Surface irregularities of calendered polypropylene

P. Prentice
Department of Mechanical Engineering, Imperial College of Science and Technology, London SW7 2BX, UK
(*Received* 11 *April* 1980)

Attempts have been made to calender polypropylene but the resulting sheets possessed an undesirable surface structure which became more severe at higher processing speeds. The pattern produced by this structure has been investigated and has been shown to be a consequence of two distinct crystal types forming in the wake of an unstable melt flow. The existence of these crystal types has been examined by differential scanning calorimetry (d.s.c.), optical microscopy and scanning electron microscopy (*SEM*). Orientation of polymer molecules in the calendered sheets was examined using optical microscopy and X-ray diffraction. A model of the microstructure has been proposed to explain the experimental observations.

INTRODUCTION

Recently the production capacity of polypropylene has increased enormously, and this has led to a need for the development of new outlets to add to the now well established uses of polypropylene in injection moulding and fibre spinning. One possible new application, in the packaging and stationery trades, gave rise to the requirement of thin sheet (125–250 μm). It was thought that polypropylene, without the adverse properties of PVC and ABS, would be well suited for use in the area of food packaging and the manufacture of stationery binders and such. Because of the high output rates that can be achieved, the processing technique frequently used to manufacture PVC sheet of this thickness is calendering, but attempts to produce polypropylene sheet by this method have met with intractable problems.

Calendering of PVC has been practised for many years with few difficulties and the process is now well established. It must therefore be assumed that the difficulties encountered with polypropylene are associated with the material rather than with the process. No work has been described in the literature relating to the calendering of polypropylene, although some references have been found describing the application of the calendering process to polyethylene.

In the most recent, and most relevant, of these references Hashimoto and coworkers[1,2] describe the preparation of test specimens of high molecular weight, high density polyethylene by means of a calender. However, the line speeds that they employ, 6 m min^{-1}, bear little relation to the speeds of 50–75 m min^{-1} common on production equipment. Even at these low speeds Hashimoto noticed that the surface of the sheets was rough and that the tensile properties were highly anisotropic. In the second of the two papers, they studied the structure of the calendered polyethylene more closely, and arrived at a model in which they propose the existence of rod-like units intermeshing with each other to form a network structure. The aim of the present work was to extend the work of Hashimoto *et al.* to explain the difficulties encountered with polypropylene.

EXPERIMENTAL

Initially a suitable grade for calendering had to be established, since it was soon discovered that few of the commercially-available grades had the required properties. A range of polymer types and grades were examined rheometrically, determining both the shear viscosity–shear stress and extensional viscosity–extensional stress flow curves on a Davenport Capillary rheometer. The extensional data was determined using the Cogswell converging flow analysis[3]. Each grade was then processed, first on a two-roll mill and then, assuming suitable results on the mill, on an EKK four roll 'Z', laboratory calender with a 12 in. bowl diameter. Pregelling was achieved in a Francis Shaw Intermix up to a temperature of 185°C. This initial work enabled the selection of a polymer grade suitable for a larger production trial to be made. The trial was carried out on a Berstorff 'Inverted L' four roll calender with 29 in. diameter bowls and a temperature regime of 167°/167°/167°/167°C. The line speed was 15 m min^{-1} and the sheet thickness was 125 μm. Samples of sheet produced on this trial were used to identify the nature of difficulties associated with the calendering of polypropylene.

Samples of about 1 cm × 1 mm were cut from the sheet at various angles with respect to the machine direction. The samples were mounted in a 57 mm diameter Debye–Scherrer camera. The camera, fitted with a strip of Ilford Commercial G X-ray film, was mounted on a Philips X-ray generator. The specimen was irradiated for 90 min with Cu Kα X-radiation (40 kV, 18 mA). X-ray diffraction patterns were obtained for the samples from which the direction of preferred orientation was established.

Samples (about 10 mg) were equilibrated in a Perkin–Elmer DSC-2 differential scanning calorimeter, at a temperature well below the melting range of the sample before increasing the temperature at various rates from 1.25°C to 40°C min^{-1}, until well past the melting point.

