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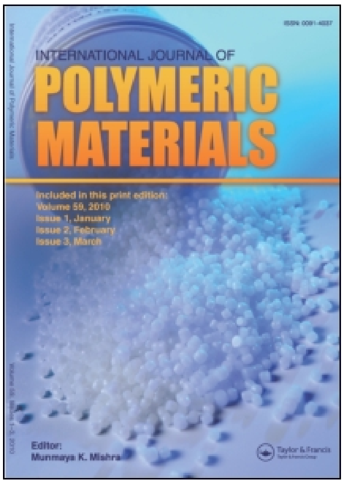

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Influences of Flow and Heat Transfer Conditions on the Solidification of Polymers by Crystallization

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Influence of flow and heat transfer conditions on solidification of polymers by crystallization is reviewed.

KEY WORDS Crystallization, polymer processing, texture, flow, cooling conditions.

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Solidification of polymers by crystallization is an important feature of polymer processing. The textures, as obtained in the products, are rather sensitive to previous flow and cooling conditions. In the absence of flow no clear influences of molar masses and/or molar mass distributions are noticeable. The contrary is true, however, if flow is involved in the process, as is normally the case. In order to obtain a better understanding of these facts, seven years ago a national working party on injection moulded articles was launched. The reported results are largely an outcome of a subdivision of this working party.

Interestingly enough, flow induced nucleation can be considered as an elasticoviscous process. It is considered as a homogeneous nucleation process in contrast to the heterogeneous nucleation in quiescent melts. Only the latter process can be influenced by the addition of nucleating agents.

For quiescent melts a method has been developed for the simultaneous integration of kinetic rate equations (Schneider *et al.*) and the equation of heat conduction. For flowing melts the kinetic model is being tested experimentally. Convection of prenucleated fluid must be taken into account together with normal heat convection.

1. INTRODUCTION

As is well-known, shear induced surface layers are found in the walls of injection moulded plastics articles.[1,2] If these layers are very thick, they cause several undesired effects, such as: stress-whitening, wharping, dome-forming, and brittleness (splitting).[3,4] With crystallizing polymers these layers can never be avoided completely. Manufacturers know from experience[5] that one should use polymers of comparatively narrow molar mass distributions (for instance rheology-controlled grades) instead of reactor products which—in particular with polyolefins—show extremely broad molar mass distributions. This practical knowledge, however, seems rather unsatisfactory. One should certainly try to understand the underlying processes. Such a knowledge seems indispensable in the age of computer simulation, when the prediction of certain textures is tried. As has been shown recently,[6] those textures may even be advantageous for special purposes.

When pertinent research was started in a National Working Party of the Austrian "Fonds zur Förderung der wissenschaftlichen Forschung," Vienna, the theoretical background was virtually unexplored. This does not mean that there did not exist a series of interesting singular experiments which are described together with our findings in a recent review,[7] where also the original literature is cited, e.g.[8,9] In this review, also the solidification processes in quiescent (i.e. relaxed) polymer melts are described. Also these processes were part of the investigations in the mentioned working party. With respect to quiescent melts famous fundamental work had been done previously. In this connection always the work of Avrami[10] has been cited. Only recently we discovered that Kolmogorov[11] did the first important step in this direction. An extension of the results of this work was necessary, however, in order to enable the treatment of non-isothermal heat transfer situations. This was achieved by members of our working party.[12] A more simple treatment of the heat transfer situation ignoring details of the crystallization kinetics, was given a little earlier by Malkov *et al.*[13] (See also Reference 14.)

In that which follows, a review will be given only on shear induced crystallization. Also for this type of crystallization the heat transfer situation is of great importance, so that the just mentioned experiences on relaxed melts are of paramount importance. In this lecture, however, we restrict ourselves to a qualitative description.

