

## A DISCUSSION OF MOLECULAR ORIENTATION IN PLASTICS PRODUCTS

H. Janeschitz-Kriegl

Linz University, Austria

Abstract - As in many engineering problems, no simple instruction can be given, how to avoid undesired orientations in plastics products. Recently, however, fundamental progress has been made in the understanding of three important aspects:

- a) The mould filling process in injection moulding (interaction of heat transfer and time dependent flow).
- b) The influence of annealing (under the condition of constrained shape) on the birefringence and on the residual capability to free recovery ("heat shrinkage").
- c) The relationship between structural parameters (molecular mass distribution, chain stiffness) and flow properties. The interplay of these aspects will be discussed.

### INTRODUCTION

In general, molecular orientation should be kept within certain limits in injection moulded articles. As is well-known, pronounced orientation leads to anisotropic mechanical properties which, in the wake of quenching stresses, can even cause spontaneous fracture of the moulded article. This is not the place, however, to discuss problems of designers who sometimes can avoid these problems by choosing proper mould designs. In the following, only results, as obtained with a strip-mould, will be discussed. One of the purposes of the present paper is to show how complex the interpretation of birefringence or crystallization patterns can be even in such a simple strip-mould. In general, we are happy if we understand the processes leading to certain features of the end-product. As indicated in the abstract, a discussion will be given of recently gained new insights into these matters.

### OUTLINE OF THE PROBLEMS

As an example for a typical birefringence pattern in a moulded strip of an industrial polystyrene the pattern obtained by Wales et al. (1) is reproduced as Fig. 1. This pattern has been used frequently for comparison with theoretic

TABLE 1. Process Data as Used by Wales et al. (1)

Strip mould: L = 30 cm, B = 7,5 cm, 2 H = 0,2 cm;

Injection time:  $t_i = 2,5$  s;

Temperatures of injection and mould:  $T_i = 250^\circ\text{C}$ ,  $T_m = 50^\circ\text{C}$ ;

Pressure gradient in the mould:  $P' = 1,33 \cdot 10^6$  Pa  $\text{m}^{-1}$ ;

Polymer properties:  $T_g = 100^\circ\text{C}$ ,  $a = 7,05 \cdot 10^{-8}$   $\text{m}^2\text{s}^{-1}$ ,

$\lambda = 1,295 \cdot 10^{-1}$   $\text{JK}^{-1}\text{m}^{-1}\text{s}^{-1}$ .

(Glass-transition temperature  $T_g$ , heat diffusivity  $a$  and heat conductivity  $\lambda$  for polystyrene from Polymer Handbook (25)).

tical predictions (2) because of the accurate characterization of the process of mould filling (see Table 1). In the lower part of the figure the birefringence distribution, as found in the direction of the propagation of the flow front, is shown. This birefringence is measured with the aid of a light beam directed perpendicular on the largest surface of the strip. This distribution shows a maximum at a distance from the (line) gate of about 20% of the total length of the strip. In the upper part of the same figure cross-sectional distributions of the birefringence are shown for four cross-sections located

at the arrows inserted into the lower part. Corresponding measurements are taken on slices cut along the 1,2-plane of preceding flow. One observes that these birefringence distributions show (primary) maxima rather close to the opposite main surfaces of the strip. In Fig. 2 another detail is shown, which has not been mentioned by Wales but which is noticeable on the original pattern of photographed isochromes of this author. This Fig. 2, which is taken from the work by Kamal and Tan (3), clearly shows that besides the just mentioned maximum (C) there is an upswing of the birefringence right into the outer surface (A) (full circles). The birefringence in the 2,3-plane (open circles) is not very pronounced.

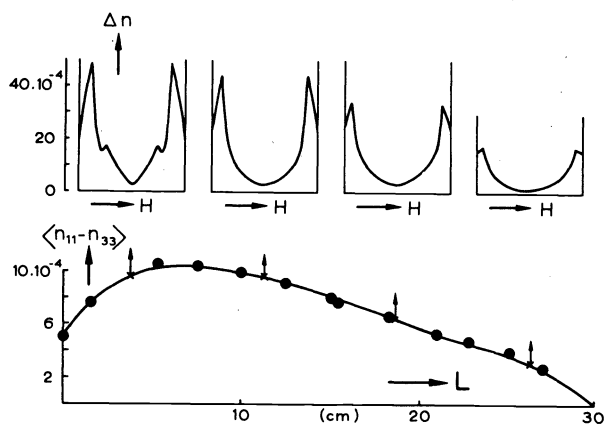


Fig. 1. Distribution of birefringence in an injection moulded strip of polystyrene according to Wales et al. (1).

