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RHEOLOGICAL FUNCTIONS AND PROCESSING BY EXTRUSION AND STRETCHING OF PVC BIAXIALLY ORIENTED SHEETS

J.C. CHAUFFOUREAUX

Central Laboratory, SOLVAY & CIE, S.A., Brussels

Abstract - A description and a general survey of the design and the running conditions of an industrial production line of biaxially oriented corrugated PVC sheets is made to show how rheology can help processing.

Choice of additives of the PVC and running conditions of the extruder are done by using friction, gelation and flow properties of the PVC in the solid and in the molten states. Stretching and corrugation parameters are related to the tensile properties of the PVC in the rubbery state. Dimensional stability of the corrugated sheet depends on the internal stresses frozen during the cooling.

INTRODUCTION

During the last ten years, a great evolution occured in the processing of PVC by extrusion, injection moulding, coating and calandering. Higher output rates, lower labour content, introduction of micro or minicomputers and the fabrication of more sophisticated products characterize that evolution.

Making manufactured products at the lowest cost, to be able to compete with other raw materials without loosing a good profit, is the guide line of the expansion of the PVC processing industries. To succeed, it was necessary to improve the basic knowledge on polymer rheology and processing. In particular, the relationships between the rheological functions of PVC, the processing modes and the properties of the manufactured product were needed to program the miniprocessors used to monitor the lines and to work out the feed back loops.

To show how rheology is a basic tool to design and to use modern industrial facilities, we have chosen to analyse the manufacturing of biaxially oriented PVC corrugated sheets at high output rates.

PRODUCTION OF BIAXIALLY ORIENTED PVC CORRUGATED SHEETS

A schematic diagram of the plan designed by Solvay & Cie to produce these sheets is given in figure 1.

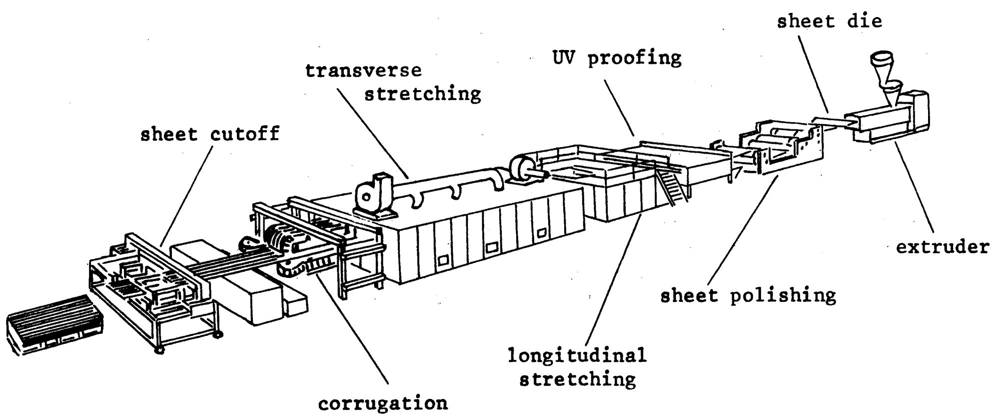


Fig. 1. Extrusion - Corrugation of biaxial oriented PVC sheets

The powder compound and the scraps are mixed, melted and shaped in a cascade single screw extruder provided with a filter and a flat die at an output which varies between 600 and 750 kg/h regarding the size and the thickness of the manufactured product. The molten sheet - 3 to 5 mm thick - is polished in the three rolls calander and a special treatment of the surfaces is made to increase the UV resistance of the PVC. The biaxial stretching is made in a two step process. The balance between the orientation in the machine and the transversal direction is made during the corrugation.

After cooling, the sheet is cut in standard size pieces. The control of the plant is made by a minicomputer.

ANALYSIS OF THE REQUIREMENTS ON THE RAW MATERIAL

The specifications on the quality of the corrugated sheets are given in figure 2.

