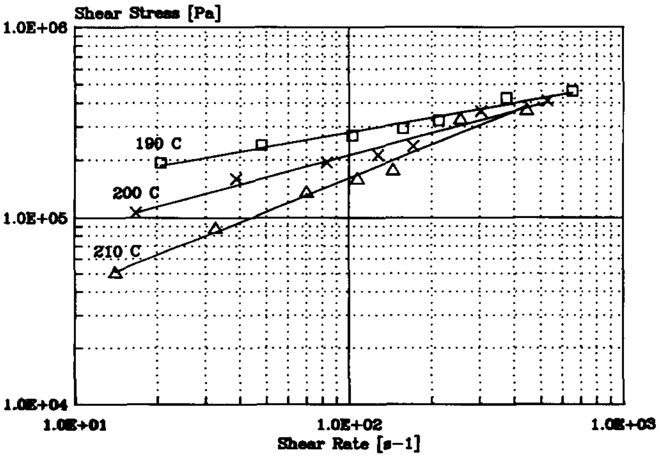

Figure 5 Shear flow curves at three temperatures for UPVC Dorlyl GPC650

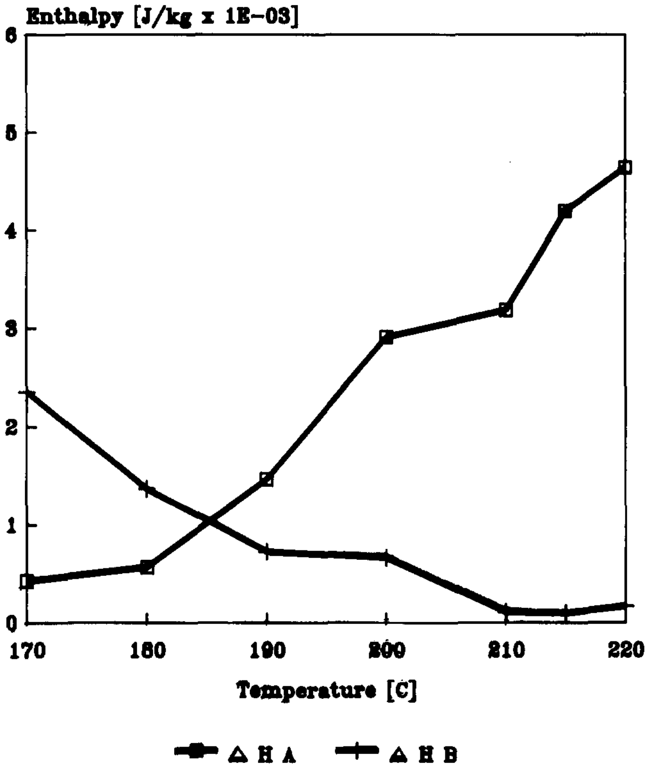

Figure 6 Evolution of crystallinity formed upon cooling (ΔH_A) and that surviving processing (ΔH_B) with temperature, for UPVC Gaplas T04/23