Optical and scanning electron microscopy were performed on samples using a Ziess polarizing microscope and a Cambridge Stereoscan 600 *SEM*. Samples for optical microscopy were mounted between two microscope

0032-3861/81/020250-05$02.00

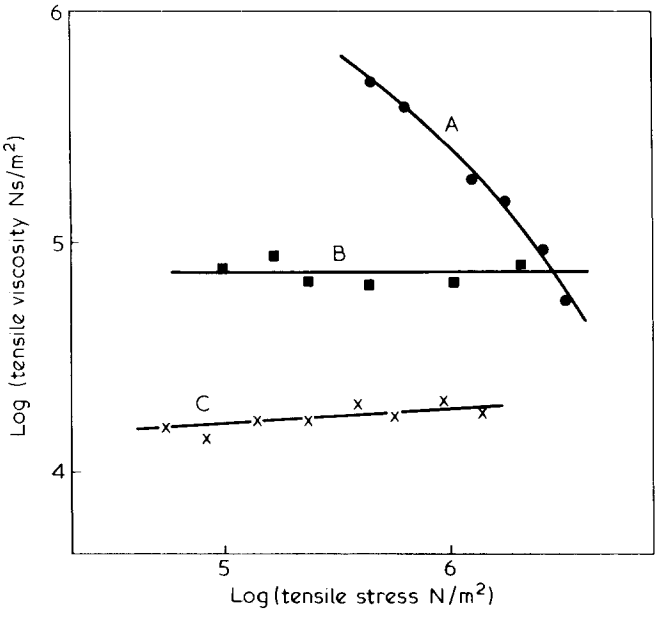

Figure 1 Log extensional viscosity vs. log extensional stress for three grades of polypropylene

slides; to prevent relaxation whilst they were examined on a Mettler micro-melting point hot stage. Specimens for *SEM* were gold coated.

RESULTS

The results of the initial study are summarized in *Figure 1* which shows the three types of extensional flow curve obtained. The tensile viscosity of sample A was found to decrease markedly with increasing stress. This material was found to be totally unprocessible on the calender under any circumstances. For temperatures at which no sticking to the calender bowls occurred, the elastic component of the melt predominated and caused the sheet, once formed in the nip, instantly to deform to give a totally unsatisfactory product, even at low line speeds. The effect was almost like passing a thick piece of rubber through a mangle; the rubber instantly regaining its former shape on removal of the stress. The vast majority of polypropylene grades examined were included in this category. The tensile viscosity of **B** was virtually independent of stress while that of C increased slightly with increasing stress. Polymer C gave the best results on the laboratory calender but is unfortunately not available commercially. **B** was the material used for the production trial described here. It is a 3% ethylene/propylene random copolymer with a *MFI* of 1.70 g/10 min at 230°C and 2.16 kg.

Using this material, sheet produced at low shear rates on the laboratory calender had a smooth surface, but that produced at high shear rates (in excess of 5000 s^{-1}) on the production equipment had a pattern on the surface. The physical appearance of the pattern was similar to that produced when water flows along a shallow channel, i.e. storm water flowing in a gutter. The structure of the pattern consisted of a series of elongated diamond-shaped ridges joined along their edges, a line connecting the apices of the diamond shapes lay parallel to the machine direction. *Figure 2* is a photographic reproduction of the surface pattern. The pattern was found to be present at the exit of the first nip. Stopping the calender during a run at a higher speed on the laboratory calender, and restarting it immediately, produced a smooth band across the sheet at the point corresponding to that at which the calender was stopped. Either side of the band the surface pattern was well defined.

X-ray diffraction showed the existence of molecular orientation similar to that found in polypropylene drawn fibres (*Figure 3*). In sheet produced at low speeds on the laboratory calender the orientation was less pronounced, the crystallographic *c*-axis was found to run parallel to the machine direction; but in the high shear sample the direction of preferred orientation was found to run at a slight angle to the machine direction and to coincide exactly with the ridges in the surface pattern.