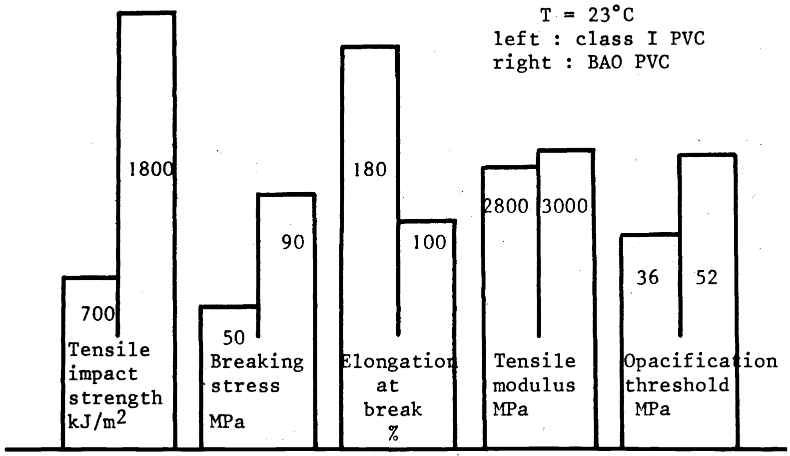


Fig. 2. Properties of the corrugated biaxially oriented sheets

To succeed in making such a sheet, it is necessary to follow severe rules for the choice of the quality of the PVC and the processing additives.

A high molecular extrusion grade of PVC and additives which allow to reach a good gelation without decreasing the HDT of the polymer must be used. These requirements are indispensable to obtain a sheet which can be biaxially stretched enough to reach the needed impact resistance and to prevent shrinkage during its life time.

Moreover, the thermal stability of the powder compound obtained by mixing the polymer and the additives must be high enough to allow a continuous extrusion at high output rate in a non stop process for a few weeks.

Only additives which do not decrease the weatherability of PVC can be used.

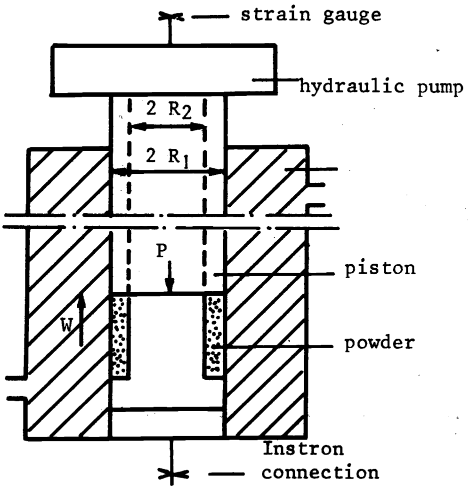
ANALYSIS OF THE MAIN FUNCTIONS OF THE PRODUCTION LINE

Starting from the feeding section and going to the sheet cutting device, we can determine a large number of processes which will have a strong effect on the running of the production unit and the quality of the sheets.

Feeding of the screw and displacement of the solid bed

In a single screw extruder, the maximum output rate is strongly related to the friction coefficients of the solid bed on the barrel and the screw surfaces (Ref. 1).

The structure of the PVC powder and the additives, mainly lubricants and fillers, can have a strong effect on these properties and modify the running of the extruder (Ref. 2). To measure the friction properties and mainly the synergistic effects generated by a combination of additives of different kinds, two apparatus have been used (figures 3 and 4).



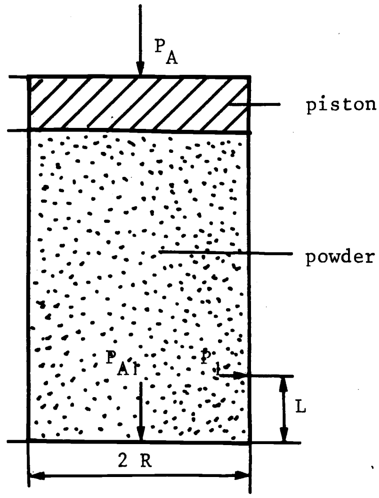


Fig. 3. Friction stress measurement
Fig. 4. Lateral pressure transmission coefficient measurement