As is well-known, investigation of the birefringence pattern is not the only way to discover molecular orientations. (In principle, superimposed on the birefringence as caused by the preceding flow there is a birefringence contribution caused by the quenching effect. This contribution has been investigated elsewhere (4). However, it does not seem to disturb the conclusiveness of the patterns with respect to their revelation of the mould filling process.) With crystallizing polymers conclusions can be drawn from the pattern of crystal texture. Another very popular method of determining orientations is the application of the so-called heat shrinkage. The most subtle way is to cut the sample into thin slices before heating these slices to a temperature above glass transition or melting temperature, where the recovery takes place and can be measured (5). (As will be seen, this is the most sensitive method of determining orientations.)

In order to understand orientation patterns in injection moulded samples one is in need of several prerequisites. In principle, a valid theoretical description of time dependent, non-linear polymer properties in non-isothermal flow is required. At the moment, however, no complete description is available, even for the simplest strip mould. So far, three approximate approaches have taught us how to understand textural patterns in a moulded strip:

a) A simplified treatment based on the boundary layer concept, ignoring details of flow, but yielding an easily interpretable result in closed form (explicit dependence on adjustable process parameters). (6) (7) This result is valid for low molecular mass amorphous polymers (no pronounced melt elasticity) and gives an upper limit of layer growth for crystallizing polymers.

b) Very detailed numerical results for an inelastic, not crystallizing, power law fluid of exponential temperature dependence (8).

c) Treatment based on a fictitious process showing some essential similarity with the real filling process, but using a realistic constitutive equation for the polymer melt (9).

As will be shown below we need all the three approaches in order to obtain a

correct qualitative picture of the mould filling process and of the molecular orientation which is a consequence of this process.

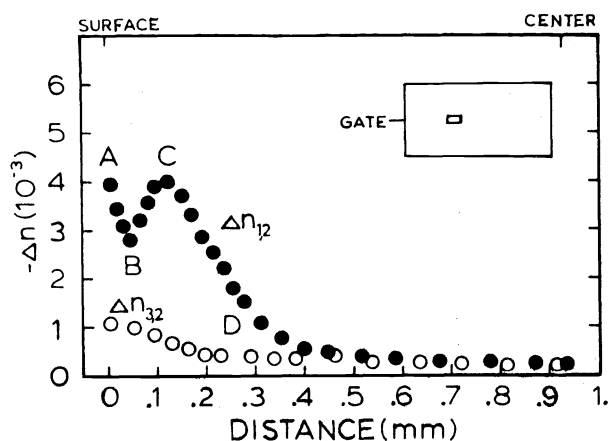


Fig. 2. Gapwise distributions of birefringence in moulded strip of polystyrene at the indicated position, with  $T_i = 218^\circ\text{C}$  and  $T_m = 60^\circ\text{C}$ , according to Kamal and Tan (3).

#### HEAT TRANSFER DURING MOULD FILLING

Two mental experiments are envisaged (7):

a) Examination of the polymer in a cooled open duct possessing inner dimensions identical with those of the strip mould, except for being open at the end: This duct is thought to be fed by a powerful extruder through a narrow line gate extended over the whole width of the duct, in order to maintain a steady polymer stream of the same mean speed as occurring temporarily during real mould filling.

b) Examination of a process familiar from the kitchen: A layer of constant thickness of the hot polymer melt is thought to be wrapped around a hot rolling-pin possessing a circumference equal to the length of the strip mould. Subsequently, after the application of a proper incision (in a direction parallel to the axis of the pin), the polymer layer is rolled down like a dough on a cold plate with a constant speed agreeing with the speed of the flow front during mould filling (this latter speed being identical with the mean speed mentioned in the first experiment).