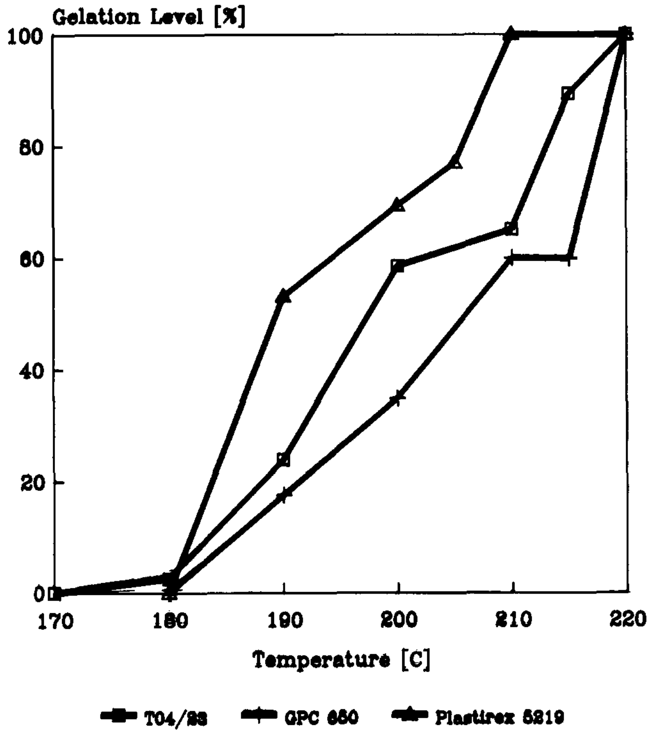

Figure 7 Normalized gelation curves for UPVC Gaplas T04/23, UPVC Dorlyl GPC650 and UPVC Rio Rodano Plastirex 5219

Figure 7 also includes the gelation curve of the Plastirex compound, which exhibits 100% gelation at 210°C. This

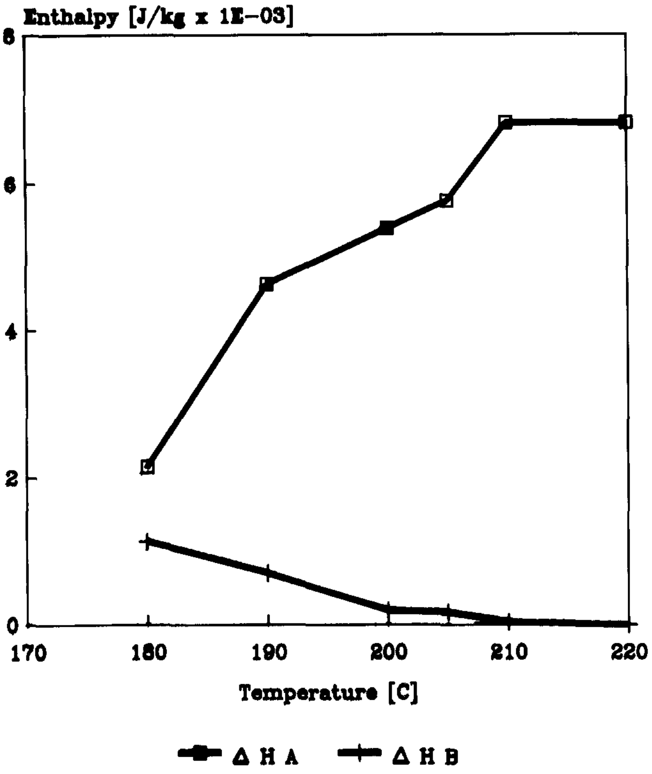

Figure 8 Evolution of crystallinity formed upon cooling (ΔH_A) and that surviving processing (ΔH_B) with temperature, for UPVC Rio Rodano Plastirex 5219

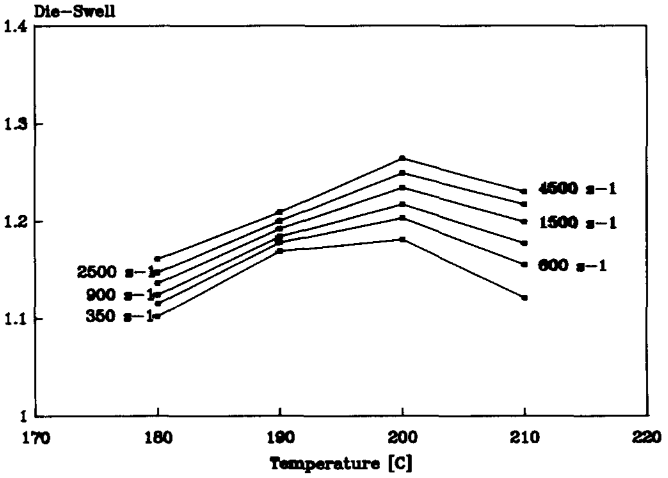

Figure 9 Variation of die swell with temperature, at constant shear rate, for UPVC Rio Rodano Plastirex 5219

could indicate a behaviour that is different from the one reported for the other materials. Indeed, when the enthalpies of the A and B peaks are plotted against the processing temperature (*Figure 8*), no evidence can be found of the presence of unmelted material beyond 210°C. Full gelation and the absence of structural order (at and above 210°C) provide the conditions for the development of a true melt flow. Thus, this compound allows one to test the applicability and validity of equations (3) and (4).