The friction stress is measured with a special device (figure 3) added to an Instron tester. The powder undergoes an hydrostatic pressure generated by an hydrolic system. During the displacement of the piston, the friction stress of the powder against the barrel is measured. The temperature can be fixed between 23°C and 240°C.

$$\mu k = \ln \frac{P + W}{P} \quad \frac{(R_1^2 - R_2^2)}{2\ R_1 L}$$

where :

μ is the friction coefficient
L is the lateral transmission coefficient of pressure
P is the external pressure applied on the powder
W is the friction stress per unit of surface
R_1, R_2 are the inner and outer radii of the ring of powder
L is the length of the ring of powder

The lateral pressure transmission coefficient is measured with the apparatus shown on figure 4 following an experimental procedure described by Wales (Ref. 3).

$$k = \frac{P_1}{P_{A1}}$$

where :

k is the lateral transmission coefficient
P_1 is the pressure measured at the wall of the cylinder at high 1
P_{A1} is the axial pressure at the same level is the powder

Some results obtained are shown on figure 5.

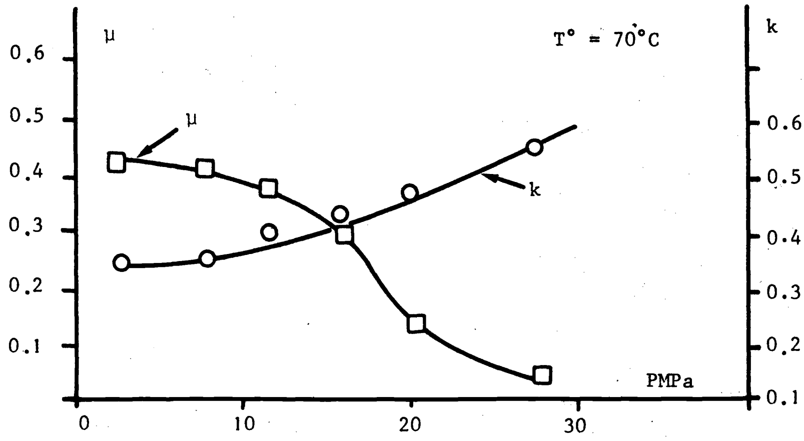


Fig. 5. Friction and lateral transmission coefficients of a rigid PVC at 70°C

They can be used to simulate numerically the work generated in the feeding section of the extruder and to correlate the effect of a modification of the composition of the compound on the processing.

Gelation of the PVC and homogeneization The gelation begins into the thread of the first screw and ends into the second screw. The cascade extruder thus breaks the solid bed when the melting efficiency is still high, mixes it with the meltpool and causes very quickly its vanishing and the homogenization of the melt.

The plastirecorder can be used to foresee the processing of the PVC powder compound and to improve its setting (Ref. 4).

Some results obtained during the mixing of a translucent composition are given in figure 6.

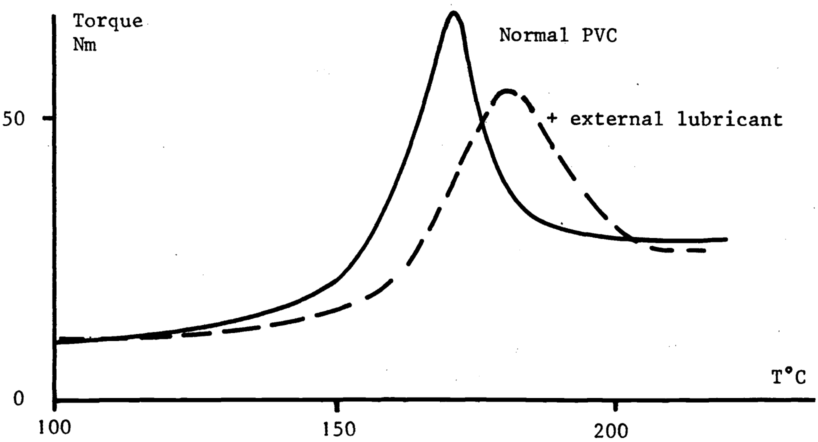


Fig. 6. Gelation of rigid PVC in a plastirecorder

The modification of the quantity of lubricant has a strong effect on the gelation conditions, mainly the maximum torque, the mixing time needed to obtain the gelation, the temperature at which this modification of structure occurs, the homogenization of the molten polymer.