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2. RELAXATION PHENOMENA

As is well-known to rheologists, a small content of rather long molecules can have a tremendous influence on the rheology of a polymer melt. As an example, the influence of less than a half percent per weight of large molecules on the shapes of the loss-and storage moduli as functions of circular frequency is shown for a polypropylene melt in Figure 1. In this work[15] the experimental molar mass distribution, as obtained with the aid of gel permeation chromatography (GPC) is properly extrapolated into the range of molar masses $M > 10^7$, where fractions are too small for being detectable. The theoretical curves, as shown in Figure 1, were calculated according to a model proposed by Schausberger.[16] One may notice that, by adding several extrapolated fractions (over one further decade in M) to the molar mass distribution, one obtains a considerable increase for both moduli in the low frequency range, which converges quickly after the 10th fraction, while the melt flow properties are completely changed. (The ω-scale is arbitrary. At the

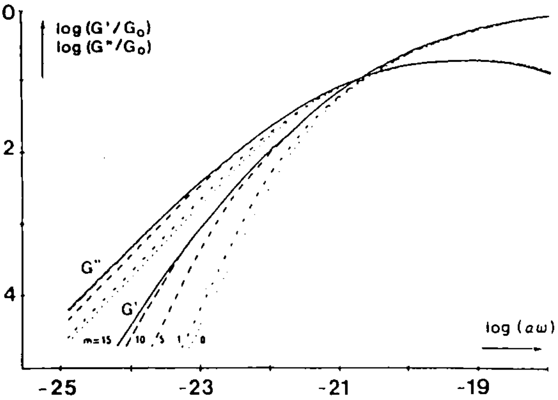

FIGURE 1 Double logarithmic plots of the reduced moduli G'/G_0 and G''/G_0 as functions of the reduced frequency $a\omega$, when extrapolated molar mass distributions with a number m added fractions are used.[15] (m = 0, 1, 5, 10 and 15). Courtesy of J. Wiley, NY.

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cross-over point one has $\omega \simeq s^{-1}$, which corresponds, according to the Cox-Merz rule,[17] to a comparable rate of shear $\dot{\gamma}$, when shear flow is considered.) Near $\omega \simeq 10^{-1}\,s^{-1}$ the storage modulus G' increases by more than one decade by the addition of immeasurable quantities of long molecules! The ultimate curves agree with the experimental ones!

As indicated in the introduction, just as tiny fractions of long molecules may influence the kinetics of shear induced crystallization. So far this knowledge, however, is only qualitative. Nevertheless, it will be shown that also in the kinetics of shear induced crystallization, a relaxation phenomenon is involved, even if the underlying process is distinctly different from the process of the diffusive disorientation of individual chain molecules taking place after cessation of polymer melt flow. As is well-known, in the latter process stored free energy (of entropic nature) is relaxed. (See the key word "storage modulus" in the previous paragraph and our knowledge about unique interconvertibility of rheological quantities.) In connection with the shear induced crystallization, however, the relaxation of a supermolecular structure has been postulated. Some preliminary remarks seem useful for a better understanding.

In our laboratory the most favourite experiment has been the extrusion through a slit die which can be kept at/or quenched to a certain level of supercooling by the circulation of a heat transfer fluid through its walls. The slit die itself is formed by a rather long duct of rectangular cross-section of a large aspect ratio ($L >> B >> H$, when L is its length, B is its width and H is its height). After a variable flow and cooling program this die can finally be quenched to a temperature far below the melting point of the polymer. After this procedure the solidified polymer can be extracted and cut on a microtome. In Figure 2 a microphotograph of such a cut is shown, as obtained with crossed polars. On either side a bright, highly birefringent surface layer is shown. These layers are due to shear induced crystallization. As is well-known, during flow the shear rate is zero in the centre but increases towards the side walls of the duct. Apparently, shear induced crystallization occurs only at shear rates larger than a critical shear rate. Otherwise, the

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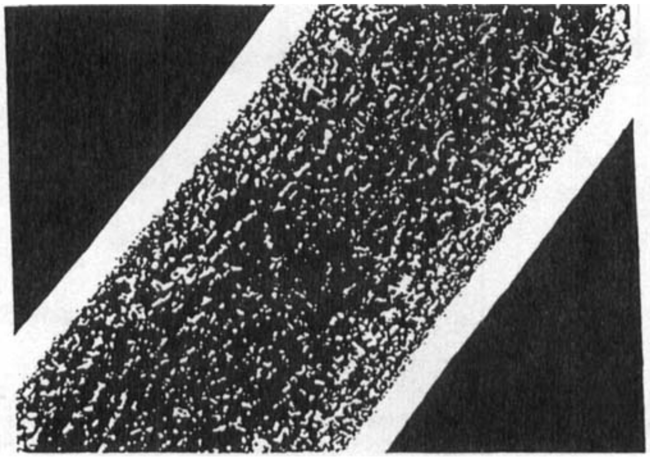

FIGURE 2 Microphotograph of 30 μm cut through a sample of polypropylene Daplen KS 10 after the extraction from the quenched duct in which shear treatment had occurred.[7] Courtesy of Pergamon Press, Oxford.

