Polymer Bulletin 14, 1–8 (1985)

Polymer Bulletin

Engineering

Crystallization Fronts in Quenched Polymer Samples

G. Krobath, S. Liedauer, and H. Janeschitz-Kriegl

Universität Linz, A-4040 Linz, Austria

SUMMARY

A relatively simple experiment is described: In a "unilateral" quench a melted disk-like polymer sample is partially solidified. The conditions are discussed which lead either to a sharp crystallization front or to the occurrence of dispersed spherulitic crystallites. The importance of this basic experiment for the understanding of industrial moulding processes is stressed.

INTRODUCTION

When in this laboratory studies on the crystallization of polymer melts were started with regard to industrial moulding processes we did not expect that there would be such a want for more insight into various aspects of this phenomenon. First of all, it has been shown in a preliminary study (1) that the famous solution of the Stefan problem (2) cannot be applied to polymer melts. This means that a generally accepted basic model for engineering calculations is ruled out - at least for polymer melt processing. With respect to mass transfer phenomena in polymers similar observations were made by Astarita, Nicolais and coworkers (3). (As is well-known, mathematics for these latter phenomena are very similar.) The reason for the failure of Neumann's solution , as used by Stefan, lies in the fact that, in steep temperature gradients, crystallization always proceeds as a nucleation controlled process, whereas Neumann's model is, per definition, heat diffusion controlled.

Instigated by preliminary experiments (4) an alternative theory (5) was developed in this laboratory. This theory is still based on the assumption that crystallization starts only at the quenching wall and proceeds into the homogeneous polymer melt in the form of a crystallization front, as in the case of Neumann. The principal difference lies in the choice of the conditions at the moving boundary: In contrast to Neumann supercooling is permitted at the boundary, whereas the speed of the front is assumed to be a polymer specific function of the crystallization temperature at this front. As a consequence of this more realistic assumptions the speed of propagation of this front is finite at zero time of contact with the "cold" wall. This is in contrast to the Neumann solution where this speed is infinitely high in the very first moment of the quench ("$\sqrt{t}$-law").

In later experiments, however, it very often happened that no crystallization front was formed at all during the quench (8). In fact, such a situation is found, if the growth of crystals is so slow that the melt is supercooled over a considerable distance from the wall before crystallization starts. If the pertinent melt temperature is still above the glass transition temperature, normal spherulitic growth takes place. An intermediate situation is when initially a crystallization front starts at the quenching wall, but is hampered on its way by spherulites growing from nuclei coming up before this front. This situation is realistic since also the melt in the area before the crystallization front is supercooled (in contrast to Neumann's view).

As in moulded polymer samples two characteristic types of texture are observed, viz sharp crystallization fronts - in particular, when shear is applied - and dispersed spherulites, we are in urgent need of a criterion on which realistic predictions can be based at least qualitatively. The purpose of this paper is to show how one can obtain such a criterion on the basis of systematic experimentation. In the beginning of this experimentation we considered also the influence of shearing - as it were in an integrated effort. However, in order to avoid too many parameters we lateron focussed our attention primarily on the "unilateral" quench of quiescent samples of molten polypropylene.

THE UNILATERAL QUENCH

First, the apparatus will be described. A schematic drawing is given in Fig. 1. In the upward face of cylindrical part A a shallow trough is turned. In this trough the disk-like polymer sample (tabloid P) is placed. The outer surface of this tabloid is then covered by the downward face of the upper cylindrical part C. Both parts of the apparatus are then heated by electric heating bands not shown in the figure. The mentioned parts are hollow and can rather quickly be quenched from inside with the aid of adequate heat transfer fluids, as schematically shown for the lower part A. The upper part can also be rotated at constant torque. This is schematically indicated. In avoiding difficulties with the electric leads during rotation, the upper part is heated by radiation: The heating band forms a narrow cylindrical gap with part C. During this electric heating there are no fluids in the interiors of parts A and C.