Figure 4 shows d.s.c. scans for both an annealed sample and a sample of the production sheet. In the high shear rate sample a second, higher melting peak is evident. The

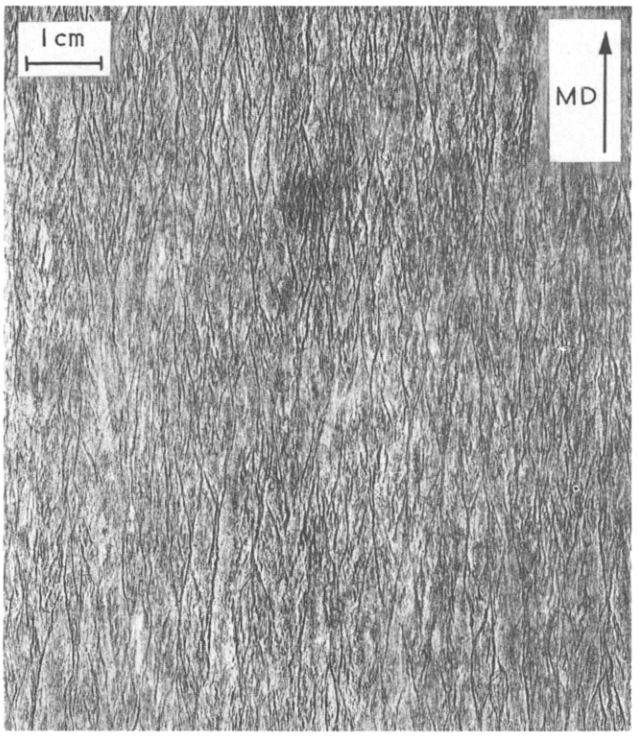

Figure 2 Surface structure of calendered polypropylene sheet: shear rate = 5500 s^{-1}

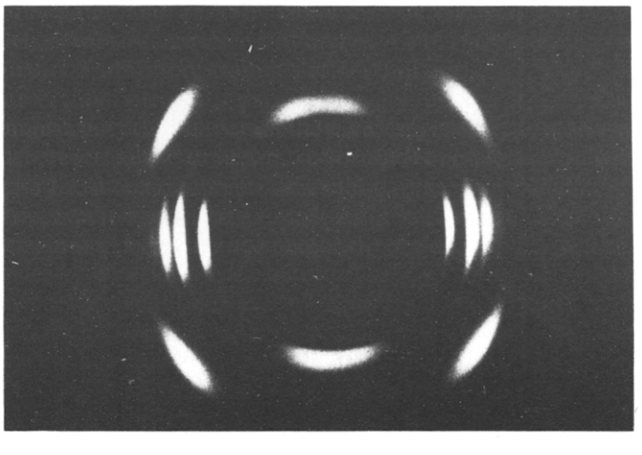

Figure 3 X-ray diffraction pattern of polypropylene calendered at 5500 s^{-1}

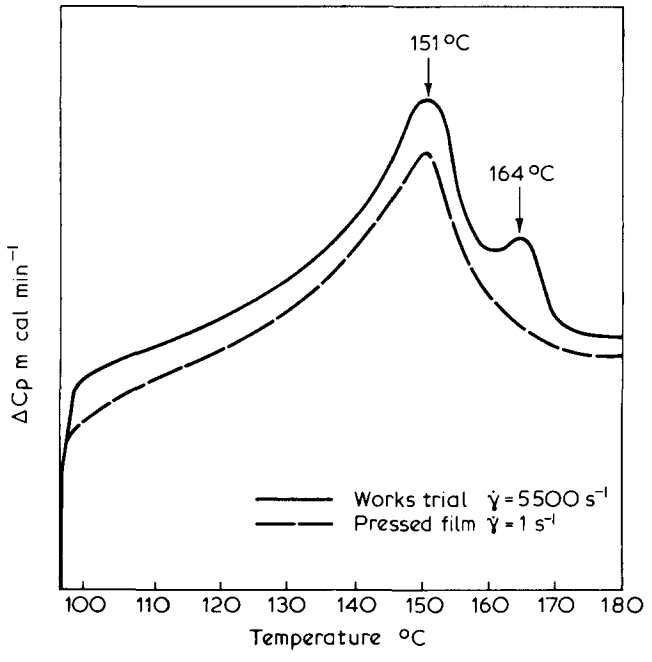

Figure 4 D.s.c. scan of polypropylene samples

two melting peaks behaved differently; the higher peak temperature was found to increase through the whole range of heating rates (*Figure 5*), while the lower peak temperature was found to decrease significantly before increasing with increasing rate.