Filtration-shaping-polishing
The quality of the thick sheet and the time length of extrusion without any thermal degradation and contamination by "black points" will depend on the flow conditions into the filter and the die. The lubrication must be efficient enough to prevent sticking and degradation of the PVC at the wall of the flow channels (external lubrication) and to keep the temperature of the melt as homogeneous and as low as possible (internal lubrication) (Ref. 5).

Migration of additives (fillers, lubricants, ...) generated by variations of pressure through the melt can create sedimentations on the walls or on other pieces of the equipment like the screw head, the pressure bar of the flat die or the walls of the converging channel at the exit of the filter (Ref. 6, 7).

The slipping effect induced by the external lubricants can be measured by using different experimental devices (Ref. 8, 9, 10).

Generally, the plastirecorder and the capillary viscosimeter are used to select the additives which will give a slip velocity at the wall high enough to prevent thermal degradation during the flow. More sofisticated methods are used when exact figures are needed to feed a computed simulation program.

An exemple of the effect of an external lubricant on the slip velocity at the wall of a die is given in figure 7.

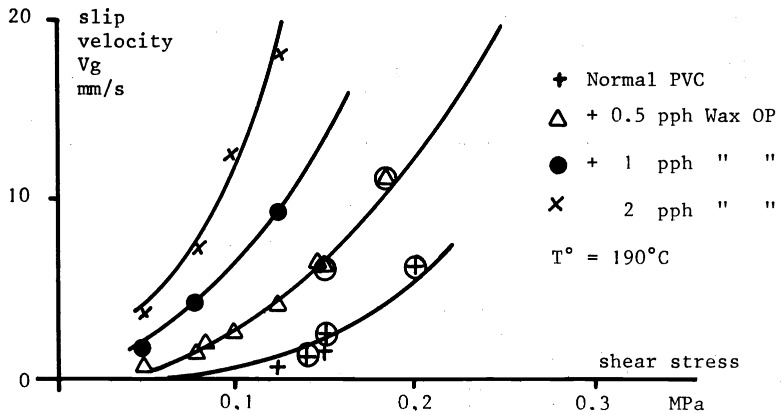


Fig. 7. Slip velocity versus shear stress at the wall

As each modification of the composition of the PVC compound can also have an effect on the running of the extruder and on the quality of the manufactured product, it is sometimes easier to fit the geometry of the flow channel to reach stationnary conditions allowing a long time length extrusion without thermal degradation. An exemple of that situation is given in figure 8 for the flow of the PVC through the filter and the converging channel (cross section decreasing continuously) which connects that part of the equipment to the die.

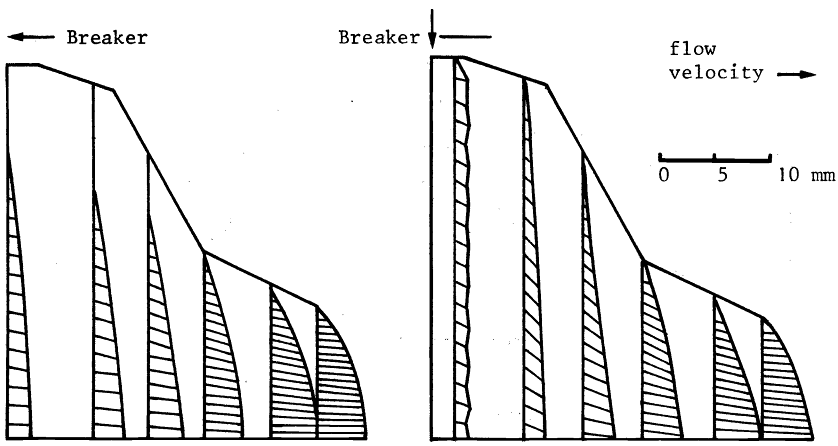


Fig. 8. Flow of rigid PVC through two filter devices

The risk of a thermal degradation are reduced without being obliged to change the lubrication. These sections were calculated by numerical simulation using a finite element program and a newtonian isothermal model to approximate the flow of the melt.