If in experiment a) the polymer melt stream is sufficiently fast, the duct remains open, the thickness of the solidified layers on the large side walls increasing, according to well-known principles, with the cubic root of the distance from the gate. On the other hand, the layer solidified during the rolling down process (experiment b), is zero at the very end of the strip, where the contact time is zero. This contact time increases linearly with the distance from this end. As a consequence, the thickness of the layer solidified during the latter process increases with the square root of this awkward distance, being highest at the gate where the layer thickness, as found according to the cubic root law, is zero. As is well-known, the cubic root dependence stems from the interaction of prevailing heat convection in the flow direction and heat conduction in the lateral direction. If there is no convection, as in the case of the rolling down experiment, the mentioned square root dependence is found. As a consequence, the layer thickness distribution of the rolling down process forms an outer envelope(2). As a matter of fact, any influence of flow (heat convection or frictional heat production) will reduce the layer thickness. It goes without saying that this envelope is also independent of the flow properties of the polymer.

The final result of these considerations can be expressed by the following equation (7):

$$\Delta = \frac{\theta_g^{-1} \zeta^{1/3} Fo^{1/3}}{\zeta^{1/3} Fo^{1/3} Br + 1} \cdot \left\{ 1 - \exp \left[ -2\theta_i^2 Fo^{1/3} \frac{(\zeta^{1/3} Fo^{1/3} Br + 1)^2}{\zeta^{2/3}} (1-\zeta) \right] \right\}^n \quad \dots(1)$$

where  $\Delta$  is the reduced layer thickness,  $\zeta$  is the reduced distance from the gate,  $Fo$  and  $Br$  are the Fourier and Brinkman numbers, respectively,  $\theta_g$  and  $\theta_i$  are reduced temperatures, and  $n$  is an exponent equal to 0,147. The pertinent definitions of these dimensionless quantities are:

$$\Delta = \delta_o / 2 H \quad \dots(2)$$

with  $\delta_o$  being the vertical distance of the isothermal line of the glass transition temperature from the large side wall, at the moment when the cavity is filled, and  $H$  being the half height of the strip-mould (length  $L$  being large compared with height  $2 H$ ).

$$\zeta = z/L, \quad \dots(3)$$

where  $\zeta$  is the reduced distance from the line gate.

$$Fo = \alpha t_i / 4 H^2, \quad \dots(4)$$

where  $\alpha$  is the (average) heat diffusivity of the polymer and  $t_i$  is the injection time.

$$Br = \frac{2P' \bar{v} H^2}{\lambda(T_i - T_\ell)}, \quad \dots(5)$$

where  $P'$  is the pressure gradient over the length of the strip mould at the moment when the mould is completely filled,  $\bar{v}$  is the speed of the flow front,  $\lambda$  is the (average) heat conductivity of the polymer,  $T_i$  is the injection temperature and  $T_\ell$  is the stagnation temperature to be discussed below.

$$\theta_g = \frac{T_i - T_\ell}{T_g - T_m}, \quad \dots(6)$$

where  $T_g$  is the glass-transition temperature of the amorphous polymer (probably to be replaced by the melting temperature for a crystalline polymer) and  $T_m$  is the mould wall temperature.

$$\theta_i = \frac{T_i - T_\ell}{T_i - T_m} \quad \dots(7)$$

The subscripts of the reduced temperatures coincide with those of the first terms in the denominators. The difference  $T_i - T_\ell$  is considered as a thermo-rheological parameter of the polymer. The stagnation temperature  $T_\ell$  is chosen to be that temperature, at which the zero shear fluidity  $1/\eta_o$  of the polymer is reduced to one per cent of its value at the injection temperature. With the aid of the thermal shift factor, as obtained for polystyrene from the usual time-temperature superposition procedure, one obtains with  $T_i = 250^\circ\text{C}$  a value of  $T_\ell = 180^\circ\text{C}$  (see Table 1).

With the aid of the process data of Table 1, as given by Wales et al. (1), Fig. 3 has been constructed on the basis of eq. (1). Curve I is the mentioned envelope according to the rolling down experiment. Curve II is obtained with  $T_\ell = 180^\circ\text{C}$  according to the concept discussed. Curve III should be valid if  $T_\ell$  would be equal to the glass-transition temperature  $T_g$ . This, of course, is a very unrealistic assumption, since in the derivations leading to eq.(1) the silent assumption is made that the relatively high fluidity, as observed at the injection temperature  $T_i$ , remains unchanged during cooling until the stagnation temperature  $T_\ell$  is reached, where this fluidity suddenly jumps to zero. With  $T_\ell = T_g$  this must lead to a tremendous overestimate of the heat

convection on the retardation of the layer growth, since fluid velocities close to the layer are tremendously overestimated. Even with a  $T_\ell$ , as chosen according to the agreement made above, a slight overestimate of the retardation of layer growth is expected for the same principal reason. An overestimate of the retardation of layer growth is also expected from the way in which the influence of frictional heat (with non-zero Brinkman number) is introduced into the theory (6).