At first, parts A and C are brought to a temperature well above the melting point of the polymer. After some time, when thermal equilibrium is reached, the temperatures of both parts are lowered to the actual starting temperature T_i at which still no crystallization takes place. In the latest experiments on polypropylene a temperature of 180°C was chosen for T_i. At time zero ($t = 0$) the upper part is quenched to some chosen temperature T_w located between the melting point of the polymer T_m and the glass transition temperature T_g. This is accomplished by pushing a thermostat fluid of proper temperature into part C. After a certain "contact time" t (this term is chosen with regard to the contact at part C) the lower part A is also quenched. This is accomplished with the aid of a fast stream of tap water. Polypropylene samples are quickly and completely solidified in this way. The solidified samples are then removed from the apparatus. On a microtom slices M of a thickness of about 30 µm are cut perpendicular to the tabloid surface at a location indicated in the right corner of the figure. This location is chosen in view of those quenching experiments which are carried out under shear. With these cuts the previously applied shear stress is rather well known in the middle of the slices. However, as indicated in the introduction, this type of experiments has not yet been carried out systematically because of a series of other experimental difficulties. In this report we restrict ourselves to results as obtained by quenching quiescent melts. One of the advantages of this latter experiments is also that crystallization proceeds much slower than under the influence of shear so that the desired step functions in temperature can be approximated much better by the described quenches.

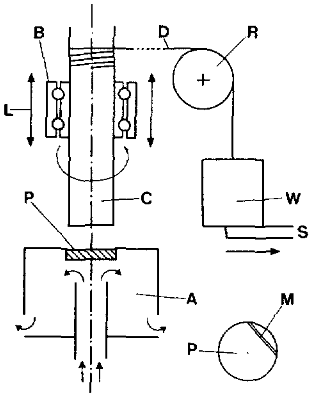

Fig. 1: Simplified view of the apparatus:
A ... pot with shallow trough,
P ... polymer sample of thickness D,
C ... hollow copper rod,
B ... bearings, D ... thread,
R ... roller, W ... weight,
S ... removable support (from D on very schematic),
M ... indication of the location of the microtom cut.

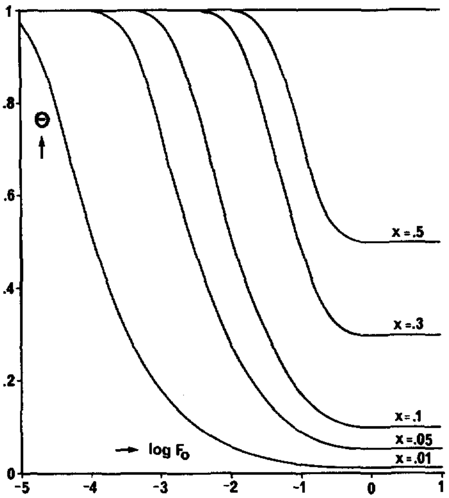

Fig. 2: Lateral quench (course of reduced temperature $\theta = (T-T_W)/(T_i - T_W)$ vs. reduced time $t^* = ta/D^2$, (Fourier number) for various reduced distances $x^* = x/D$ from the quenching wall. A constant heat diffusivity a of the sample (no phase transition) is assumed throughout.

At this point one arrives at the theoretical implications. As will become obvious from the pictures to be shown, in quiescent polypropylene melts any crystallization front moves so slowly that the relevant dimensionless times of contact at the face of part C (Fourier numbers) are considerable, viz of the order of ten. However, already after a dimensionless contact time of only unity, a linear temperature profile, extending over the whole thickness D ($\simeq$1 mm) of the sample, from T_i at part A to T_w at part C, is established before any crystallization becomes manifest. (For the development of such a linear temperature profile see Fig. 2.) As a consequence a curve showing the (dimensionless) crystallized layer thickness vs. (dimensionless) contact time reflects the result of quasi steady state growth: The only change developing during this layer growth is the occurrence of a slight kink in the temperature profile at the crystallization front, which reflects the difference in heat conductivities between solid and liquid phases.

Our experience is that the growth speed of the crystallized layer can be enhanced by at least a factor ten when shear is applied. However, before one can decide whether such a layer growth can take place on the whole (shear or no shear), one has to consider the influence of the temperature of the quenching wall (face of part C in our experiment). One may guess that crystallized layer growth only occurs, if T_w is well beyond the temperature T_p at which the growth speed of nuclei shows a maximum.*) In this range ($T_p << T_w < T_m$) one will have to resort to the non-equilibrium theory of ref. (5) if the growth speed is considerably higher than that in the quiescent melt of polypropylene. On the other hand, in the range $T_g < T_w < T_p$ the quenching wall is no longer expected to be of noticeable influence on the crystal growth in the melt, since nuclei in the melt grow faster anyway than those at the wall. In our type of experiment a linear temperature profile is established in the melt long before crystal growth becomes evident, when polypropylene is investigated. This means that with $T_w < T_p$ the size distribution of spherulites reflects this temperature profile. This has been shown in a previous communication (8). In accordance with Van Krevelen's (7) estimate of the number of nuclei vs. temperature this size varies by a factor of roughly 10^5 between an area close to the quenching wall at $T_w \simeq T_g + 20$ K and the area where crystallization comes to a halt since the temperature in the melt approaches the melting point. (The mentioned linear temperature profile extends from T_w to $T_i >> T_m$!) More facts will be published in a detailed publication in the near future. In the present communication the evidence will be presented that at $T_w >> T_p$ the expected crystallization front is actually formed even in a quiescent melt. In this way our expectations with respect to the role of the wall temperature are confirmed (see the Conclusions).