Figure 9, presenting the variation of die swell with temperature at several shear rates for the Plastirex compound, confirms the relevance of the data presented in *Figure 8*. Die swell increases with temperature while the material develops a particulate flow, but in the higher temperature range, once all the material is melted, a more conventional behaviour is observed. The existence of a transition temperature, where there is a change in the rheological properties of the material, is also apparent in *Figure 10*, which presents the flow curves at temperatures ranging from 170 to 210°C. The curves are nearly linear in the double-logarithmic plot at lower temperatures. At 210°C the shape of the flow curve is more similar to that observed with conventional polymers such as polystyrene[13], with the development of a region with a Newtonian-like behaviour at low shear rates. The levelling-off of the flow curve at high shear rates could be due to slip at the wall, although these effects are usually expected to decrease with increasing temperature[24].

If the proposed methodology of predicing the elastic behaviour of the Plastirex compound is to be applied, T_x should be defined from knowledge of the variation of the flow activation energy with temperature. When a_T (which is directly related to ΔE) is computed at constant shear stress (*Figure 11*), no change in the slope can be detected with certainty. When the process is carried out at constant shear rate, as recommended by Collins and Krier[25] (*Figure 12*), and special care is taken in analysing the curves corresponding to the lower shear rates, two slopes can be distinguished, below and above 200°C. In

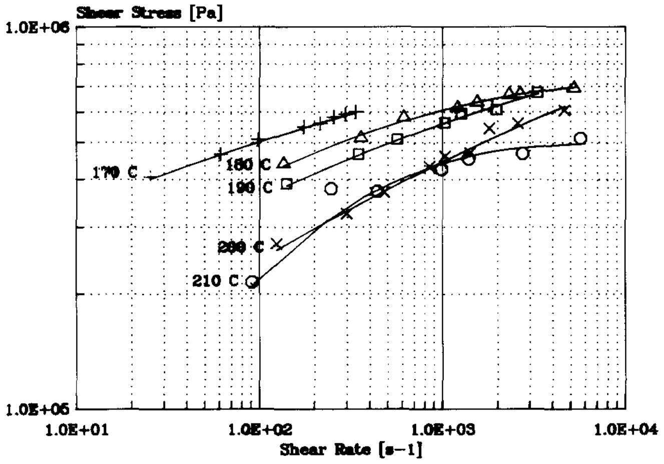

Figure 10 Shear flow curves for UPVC Rio Rodano Plastirex 5219

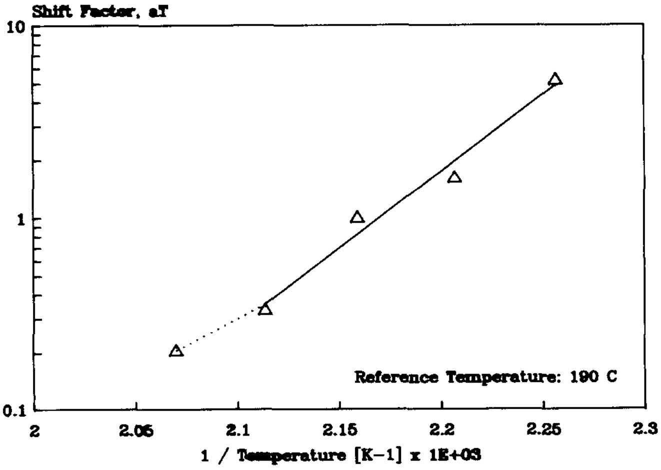

Figure 11 Shift factor, a_T, computed at constant shear stress, using 190°C as reference temperature (UPVC Rio Rodano Plastirex 5219)