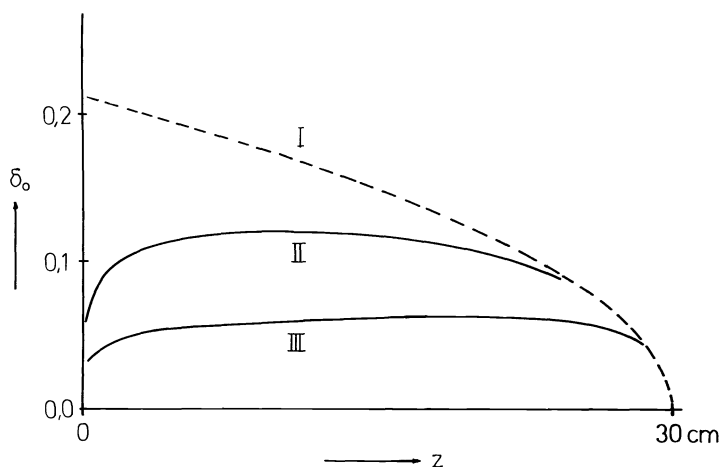


Fig. 3. Isothermal lines of  $T_g$  according to Table 1 and eq. (1): I ... simple penetration theory, II ...  $T_\ell = 180^\circ\text{C}$ , III ...  $T_\ell = T_g = 100^\circ\text{C}$ .

In this respect a look on Fig. 4 is very interesting. Isothermal lines, as calculated recently for the same process conditions by Van Wijngaarden, Dijkstra and Wesseling (8) with the aid of numerical techniques, are shown. These isothermal lines for the glass-transition temperature  $T_g$  hold for several moments during mould filling. If the isothermal line for  $t = 2,5\text{s}$  is considered, one finds a very reasonable agreement with curve II of the previous figure. (It goes without saying that a guess of  $T_\ell$  was no longer necessary for these calculations, in which the fluidity was assumed to change continuously with temperature.) Experimental birefringence distributions like those depicted in the lower part of Fig. 1, as obtained by Wales et al. (1) for incompletely filled moulds, form a striking evidence for the usefulness of Fig. 4.

Finally, two remarks should probably be made. The distribution of the layer thickness will certainly be disturbed in the neighbourhood of the gate, if the design of the gate deviates from that of a narrow line gate. Wales (1) has shown this indirectly with the aid of birefringence patterns. Secondly, one may expect that, with crystallizing polymers, the layer thickness will be smaller than according to eq. (1) (with  $T_g$  replaced by melting temperature) for three reasons: 1) The fluidity will actually show a discontinuity at the boundary of the layer when crystallization occurs. 2) The heat of crystallization must be removed in addition. 3) Undercooling (delay of crystallization because of insufficient nucleation) can cause an additional, unpredictable retardation of layer growth.

#### INTERRELATION BETWEEN BIREFRINGENCE PATTERN AND MOULD FILLING

In his original paper (6) the present author has supposed that, at any distance  $z$  from the gate, the ordinate of the isothermal line for  $T_g$  is identical with the distance of the primary birefringence maximum from the surface

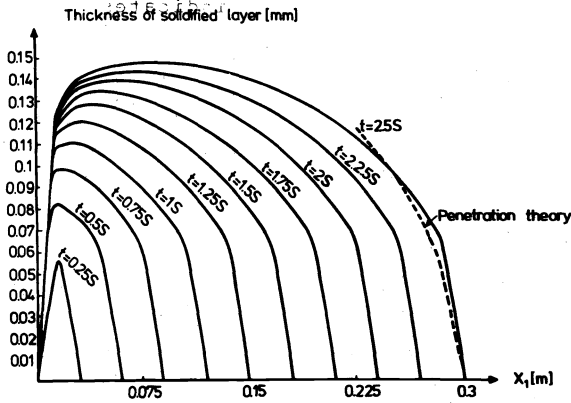


Fig. 4. Isothermal lines of  $T_g$ , as calculated with Table 1 for several moments during injection, according to Van Wijngaarden, Dijksman and Wesseling (8).