RESULTS

In Fig. 3 a microphotograph is shown as obtained from a sample of industrial (mainly isotactic) polypropylene Daplen KS 10 after a unilateral quench from $T_i = 180°C$ to $T_w = 110°C$, with a contact time of 40 seconds at T_w. (After 40 seconds the final quench with the aid of

---

*) Footnote: It is well known that the growth speed of nuclei is zero at the melting point T_m and at the glass-transition temperature T_g. At some intermediate temperature T_p the growth speed shows a maximum (cf.e.g. refs.(6) and (7)).

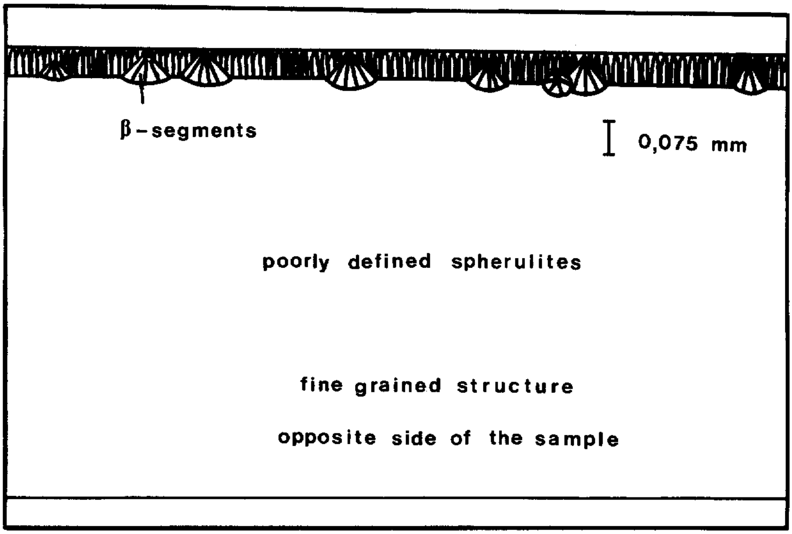

Fig. 3: Drawing from microphotograph, as taken in polarized light from a cut of a sample of industrial polypropylene Daplen KS 10 after a unilateral quench from 180°C to 110°C. The final quench was carried out after 40 seconds.

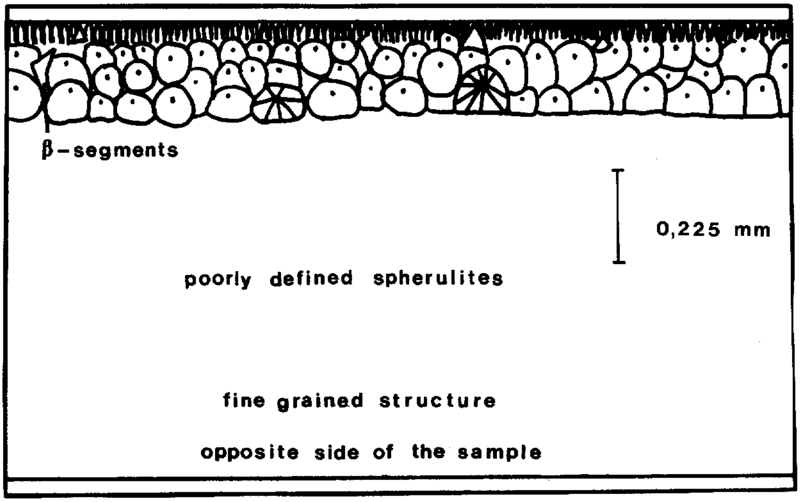

Fig. 4: Drawing from microphotograph as in Fig. 3, but after a unilateral quench from 180°C to 100°C and a final quench after 45 seconds.

tap water, as described in the previous section, was carried out.) On the upper rim of the sample one clearly discerns the said crystallization front. One notices that crystallization has started at a great number of points at the surface. One also notices that the main layer, which is striated in a direction perpendicular to the surface, is interrupted by very bright circular segments. These are segments of spherulites of the β-modification which grow faster than the α-modification, showing a much lower birefringence. From the angle of the opening of almost 90° of these segments one can conclude that the β-modification grew faster by a factor of about 1,4 ($\sim \sqrt{2}$). On the basis of literature data (9),(10) these facts are not surprising. For our investigation the thickness of the α-layer has been used. The texture of the main part of the microtom cut is formed during the final quench. It remains to be said that the temperature of 110°C is not too far above the temperature T_P for polypropylene. Similar pictures were found at a number of other contact times and also at a higher wall temperature T_W of 120°C. (See the curves in Fig. 5 below.) Apparently, the layer grew into a homogeneous melt free of impeding nuclei, as in zone crystallization (11).