When a sample of the production sheet was mounted between two microscope slides in a hot stage and heated to 160°C, just above the lower peak melting temperature, a high degree of birefringence was still evident, indicating a large amount of residual order. When the sample was heated to 185°C, where no further melting was evident in the d.s.c. all traces of birefringence disappeared. However, when the sample was cooled to 130°C, nucleation was seen to occur almost immediately along lines lying at a slight angle to the machine direction. These lines appeared as bundles in a criss–cross pattern, suggesting a macroscopic flow instability. Crystal growth then occurred normal to the nucleating lines resulting in long sausage-shaped crystals (*Figures 6a–6d*). Normal nucleation and spherulitic growth was not observed until about 15 min after the line nuclei first appeared. These nucleating lines were still evident when the original sample was heated to 200°C and subsequently cooled. They were finally destroyed by heating the sample to 210°C and annealing at that temperature for 5 min before cooling to 130°C, at which point normal spherulitic growth occurred, again after about 15 min, producing well defined spherulites nucleating at isolated sites.

The scanning electron microscope showed a well defined bundle from which ribbons appear to have grown (*Figure 7*).

DISCUSSION

The surface pattern observed on the sheet produced at high shear rates was similar to, although more severe than, that described as 'nerve' by Chong[4] when he processed high molecular weight cellulose acetate at high speeds and low temperatures. The fact that the pattern is eliminated by stopping the calender for just a few seconds suggests it is governed by the parameter, δ, proposed by Ziabicki[5]:

$$\delta = \tau_{or}/t_{1/2}$$

where τ_{or} is the characteristic time for disorientation and is related to a macroscopic relaxation time, and $t_{1/2}$ is the crystallization half-life. If the value of δ is much greater than unity; i.e. crystallization is much faster than disorientation (relaxation) the entire crystallization process will occur in the state corresponding to the orientation present in the melt and a highly oriented texture will result. If, however, δ is much less than unity; i.e. crystallization is slow compared with disorientation, the order present in the melt will disappear before crystallization occurs. Here lies the difference between PVC and polypropylene. In the case of PVC where the tendency to crystallize is low, any frozen in 'nerve' may be eliminated by increasing the temperature and thus lowering both the value of τ_{or} and δ. This is in complete contrast to the case of polypropylene, where the tendency to crystallize is high and the temperature/viscosity relationship is such that any attempt to lower the rate of crystallization, by raising the temperature, results in a melt viscosity that is so low that the sheet sticks to one or other of the calender bowls.

D.s.c. and optical microscopy both indicate the presence of two crystal types in the production sample. The lower melting peak, exclusively present in the pressed sample, is attributed to a chain-folded lamellar structure. The initial decrease in the peak temperature is associated with an annealing mechanism at the low heating rates, the larger crystals growing at the expense of the smaller ones.