of the moulded strip. This view is explained with the aid of Fig. 5. This figure sketches the change of the course of the shear stress with time at an arbitrary cross-section of the strip mould. Very soon after the passage of the flow front the shear stress shows a linear gapwise distribution. The value of the shear stress increases from zero at the central plane up to a value  $\sigma_r$  at the wall. This is the consequence of a simple balance of forces in

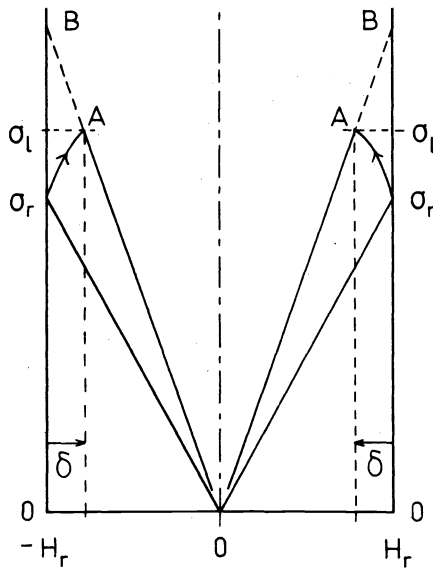


Fig. 5. Sketch elucidating a naive interpretation of the primary birefringence maxima, according to ref. (6).

a system symmetric with respect to the central plane. When the layer  $\delta$  grows, the gap available for the passage of the fluid decreases.

As a consequence, the straight line showing the dependence of the shear stress on the distance from the central plane becomes steeper, ending up at B. Above the glass-transition temperature gapwise distribution of shear stresses is depicted by the flow birefringence, in accordance with the linear

stress-optical rule. However, as soon as the glass-transition temperature is crossed in a downward direction, the balance of forces is taken over by other mechanisms than those known from rubber elasticity. As a consequence, the stresses which are small compared with the modulus of a solid, are no longer depicted by the birefringence. The line drawn from  $\sigma_r$  at the mould wall to the point A, where a shear stress  $\sigma_\ell$  is reached, indicates the shear stress growth during mould filling, as it occurs on the penetrating frontier of the "cold", as characterized by  $T_g$ . This may explain, why at A a maximum in the birefringence can be expected. ( $T_g$  has been chosen as the characteristic temperature instead of the stagnation temperature  $T_\ell$ , since the relatively low fluidity at  $T_\ell$  is supposed to be caused by a high entanglement life time rather than a lack of internal equilibrium in the chain segments between entanglements. But the latter internal equilibrium is considered to be responsible for the validity of the linear stress-optical rule. The reader is reminded in this connection of a recent paper by Doi (10). Doi distinguishes three relaxation phases with vastly differing relaxation times.)

Notwithstanding the fact that this picture will be shown to be amenable to a considerable improvement in view of the desired quantitative agreement with the experimental findings, it gives qualitatively correct results. A look on the lower part of Fig. 1 shows that the maximum of the average birefringence in the 1,3-plane is at a place corresponding to that of the maximum in the layer thickness, as indicated by curve II in Fig. 3. The upper part of Fig. 1 shows that, except for the neighbourhood of the line gate, the distance of the primary maximum from the surface decreases (together with its height) with increasing distance from the gate. Also these facts are in agreement with Fig. 3. No explanation, however, is given for the upswing of the birefringence into the surface of the strip, as shown in Fig. 2. The explanation of this upswing has previously been given by Tadmor (11). It seems to be caused by one-sided compression of the fluid behind the flow front. This compression is caused by the fact that the maximum speed in a nearly parabolic flow profile is about twice the average speed. This effect must produce a highly oriented layer in the flow front which is unrolled at the cold wall of the mould.

A serious shortcoming of the given interpretation of the primary birefringence maxima becomes apparent, if a quantitative comparison is made between the experimentally determined distances of the birefringence maxima from the surface and those predicted with the aid of Figs. 3 and 5. It appears that the experimental distances are about twice those predicted. This means that the envelope given by curve I of Fig. 3 is surpassed by the experimental distances. The only possible conclusion must be that the birefringence maximum occurs at a temperature above the glass-transition temperature.