The result of Fig. 4 is of particular interest in this connection. In this figure the result of a quench from T_i = 180°C to a little lower wall temperature of T_W = 100°C is shown for a contact time of 45 seconds. In this figure the layer, as crystallized during this contact time, is no longer uniformly striated in a direction perpendicular to the contact surface. Apparently, such a striation is only formed in the beginning of the quench. But in this respect we must be careful: We have found rather thick, beautiful layers of uniform striation without interspersed β-segments when the contact surface is cooled down at a very low rate. So it may be that, for short nominal contact times, the presupposed step-function in the wall temperature is not sufficiently realized. In this difficult field of experimentation we still have to make progress. When looking at Fig. 4, our main interest is focussed on the fact that, in agreement with expectation, a rather large number of nuclei got the chance to grow out in the adjacent melt before the crystallization, which started at the wall, could reach the locations of these nuclei. Nevertheless, in the whole there is still a clearly distinguishable crystallized layer of about 20% of the total thickness of the sample. It will be clear to the reader that such a "multi-nucleated" layer grows considerably faster than a layer nucleated solely at the wall. When shear is applied, such a "multi-nucleated" layer grows out to a layer with a sharp boundary and high orientation parallel to the wall.

The results of quenches to wall temperatures far below T = 100°C cannot easily be reproduced in this type of publication because of a lack of contrast in the pictures. But it becomes evident that no crystallization fronts occur under these circumstances. However, these circumstances are characteristic for normal processing of industrial (mainly isotactic) polypropylenes.

In Fig. 5 reduced thicknesses $x^*_c = x_c/D$ of crystallized layers are plotted versus reduced contact times $t^* = t\,a/D^2$ (Fourier numbers) for three contact temperatures, viz 100, 110 and 120°C. Remarkably, the initial slopes of these curves are in reasonable agreement with linear growth rates, as obtained by Padden and Keith (9) and by Von Falkai (12) in microscopic investigations of the spherulitic growth of polypropylene samples of widely varying molar masses. The same type of agreement is found with the results of zone crystallization by Lovinger and cooperators (11). Assuming quasi steady state growth one arrives at the following relation for

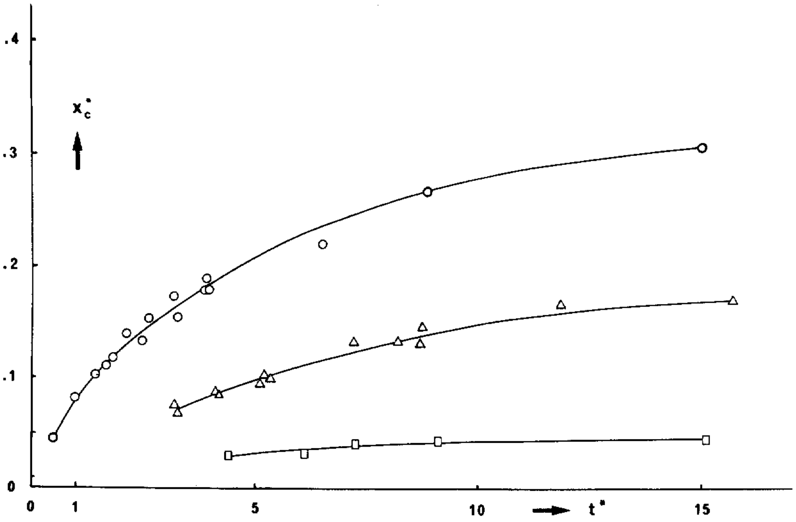

Fig. 5: Reduced thickness $x^*_c = x_c/D$ of crystallized layers as functions of reduced times $t^* = t\ a/D^2$ for various temperatures T_w of the primary quenching surface: O ... 100°C, Δ ... 110°C, □ ... 120°C.