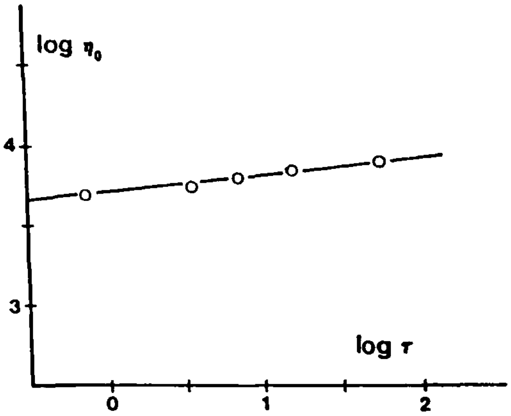

FIGURE 3 Double logarithmic plot of zero shear viscosity against the relaxation time of the precursors for polypropylene Daplen KS 10.[7] Courtesy of Pergamon Press, Oxford.

occurrence of distinct surface layers cannot be explained. At higher resolutions it can be shown that the surface layers have a lamellar structure.

As already mentioned, the conviction has been gained that reversible structures are stabilized by shear at temperatures high enough that no direct onset of crystallization can be observed even at severe shearing conditions.[7,18,19] After cessation of flow these structures apparently decay with time. This is what we called a relaxation phenomenon. In the present context only the most recent of these experiments will be discussed[20]: For the melt of an industrial polypropylene an identical flow history was realized at several temperatures well above the melting point, before flow was suddenly stopped. After cessation of flow waiting times of varying lengths were introduced, before the flow unit (our above mentioned duct) was quenched to a sufficiently low temperature where the content of the duct quickly solidified. The logarithms of the birefringences measured in the surface

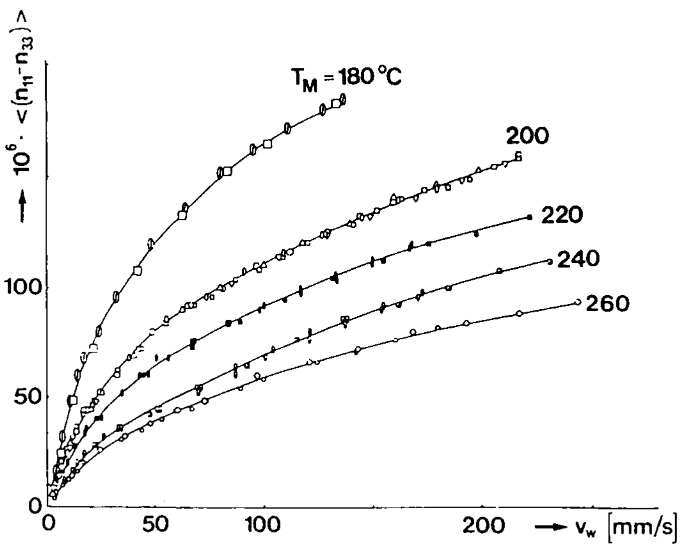

FIGURE 4 Flow birefringence (average over the duct height) against extrusion speed, as measured near the duct exit for polypropylene Daplen KS 10.[18] Duct lengths vary from 12 to 121 mm. Temperatures are given in the graph. No influence of duct lengths can be noticed in the interesting temperature range between 180 and 220°C. Courtesy of Steinkopff-Verlag, Darmstadt.

layers is plotted against the waiting times applied. In this way one gets a straight line for every shearing temperature applied. From the slopes of these lines relaxation times are deduced. In Figure 3 a double logarithmic plot is given of the zero shear viscosities of the melts against the said relaxation times. The temperature of shear flow varies from 210°C to 190°C along the straight line of this plot. In this range of temperatures the zero shear viscosity increases by a mere factor two, whereas our relaxation time grows by a factor 70. As the relaxation of individual molecules goes with the viscosity, a cooperative process is clearly indicated. It seemed that we could follow the decay of submicroscopic lamellar precursors which had been stabilized by the shear flow. The geometry of these precursors can be deduced only from the appearance of so-called "shear lines" on microphotographs taken after the solidification, where the traces of these lamellae show an increased thickness caused by subsequent lateral growth. There seems to be no way to identify these tiny structures during shear flow at elevated temperatures, as McHugh has been hoping in analogy to the vizualisation of liquid-liquid phase separation in flowing solutions.[21] As we concluded from previous experiments, in which thickness and birefringence of the surface layers were investigated after flow through ducts of widely varying lengths,[7,18,19] the mentioned precursors do not only decay after cessation of shear flow, but first are built up at measurable rates during shear flow. But isothermal flow birefringence measurements near the ends of ducts of widely varying lengths did not show any influence of these die lengths on the optical path difference (Figure 4). It goes without saying that the interesting range of temperatures was investigated.