An explanation for this fact has been given by Isayev and Hieber (9). For the purpose, however, these authors used a very simplified process. They assumed an infinitely long duct with a cross-section equal to that of the strip mould ( $B \gg 2H$ ). At times smaller than zero in this duct a steady stream of polymer melt is assumed with an average speed equal to that occurring during mould filling. The walls of the duct are kept at a uniform temperature  $T_1$ , equal to the injection temperature. At time zero, however, the wall temperature is suddenly lowered to a uniform temperature  $T_m$ , equal to the mould temperature. The process is now investigated, which takes place if the throughput is kept constant. The mathematical advantage of this simplified process is that momentum and energy equations can be treated separately, since there are no temperature gradients in the flow direction: The penetration of the "cold" can be treated as in the rolling down experiment. After a look on Fig. 3 we can guess that this simplified process will resemble the real process in the part of the mould which is remote from the gate. Leonov's constitutive equation (12) has been used by the mentioned authors because of its particular usefulness for numerical calculations. The desired relaxation time spectrum of the polystyrene was extracted from rheological measurements published by Wales (13) on the same polystyrene.

Emphasis will not so much be laid on the calculated quantitative results, however, because of the fact that the obtained results can also easily be understood qualitatively. For the purpose let us look on the equation which dissects the birefringence in the 1,2-plane:

$$\Delta n = \sqrt{4n_{12}^2 + (n_{11} - n_{22})^2} \quad \dots(8)$$

In this equation  $n_{12}$  is equal to the stress-optical coefficient times the shear stress  $\sigma_{12}$ , whereas  $n_{11} - n_{22}$  depends in the same way on the first normal stress difference  $N_1$ . This means that both quantities are firmly connected to the respective stresses. As a consequence of the mentioned balance of forces the shear stress will always show a linear dependence on the distance from the central plane as long as the process is symmetric with respect to this plane (Cf. Fig. 5). If this shear stress is increased due to the cooling process, the first normal stress difference  $N_1$  will show, in principle, only a delayed growth. This delay will be the more pronounced the lower the temperature becomes. This is shown in Fig. 6 where the gapwise distribution of  $N_1$  is shown according to the calculations of Isayev and Hieber for several cooling times ranging from zero to 2,5s (the latter time being in agreement with the injection time chosen by Wales). The dashed lines show the results expected from the equations given by Leonov for the case that steady state flow is immediately realized ("inelastic" model). In this way the birefringence maxima can be explained without difficulties. In reality, there will

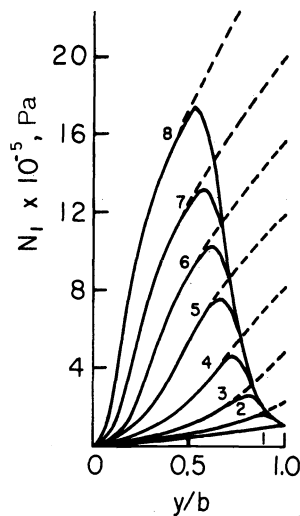


Fig. 6. Gapwise distribution of first normal stress difference according to Isayev and Hieber (9); 1 ... 0; 2 ... 0,05; 3 ... 0,2; 4 ... 0,5; 5 ... 1,0; 6 ... 1,5; 7 ... 2,0; 8 ... 2,5 seconds.

also be some stress relaxation in the core of the sample which is still hot after the moment of complete mould filling. If flow is stopped in the described model at the injection time ( $t = 2,5s$  in the present case), the influence of this stress relaxation can also be described. This is shown in Fig. 7, as taken from the work by Isayev, Hieber and Crouthamel (4), where line 1 holds for the "inelastic" model and line 2 for the "elastic" model at the moment of complete mould filling, whereas line 3 is valid for the latter model after relaxation. Circles give experimental results, as obtained at a sufficient distance from the gate. (Near the gate the height of the maximum is underestimated by this theory. At the same time too big a distance from the wall is predicted. This is in accordance with our considerations in the previous section: Near the gate the steady state situation is approached more closely.)