the temperature T_c at the crystallization front:

$$T_c - T_w = \frac{\varepsilon\, x^*_c}{1 - (1-\varepsilon)\, x^*_c}\,(T_i - T_w) \qquad (1)$$

where $\varepsilon = \lambda_f/\lambda_c$ is the ratio of the heat conductivities of the fluid and of the crystalline area, being about 0,6 for polypropylene. According to this formula the last points obtained at about $t^* \simeq 15$ on the curves for the wall temperatures T_w = 100°C (O) and T_w = 110°C (Δ) correspond with about the same T_c of 117°C. Actually the tangents at these points have very similar slopes. So one is tempted to derive the growth speeds at various temperatures, as calculable from eq. (1), from these slopes. However, the observation has been made that the crystallization fronts continue to grow, sometimes even at a faster pace during the final quench. The relative error obtained in this way is particularly large for thin layers. Another point, which has already been mentioned, is that at intermediate Fourier numbers the layer for the quench at T_w = 100°C grows much faster, as it is "multinucleated".

CONCLUSIONS

Notwithstanding the fact that the growth speed of crystallites of industrial (isotactic) polypropylenes is rather low, sharp crystallization fronts are formed when their melts are quenched at thermostated walls of temperatures higher than the temperature T_p of maximum speed of crystal growth from the melt.

Such a crystallization front has, from a physical point of view, nothing to do with the type of crystallization front assumed by Neumann in his solution of the pertinent moving boundary value problem. In fact, in reality the speed of propagation is controlled by the rate at which (secondary) crystal growth is nucleated, and not by the speed at which released latent heat is conducted away from the crystallization front (1),(4),(5). This conclusion is of major interest in view of any type of theoretical predictions of the occurrence of discrete layer structures.

If the temperature of the quenching wall is below T_p, the situation is unfavourable for the formation of a crystallization front. In fact, under this condition nuclei, which still may come up at the wall, have a lower growth speed than those located in the bulk of the melt. Preliminary shear experiments show that this conclusion retains its validity also under the circumstances of industrial processing (8).

For industrial polypropylenes the discussion of the origin of crystallization fronts is certainly of a lower priority than for polymers of higher speed of crystal growth like polyethylene. In this respect, however, the discussion cannot be settled so far, because of a grave lack of experience with the latter polymer and with the application of shear.

With the aid of the described method the speed of layer growth can be measured at lower temperatures, closer to T_p , than with microscopic investigation of spherulitic growth (down to 110°C, ref. (9)) or with zone crystallization (down to 125°C, ref. (11)). There is realistic hope that the initial layer growth will be measurable also under well defined shearing conditions. Such a measurement should furnish relevant data for engineering calculations.

ACKNOWLEDGEMENTS

The authors are very much indebted to Prof. G. Astarita for claryfying discussions during his two weeks' stay as a visiting professor at Linz University. Special thanks are due to Mr. M. Lipp as instrument maker, for his unreserved active help in many situations when the apparatus had to be changed quickly. For valuable discussions the authors also wish to thank Mr. G. Eder of this laboratory. The Austrian "Fonds zur Förderung der wissenschaftichen Forschung" is gratefully acknowledged for sponsoring this research in the course of a national research program on injection moulded articles (project S 3302).

REFERENCES

1. H. Janeschitz-Kriegl and F. Kügler, "Polymer Processing and Properties", G. Astarita and L. Nicolais, eds., Plenum Publ.Corp. 1985,p.159.
2. J. Stefan, Ann.Phys. und Chem.(Wiedemann) N.F. 42, 269(1891).
3. G. Astarita and L. Nicolais, Pure & Appl.Chem. 55, 729(1983).
4. H. Janeschitz-Kriegl, G. Krobath, W. Roth and A. Schausberger, Eur.Polym.J. 19, 893(1983); H. Janeschitz-Kriegl and G. Eder, Plastics and Rubber Processing and Application 4 ,145(1984).
5. G. Eder and H. Janeschitz-Kriegl, Polym.Bull. 11, 93(1984).
6. A. Gandica and J.H.Magill, Polymer 13, 595(1972).
7. D.W. van Krevelen, Chimica 32, 279(1978).
8. H. Janeschitz-Kriegl and G. Krobath, Proceedings of the Rolduc Polymer Meeting, Elsevier 1985.
9. F.J. Padden, Jr., and H.D. Keith, J.Appl.Phys. 30 , 1479(1959).
10. A.Turner-Jones and A.J.Cobbold, Polymer Letters 6 , 539(1968).
11. A.J. Lovinger, J.O.Chua and C.C.Gryte, J.Polym.Sci., Phys.Ed., 15 ,641(1977).
12. B. von Falkai, Macromol.Chemie 41 , 86(1960).

Accepted June 26, 1985