The shaping of the PVC is made with a 740 to 870 mm width slit die. The internal structure of the PVC particles as well as the processing conditions like the stability of the extruder can have a strong effect on the quality and the steadiness of the sheet.

The three curves given in figure 9 are related to PVCs of same K number and molecular distributions.

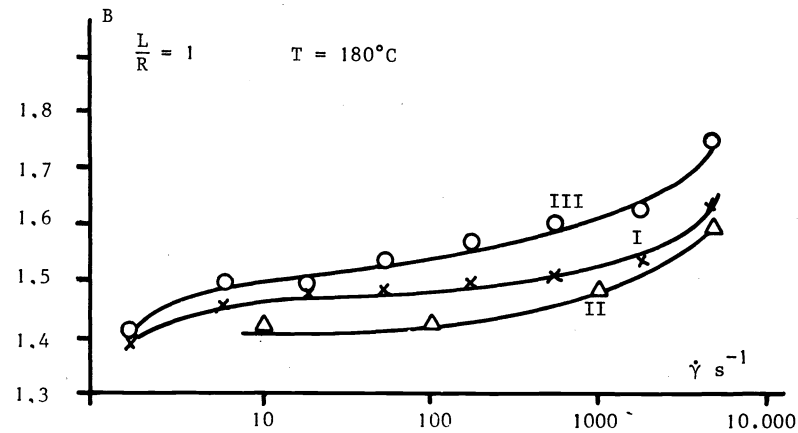


Fig. 9. Effect of the structure of PVC on the swelling

A modification in the structure of the PVC particles (curves I and II) or in the processing conditions (curves I and III) changes the swelling of the extrudate and the viscoelastic behaviour of the melt. This very well known phenomenon (Ref. 11) is a result of the nature of the rheological units which can be found in the flow of PVC. In normal processing conditions, time, temperature and shear stresses have an effect on the size of these units. More and more elasticity is developed in the flow when the temperature increases but stays below a limit value of about 210°C for a 65 K value PVC. Above that value and in the limits of the normal processing conditions, the structure of the rheological units seems to stay less dependent on temperature and the viscoelastic properties of the melt changes with the temperature by the same way than other polymers like PS, PE, PP (Ref. 12).

The shaping of the melt is characterized by strong elastic effects and a long memory of what has happened before flowing through the die. That is the reason why it is often necessary to add in the compound high molecular weight additives which have an effect on the long relaxation times of the melt (figure 10).