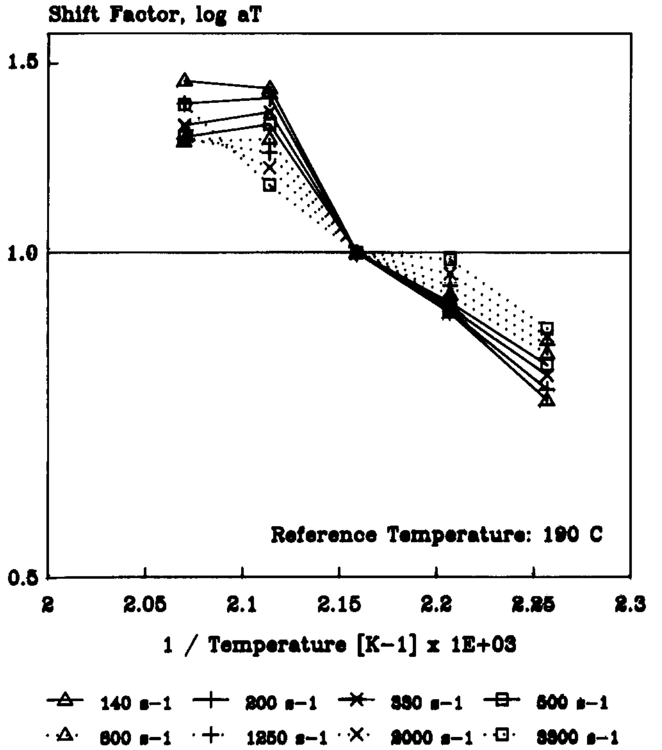

Figure 12 Shift factor, a_T, computed at several constant shear rates, using 190°C as reference temperature (UPVC Rio Rodano Plastirex 5219)

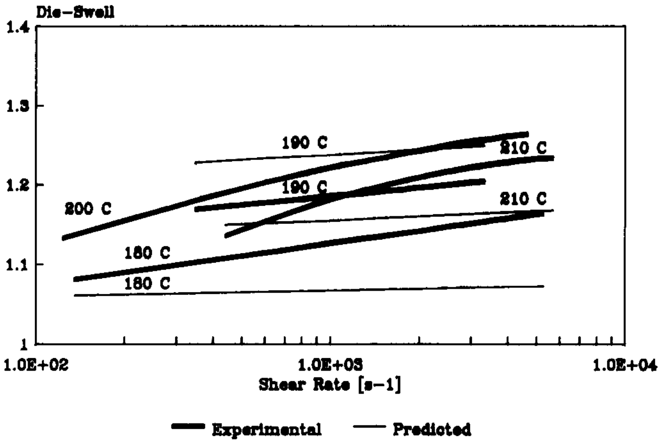

Figure 13 Experimental and predicted die swell for UPVC Rio Rodano Plastirex 5219

both cases 190°C was taken as the reference temperature, i.e. at this temperature $a_T = 1$. Thus, 200°C should correspond to T_x, which correlates well with the values reported in the literature[12,21,25].

When equations (3) and (4) are applied in their respective range of validity, the curves presented in *Figure 13* are obtained. The figure compares the predictions with the values measured. The model predicts an increasing die swell with increasing temperature up to 200°C and a decrease thereafter. It also predicts similar values of die swell at 190 and 210°C, which is confirmed in practice. The predicted die swell for 200°C lays outside the graph scale. The corresponding significant error in the prediction (around 20%) is the result of assuming a linear dependence of the die swell upon temperature throughout the two types of rheological behaviour, whereas, in practice, the transition between particulate and true melt flows is probably gradual. With the exception of this temperature, errors are kept below 5%.

CONCLUSIONS

Despite the obvious lack of further data to support this hypothesis, the methodology presented in this work seems to be able to predict adequately the elastic behaviour of PVC melts in the practical range of processing conditions.

The elastic properties of PVC melts correlate well with the current ideas on gelation and are well explained by the development of a particulate flow at lower temperatures and the progressive tendency for a true melt flow at high temperatures.

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