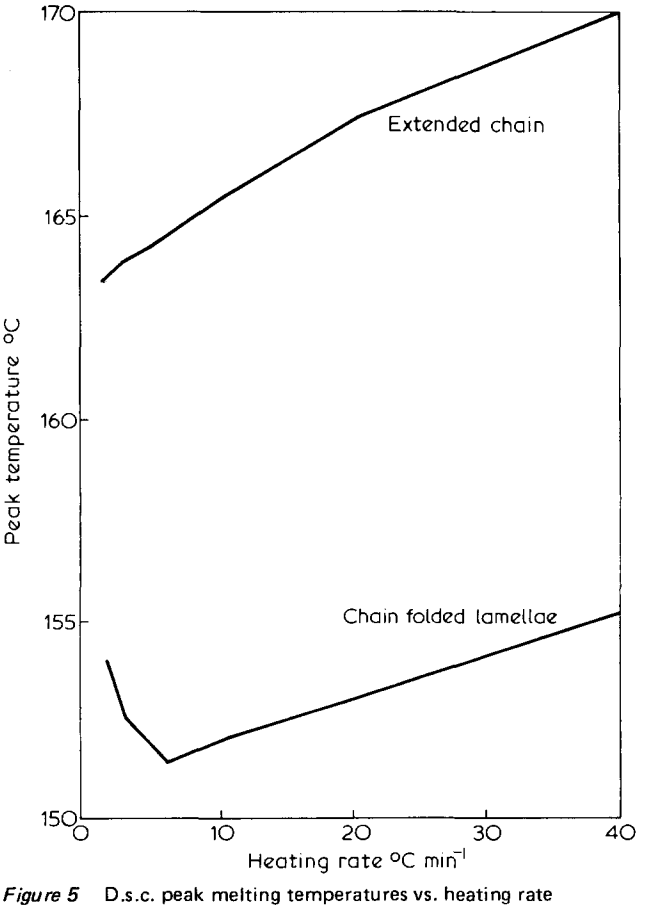

Figure 5 D.s.c. peak melting temperatures vs. heating rate

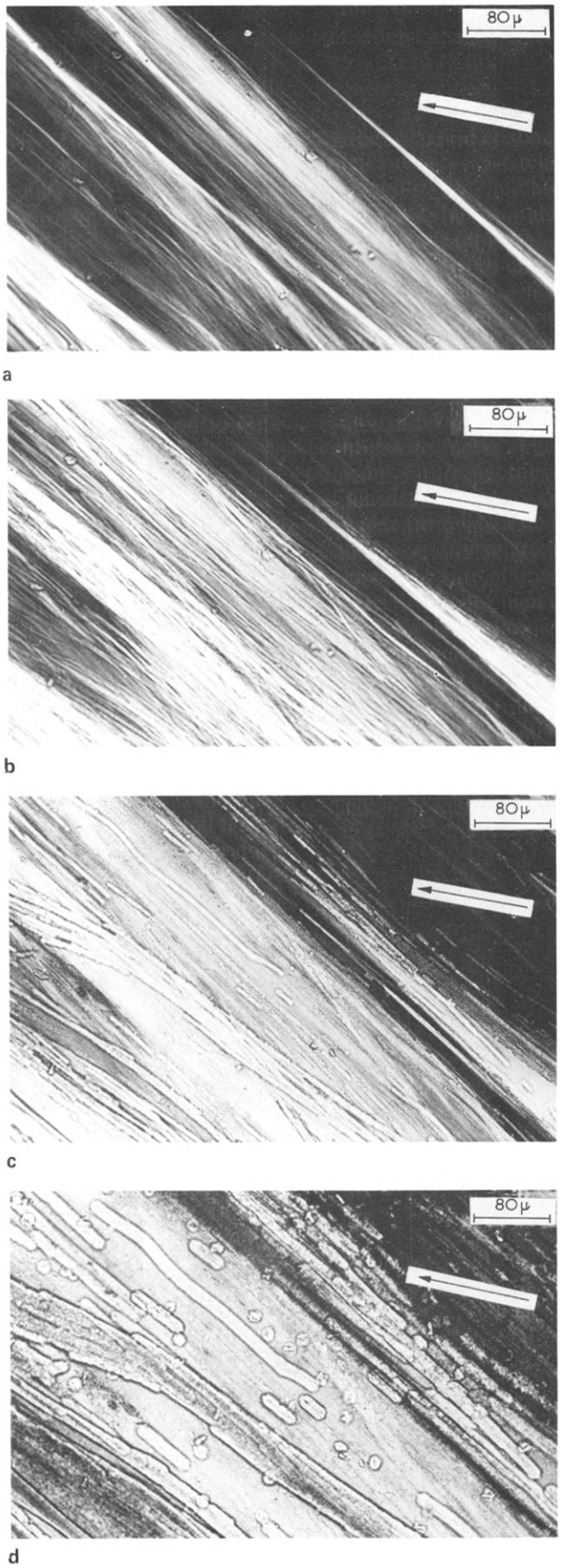

Figure 6 Crystallization of calendered polypropylene. The arrow indicates the machine direction.
(a) heated to 185°C then cooled to 130°C;
(b) after 5 min at 130°C;
(c) after 10 min at 130°C;
(d) after 15 min at 130°C