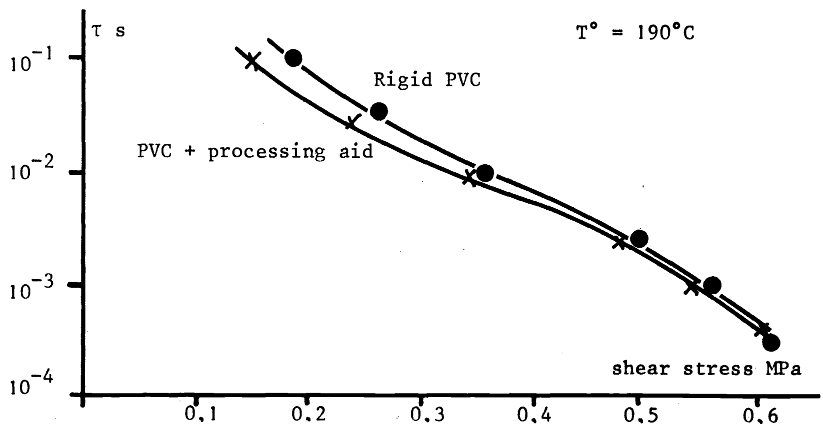


Fig. 10. Effect of MBS processing aid on the relaxation time of PVC

For the same reason these additives act as processing aids. They decrease the dependence on the gelation in small variations of the processing conditions, increase the stability of the flow through the extruder and allow an easier polishing of the surfaces of the sheet between the rolls of the calender. These effects are a result of the interactions between the processing-aids and the external lubricants of PVC.

Biaxial stretching

The impact resistance of rigid PVC decreases very quickly when the temperature falls from room conditions below 0°C. It is mainly true for cristal clear PVC sheets which are stabilized with organic tin molecules and do not contain impact modifiers. The biaxial orientation of the PVC molecules in the sheet plane increases strongly the impact resistance at room temperature and reduces its temperature dependence as shown in the next table.

TABLE. Impact resistance of a rigid PVC sheet

Temperature	Resilience in tensile impact test	
	Normal PVC grade	Biaxially oriented PVC
23°C	600 kJ/m^2	1600 kJ/m^2
0°C	280 "	1600 "
-20°C	215 "	1600 "
-40°C	<200 "	1580 "
-60°C	<200 "	1570 "

It is chiefly true for the resistance to the impact of hailstones for sheets used as roof covering.

By the same way, the laminated structure created in the PVC by biorientation decreases the effect of weathering on the impact resistance (figure 11).

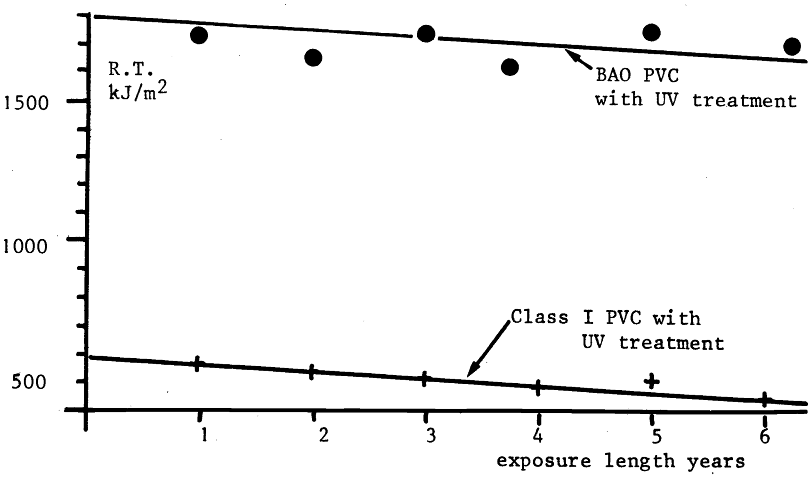


Fig. 11. Effect of biaxial orientation on weathering resistance of PVC - Impact Test

These are the main reasons why a biaxial orientation treatment is made on the extruded sheet before corrugation.

Above their glassy temperature, most of the amorphous polymers behave as gaussian rubbery networks with junctions points depending of time and temperature (Ref. 13). In rigid PVC the stability of these bonds is rather high because they are mainly induced by the small cristallites of the subprimary particles.

This can be seen in figure 12.