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3. THEORY OF SHEAR INDUCED CRYSTALLIZATION

Using the experiences gathered in the previous section, we were able to develop the first theory of shear induced crystallization.[7,22] This theory is based on a very simple differential equation containing a growth term and a decay term for a probability function Φ for the occurrence of shear induced crystallization:

$$\tau\dot{\Phi} = (\dot{\gamma}/\dot{\gamma}_a)^2(1 - \Phi) - \Phi \qquad (1)$$

Later we identified this Φ tentatively with the said internal nucleation surface per unit of volume. The growth term is governed by a critical shear rate $\dot{\gamma}_a$ of activation, whereas the decay term is characterized by the said relaxation time τ (Divide Equation (1) by τ!). As we can guess from Figure 3, the ratio t_s/τ of the shearing time over the relaxation time τ becomes always small at temperatures where shear induced crystallization is readily proceeding. This is because of the expected large values of τ. (With polypropylene one has a value of 68 s at 180°C. This is the lower temperature limit for the shearing experiments of the previous section. If the temperature is lowered by other 20 degrees to 160°C, the usually assumed melting point of polypropylene, one can expect another 70 fold increase of τ.) Since the kinetics of shear induced crystallization cannot depend on the direction of shear, there must be a quadratic dependence on the shear rate as a first approximation. (See Equation 1.) So, at temperatures where shear induced crystallization readily proceeds, we must simply have

$$\Phi(\dot{\gamma}, t_s) = (\dot{\gamma}/\dot{\gamma}_a)^2 t_s/\tau \qquad (2)$$

which forms the solution of Equation (1) for short times. Equation (2) forms a good basis for isothermal shearing experiments, as we will see. For more involved experiments or for practical processing conditions, however, where no constant temperature can be assumed, the full differential equation with temperature dependent parameters $\dot{\gamma}_a$ and τ must be used. In fact, it may happen that a so-called "shear-line" in an injection moulded article must be traced back to previous shearing above the usual melting point. Those "lines" can often be found near the gate. Furthermore, we should not forget the third parameter of this theory, which can be called the growth factor (for lateral growth on the lamellae). Also this factor has its own temperature dependence.

4. ISOTHERMAL SHEARING EXPERIMENTS

In contrast to the experiments mentioned in Section 2, which were extremely non-isothermal (shearing occurred at rather high temperatures, growth occurred only after the quench), we now concentrate on simpler, but more accurate experiments at constant levels of supercooling. First experiments of this type were carried out by other authors (see References 7, 8 and 9). In these experiments, however, shearing was continued until shear induced crystallization fully set in. One of the

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predictions of our theory is that one does not need to continue shearing up to this onset, which also will not be sharp under all conditions or with all polymers. A much more subtle experiment is, when shearing at a chosen rate of shear is stopped already after a short time and the development of the crystallization, as induced in this way, is monitored by polarization-optical means. This seems possible because of the experience that highly birefringent lamellar structures are formed, so that the optical retardation can be assumed to be proportional to number and thickness of the formed lamellae. One of our ducts, as described in Section 2, was adapted for this purpose near its exit. On either side of the slit, viz. in the large side walls of the duct, glass windows were placed. First the duct was filled with the melt of the polymer at a normal extrusion temperature. After the application of a proper period of relaxation the temperature of the whole duct was lowered to a previously chosen level of supercooling. Then extrusion was started up again at constant pressure for a time t_s. This time was chosen short enough to prevent the hot melt, as discharged by the extruder, from penetrating too far into the duct. (This measure was necessary as a supercooled melt would crystallize by stretching flow in the entrance region.) Mr. Liedauer at our laboratory, who also built the whole equipment, chose three temperature levels for polypropylene, viz. 157, 150 and 143°C, where normal spherulitic crystallization takes a much longer time than shear induced crystallization, so that the latter can be observed without noticeable disturbance by the former.