At the higher heating rates superheating becomes predominant; the temperature rises faster than the melt front can travel through the crystal[6]. The higher melting peak is associated with extended chain crystals (Hellmuth and Wunderlich[7,8]) and exhibits superheating over the whole heating rate range. The higher melting point indicates that extended-chain crystals of polypropylene are thermodynamically more stable than chain-folded lamellae, the reason the lamellar structure predominates lies in the kinetics. Normally it is unfavourable kinetically to unravel a polymer chain to such an extent that it forms extended chains. However, in the calendering process, fluid elements in the nip are subjected to pure extensional flows as well as shearing flows at the walls. It is these extensional flows that give rise to the extended-chain crystals. Ziabicki[9] showed for spun polyester that the nucleation rate increases catastrophically once a molecule has been extended to about 40–50% of its contour length and the crystallization half-life can be reduced by 2 5 orders of magnitude; McHugh and Sibeli[10] show that the reduction may be even greater, perhaps 40 orders of magnitude. This, of course, would result in a massive increase in the value of δ. The extended-chain crystals once formed act as nucleating sites for normal chain-folded lamellae[11]. This is the explanation for the results of optical microscopy; the thermodynamically more stable extended chain crystals nucleating chain-folded lamellar growth until being destroyed at higher temperatures. The observation that materials with a lower tendency to thin in tension produced the best results on a calender must be related in some way to the ease with which a melt will orient, since one explanation for extensional thinning suggests that at low extension rates the polymer chains are intertwined and that the frequency of physical entanglements is high, while at higher rates of extension the chains gradually become unravelled. In the case of a linear, stereoregular polymer such as polypropylene this would mean that the chains could more easily slip past each other and hence have a higher tendency to orient during processing.

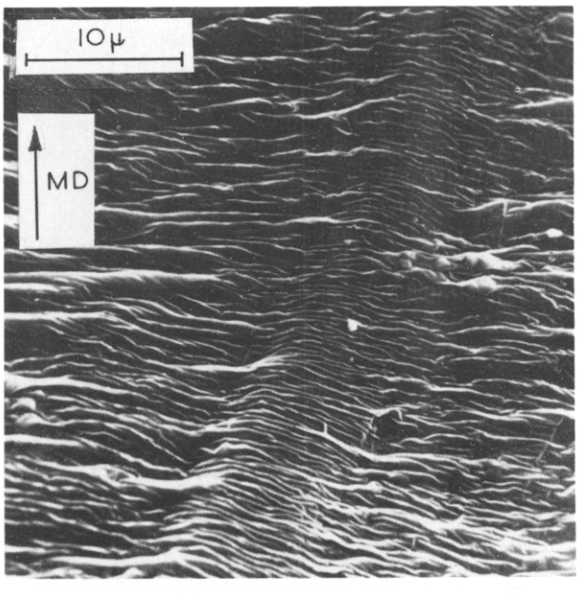

Figure 7 Scanning electron micrograph of calendered polypropylene showing chain-folded lamellae emanating from a central extended chain core

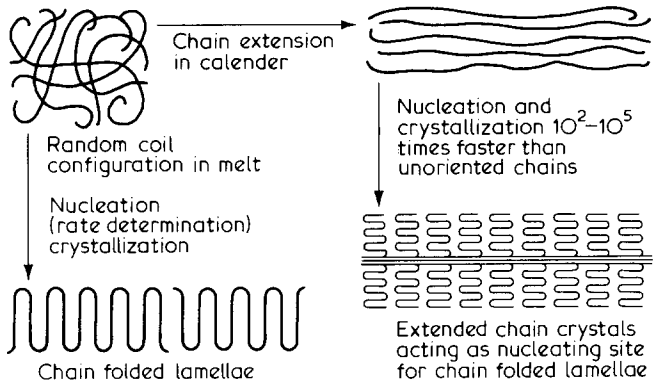

Figure 8 Summary diagram

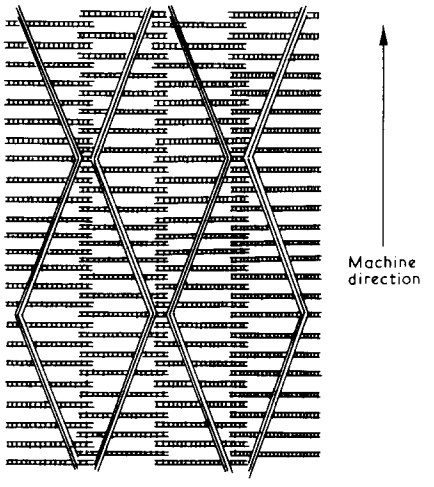

Figure 9 Schematic diagram of the extended-chain crystals forming a zigzag pattern as a result of unstable flow. Chain-folded lamellae grow from the nucleating line