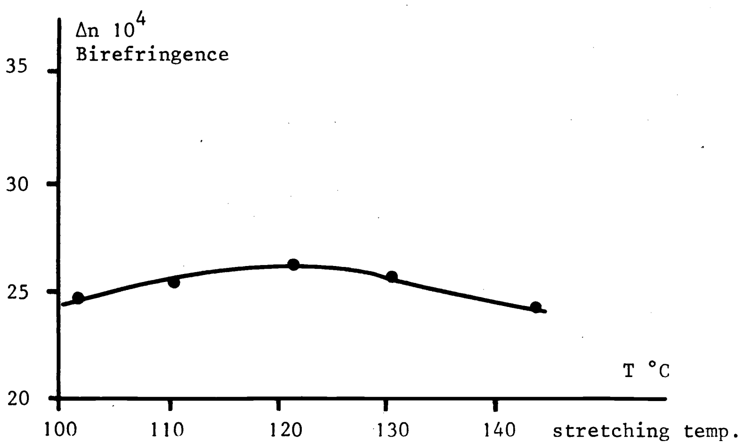


Fig. 12. Effect of temperature on the biaxial orientation of PVC

The temperature dependence of the birefringence induced in a PVC stretched at 200 % of its initial length is very small in the rubbery state. Between 90 and 110°C, for this specially formulated PVC, an increase of the birefringence can even be seen as in a real crosslinked rubber.

By stretching a PVC sheet at the beginning of the rubbery state in two principal directions of its plane, it is thus possible to extend the molecule fractions between the junction points and to form a biaxially oriented structure.

The internal recoverable stresses which can be frozen in the polymer by cooling down to room temperature depends of the elongation, the time length and the temperature of stretching. σ_i can be decomposed in two parts

$$\sigma_i = \sigma_d + \sigma_e$$

σ_d is called hookian or distorsion stress. It is related to a modification of internal energy brought by distorsion of the molecular configuration (bond angles, ...) not related to molecular orientation.

σ_e is the entropic stress generated by the molecular orientation of the PVC.

As σ_d and σ_e are respectively depending of the short and long times of the relaxation spectrum, their own values can easily be found during a stress relaxation experiment above Tg.

Following the gaussian network theory, σ_e is a measurement of the orientation of the PVC (Ref. 14).

$$\sigma_e = G\,(\lambda_r^2 - \frac{1}{\lambda_r^4})$$

where :

G is the shear modulus at the equilibrum
λ_r is the recoverable strain.

The experimental results given in figure 13 show that this theory can be applied to PVC. For the special grade used, temperature (100 to 120°C) and stretching rate (3 to 25 min^{-1}) have a very small effect on σ_e.

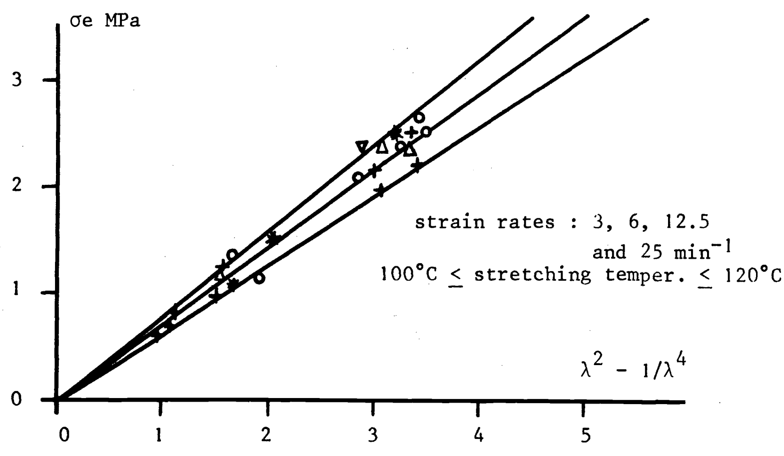


Fig. 13. Biaxial orientation of PVC - Entropic stresses versus recoverable strain

If additives which increase the mobility of the PVC molecules are used (internal lubricants, ...), time and temperature can have a stronger effect on the molecular orientation as shown in figure 14.