Finally, it should be mentioned that a delay of the first normal stress difference behind a suddenly imposed shear stress (shear creep experiment) is not merely a theoretical prediction borne out by Leonov's theory. It has been observed by Wagner and Laun (14) for a low density polyethylene at  $150^{\circ}C$  and interpreted with the aid of Wagner's theory (15). The steady state value



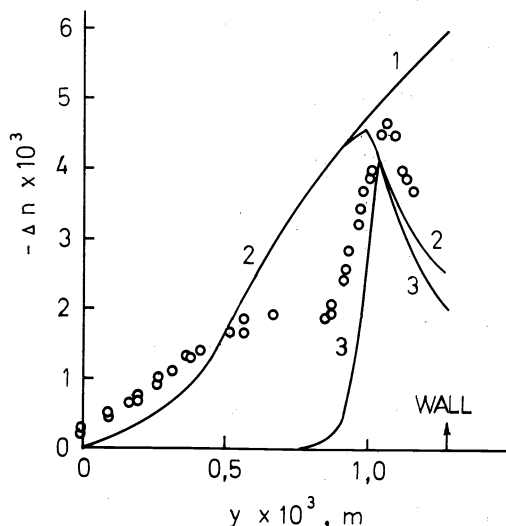


Fig. 7. Experimental and theoretical gapwise birefringence distributions in moulded strip according to ref. (4), with  $T_i = 223^\circ\text{C}$  and  $T_m = 40^\circ\text{C}$ , injection speed  $0,465\text{ms}^{-1}$ , location  $0,16\text{m}$  from the gate.

of  $N_1$  was reached only 10 seconds after the imposition of a shear stress of  $10^4$  Pa. This is a long time compared with a normal injection time.

#### ANNEALING

If one considers the practical application of an annealing procedure on a plastic article, one sometimes has in mind a reduction of the molecular orientation. However, experience has shown that one can better try to avoid orientations than to reduce them by annealing, since the latter process is rather time consuming. Nevertheless, for special applications a combination of optimum injection conditions and subsequent annealing can be obligatory. This may be one reason why a consideration of this latter process gained interest.

For experiments in this field one also needs a criterion. If the samples are opaque, birefringence measurements become impossible. Under such circumstances the only remedy is offered by so-called heat-shrinkage measurements (5) (16): The sample is annealed under exact shape constraint at a temperature a little lower than the glass-transition temperature for a chosen time, and is then ejected and heated to a temperature well above the glass-transition temperature, where it is allowed to "recover", until equilibrium is reached. Laun (17) has recently shown that this recovery is an extremely sensitive indication for residual molecular orientation.

In the present context only a few results, as obtained by Laun for deformations in the linear range, will be reproduced. This author discerns three important types of time dependencies characterizing the annealing process:

- a) Stress relaxation after a step in strain.
- b) Relaxation of the capability to recover after a step in strain.  
The same time dependence holds for stress relaxation after steady flow.
- c) Relaxation of the capability to recover after steady flow.

In all these cases the shape constraint is thought to be applied at the moment (time zero) that a certain total strain is achieved. Recovery is thought to occur when the constraint is removed after some chosen time  $t$ . In this way, isothermal processes are considered. If annealing occurs at another temperature than that at which the previous flow is applied, the previous flow rate can be transformed to the flow rate corresponding to the annealing temperature with the aid of the time-temperature superposition principle (18). The most interesting point is formed by the different time scales represented

by the time dependencies a), b) and c) under identical annealing conditions.

Laun's results are most easily presented in terms of a line spectrum ( $g_i, \tau_i$ ) of relaxation strengths and times. One has for shear:

$$a) \sigma_{r,i} = \gamma_0 \sum g_i e^{-t/\tau_i} \quad \dots(9)$$

$$b) \gamma_{r,i} = (\gamma_0/\eta) \sum g_i \tau_i e^{-t/\tau_i} \text{ and} \\ \sigma_{r,s} = q \sum g_i \tau_i e^{-t/\tau_i}, \quad \dots(10a,b)$$

$$c) \gamma_{r,s} = (q/\eta) \sum g_i \tau_i^2 e^{-t/\tau_i}. \quad \dots(11)$$

where  $\sigma_r$  is a relaxing shear stress and  $\gamma_r$  is the total shear recovery after a time  $t$  of relaxation under shape constraint, subscripts  $i$  and  $s$  pointing to the history (instantaneous deformation and steady flow, respectively),  $\gamma_0$ ,  $q$  and  $\eta$  are step shear strain, (constant) shear rate and Newtonian viscosity, respectively.