The results of X-ray diffraction studies imply the presence of an unstable flow in the nip of the calender. Cogswell has shown that the viscosity in tension may be orders of magnitude greater than those in simple shear and in particular that stretching flows tend to be more elastic[12]. It is probably the recovery of these elastic extensions that contribute to any flow instabilities. A second explanation for the preferred orientation following the surface pattern would be to assume that in the nip the extended chain crystals are formed in laminar extensional flow simply to recover elastically on emergence from the nip. Either case would result in a zigzag pattern.

CONCLUSION

An undesirable surface pattern in the calendering of polypropylene results as a consequence of the material characteristics of polypropylene and the high extension rates present in the nip of a calender. The pattern has been shown to result from two distinct crystal types formed the instant the sheet leaves the calender nip. The explanation proposed is that the high extension rates in the nip effectively remove the rate determining step from the crystallization process by unravelling the chains from their random-coiled configuration in the melt causing nucleation to occur instantly. *Figure 8* is a schematic representation of this proposal. This means that Ziabicki's parameter δ is much greater than 1 and, as such, crystallization occurs in the state corresponding to that of the melt immediately leaving the nip. The zigzag pattern frozen into the sheet at high shear rates is a result of elastic recovery of the deformed melt.

Simple examination of the tear strengths of the sheet produced in this work and analysis of the tensile data described in Hashimoto's paper both suggest that the model proposed, i.e. an intermeshing network of rods, may not be correct. In both cases the results were highly anisotropic. In this study the tear strength was found to be three times greater than that of an annealed sample perpendicular to the machine direction, while parallel to the machine direction it was found to approach zero. This suggests that the bundles of extended chains do not cross paths and that a tear propagates between the bundles. *Figure 9* is a schematic representation of a possible model which would satisfy these observations. The bundles of extended chains run approximately in the machine direction, with slight kinks resulting from some elastic recovery. The chain-folded lamellae ribbons grow approximately at right angles to the nucleating lines. A tear running in the machine direction would propagate by breaking the weak interspherulite links while in the perpendicular direction chains must be broken before a tear will propagate.

ACKNOWLEDGEMENTS

The work described in this paper was carried out at Storey Bros., Brantham Works and the author is sincerely grateful for their permission to publish. The errors are the author's alone but thanks are due to Drs N. C. Billingham and P. D. Calvert of the University of Sussex, Dr M. R. Mackley, now of the University of Cambridge, and Dr G. C. Maitland of Imperial College for their comments.

REFERENCES

1 Hashimoto, T., Nagatoshi, K., Todo, A. and Kawai, H. *Polymer* 1976, **17**, 1063
2 Hashimoto, T., Nagatoshi, K., Todo, A. and Kawai, H. *Polymer* 1976, **17**, 1075
3 Cogswell, F. N. *Polym. Eng. Sci.* 1972, **12**, 64
4 Chong, J. S. *J. Appl. Polym. Sci.* 1968, **12**, 191
5 Ziabicki, A. *Colloid Polym. Sci.* 1974, **252**, 207
6 Blundell, D. J., Cogswell, F. N., Holdsworth, P. J. and Willmoth, F. M. *Polym. Lett.* 1977, **18**, 204
7 Hellmuth, E. and Wunderlich, B. *J. Appl. Phys.* 1965, **36**, 10
8 Wunderlich, B. *Thermochim. Acta* 1972, **4**, 175
9 Ziabicki, A. Unpublished work.
10 McHugh, A. J. and Sibeli, C. *Polym. Eng. Sci.* 1967, **16**, 153
11 Keller, A. and Machin, M. J. *J. Macromol. Sci. (B)* 1967, **1**, 41
12 Cogswell, F. N. 'Le Calandrage' Journee, Published by Villeurbanne, Lyon, 1975