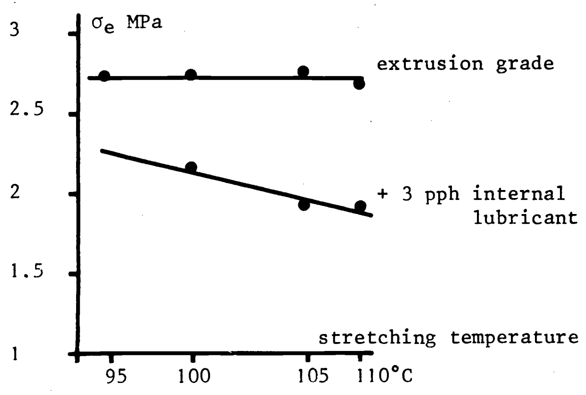


Fig. 14. Biaxial orientation of PVC - Effect of an internal lubricant

As the relative increase of the mechanical properties depends only of the orientation (figure 15), the temperature of treatment must be adapted to the kind and quantity of additives used to process the PVC.

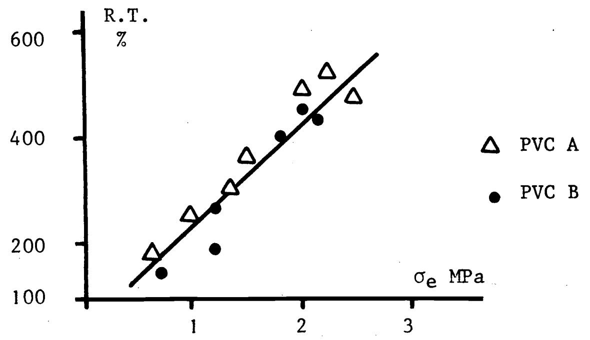


Fig. 15. Biaxial orientation of PVC - Effect of the orientation on the impact strength

Another very important functional property of the sheet is its dimensional stability. Internal stresses frozen in bring a shrinkage when the temperature is increased from room temperature up to the rubbery state. Below Tg, the shrinkage mainly depends on the distorsion stresses and thermal stresses generated by the cooling. Figure 16 shows the difference in shrinkage between two samples which have the same orientation but different internal distorsion stresses. Of course, above Tg, the difference in shrinkage vanishes and all the orientation is lost in both cases.

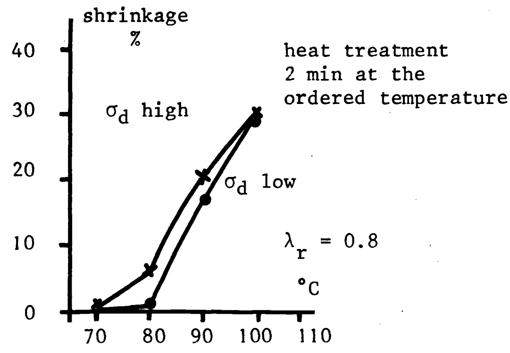


Fig. 16. Shrinkage of biaxially oriented PVC sheets

Additives have also an effect on the shrinkage of biaxially oriented PVC. As they can lower or increase the glass temperature, they can change the mobility of the PVC molecules at a fixed temperature and modify the shrinkage.

In practice, a well formulated and processed PVC can have less than 1 % of shrinkage after 24 h at 70°C. If wrong additives are used, in the same conditions, the shrinkage can reach more than 10 %.

Corrugation and cooling

To keep the molecular orientation brought by the stretching and to balance the internal stresses in the machine and the transversal directions, corrugation is also made in the rubbery state, just above Tg.

The shape and the dimensions of the cooled sheet strongly depends on the temperature of the shaping components. The best stability is obtained when both sides of the corrugated sheet are cooled simultaneously through the Tg to the glassy state. If the cooling is not symetrical, distorsions of the waves can happend when the sheet is reheated to the HDT point.

Conclusions - Control of the process

The control and the monitoring of the plant is subordinated to a good knowledge of the variation effect of the processing parameters upon the quality of the corrugated sheet. Running conditions of the extruder will be automatically adjusted by using the friction, the gelation and the flow data (temperature - torque - pressure - thickness of the sheet). Stretching and corrugation parameters will be related to the tensile properties of the PVC in the rubbery state.

The knowledge of these relationships obtained by the rheological studies of the rigid PVC powder compound in the solid state during the melting and mainly in the molten state are sufficient to allow a monitoring of the process by a computer.

Aknowledgment

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