For tensile experiments  $\sigma_r$  will be the relaxing tensile stress, if  $\gamma_0$  and  $q$  are replaced by  $3\epsilon_0$  and  $3\dot{\epsilon}_0$ . If  $\gamma_r$  is replaced by  $\epsilon_r$  and the just mentioned replacements of  $\gamma_0$  and  $q$  are maintained, one obtains the pertinent (tensile) recoveries  $\epsilon_r$ . A factor three in front of the equations for the tensile recoveries is only needed, if also the Newtonian viscosity  $\eta$  is replaced by the Troutonian viscosity  $\bar{\eta} = 3\eta$ . (It goes without saying that the relaxation strengths  $g_i$  remain those determined from a cyclic shear experiment.)

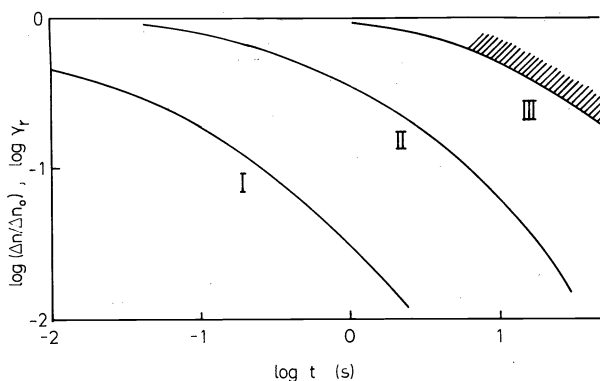


Fig. 8. Normalized courses of the curves given by eqs. (9), (10) and (11), as calculated with the aid of a relaxation time spectrum determined by Laun (17) for a low density polyethylene at 150°C.

From the relaxation spectrum determined by Laun for a low density polyethylene at 150°C one can easily calculate the normalized curves I, II and III for cases a), b) and c), as reproduced in Fig. 8. For this spectrum one finds a difference in time scale of about one decade between the time dependencies of the three mentioned cases.

Because of the validity of the linear stress-optical rule for polymer melts, in the normalized curves one can put  $\Delta n/\Delta n_0$  instead of  $\sigma/\sigma_0$ , if tensile ex-

periments are considered. For experiments in shear the situation is a little more complicated because of the validity of eq. (8), which contains the optical equivalents of the shear stress and of the first normal stress difference  $N_1$  as well. The latter quantity  $N_1$ , however, shows a deviating relaxation behaviour: After a step in shear strain it behaves according to the time dependency given by eq. (9). But after steady flow it behaves according to the time dependency of eq. (11) (instead of eq. (10b)!).

These facts are important for a judgement of the success of reducing the birefringence in injection moulded articles by annealing. Since the main contribution to the mentioned birefringence is apparently frozen in during the filling procedure, the relaxation of birefringence during annealing will proceed more according to the time law given by eq. (9) than according to that given by eq. (11). (This is in accordance with the considerations by Isayev and coworkers with respect to the mechanism for formation of the primary birefringence maximum.) The conclusion is that heat shrinkage measurements will probably be oversensitive, as their results will follow eq. (10a). Apparently, if one speaks in terms of entanglement networks, a very loose network of sufficient connectivity, which survives a long period of relaxation, is still able to produce a pronounced recovery if no constraints are present. On the other hand, the stresses pertinent to this loose network are apparently very weak and probably of no practical importance.

Recently, E.G. Kiel (Philips, Eindhoven) (19) has investigated a great number of injection moulded strips of various types of polymers. In all cases he found that the birefringence relaxed much faster than the capability to recover. (Difference in the time scales about one decade.) This is completely in agreement with Laun's views.

#### PROGRESS IN THE UNDERSTANDING OF THE INFLUENCES OF MOLECULAR PARAMETERS

In the present context recent progress in the understanding of molecular flow processes should at least be mentioned. In fact, one of the questions is always which type of polymer and which molecular mass distribution of this polymer will lead to an optimum result with respect to the properties of the end-product, in particular the degree of molecular orientation. The success of Leonov's theory has already been demonstrated. On one side, this success seems to be based on mathematical advantages with respect to the computational demands. On the other hand, quite recently a link has been discovered between this theory and the already well-known reptation concept. (De Gennes (20), Doi-Edwards (21), Curtiss-Bird (22)). This has recently been reported by Gieseke (23). So far, however, no useful relaxation spectra have been derived from this type of calculations. A review of this and other subjects has recently been tried by the present author (24).

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