In Figure 5 the optical retardation is shown as a function of time for polypropylene Daplen KS 10 at 150°C after a shearing time of 4.1 s at a shear rate of 133 s^{-1} at the large duct wall. The full line corresponds to an Avrami exponent equal to one. This can only be interpreted as the consequence of a one-dimensional lateral growth of the preformed lamellae. One may observe that t_s is very small compared with the duration of the experiment.

There is still another, important evidence for the correctness of the crystallization model: A great number of these experiments has been evaluated. The initial slopes

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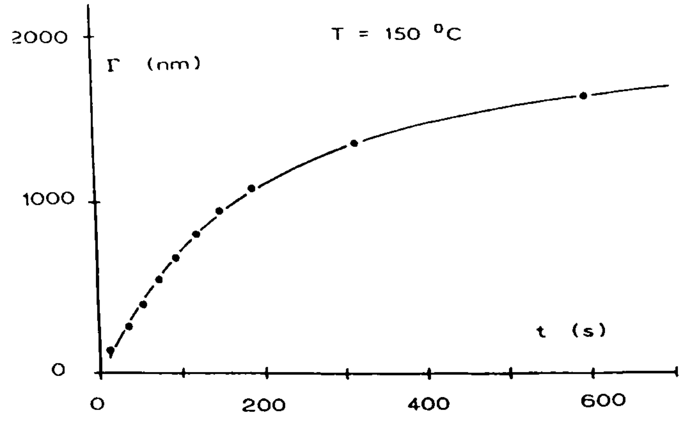

FIGURE 5 Optical retardation over the height of the duct as a function of time after a shearing time t_s of only 4.1 s at a (maximum) shear rate of $\dot{\gamma} = 133\ s^{-1}$ (at the large duct wall) at a temperature of 150°C for polypropylene Daplen KS 10. The full line gives a theoretical curve for Avrami-exponent one.[26] Courtesy of Hemisphere Publ. Corp., Washington, DC.

of the curves of the type shown in Figure 5 turned out to be proportional to the second power in t_s and to the fourth power in $\dot{\gamma}$. In other words, these slopes are proportional to Φ^2 according to Equation (2). This would be in agreement with the assumption that the submicroscopic nucleation surface (per unit of volume) grows with the shearing time and that also the ultimate degree of shear induced crystallization increases linearly with shearing time. The latter assumption becomes intelligible if one assumes that also the perfection (for instance the connectivity) of the nucleation surfaces increases with Φ, so that a more orderly lateral growth is enabled. In this respect the reader is reminded of the fact that only the β-modification of polypropylene crystals shows a big birefringence effect[23] like our surface layers, whereas the birefringence of the α-modification is low due to epitactic growth.[24] In fact, one finds varying amounts of both modifications in the surface layers.[25]

Another point is that the general form of Φ, as given by Equation (2), is established by these experiments (twice the power in $\dot{\gamma}$ when compared with t_s).

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5. DISCUSSION

The results quoted in Section 4 look very promising. Nevertheless, one should be cautious in several respects. The simple interpretation of the isothermal shearing experiment in the duct only holds as long as the induction time for the highest shear rate at the (large) duct walls is larger than the shearing time t_s. At lower temperatures, even at 143°C for polypropylene, this will no longer be the case. Then the interpretation becomes much more complicated.

As Φ is assumed to be proportional to the nucleation surface per unit of volume, its reciprocal value is proportional to the average distance between the nucleation lamellae. In this way one obtains quite realistic distances just around the dissolution power of the light microscope. For this calculation one must assume that the lateral growth speed is equal to the well-known linear growth speed of spherulites.

If the latter assumption is correct, one is also released from the problem to measure the temperature dependences of the "nucleation parameter" $\tau\,\dot{\gamma}_{a^2}$ and of the growth parameter g separately. Then isothermal experiments at several levels of supercooling, which give us the temperature dependence of $\tau\,\dot{\gamma}_{a^2}\,g^{-1}$, can be used for a calculation of the temperature dependence of $\tau\,\dot{\gamma}_{a^2}$, since the temperature dependence of the linear growth speed of the spherulites is well-known.[7] If, however, shearing starts already at temperatures above the melting point, one needs the temperature dependences of all the three parameters. This is still the most simple model to be imagined. So, we should warn artists in numerical techniques to suck their parameters out of their thumbs.

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