

# Crystal Orientation Distributions in Injection-Molded Polypropylene Compounds

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## SYNOPSIS

The crystal orientation distribution in injection-molded bars made from several polypropylene compounds has been investigated using pole figure analysis. The fillers used were glass fibers, chalk, and talc, and some compounds contained one filler and others contained glass fibers plus one or both of the others. All compounds showed strong orientation in the skin with the *b*-axis of the monoclinic crystals lying preferentially normal to the flow direction and in many cases parallel to the normal to the bar face. This normal direction orientation was very strong in compounds containing talc and is probably caused by crystals forming with their (010) planes on the talc platelet faces, which align themselves parallel to the mold face. Strong orientation persists into the interior of the moldings containing talc, whereas in the other compounds, the orientation at intermediate depths is much less pronounced than in the skin. © 1992 John Wiley & Sons, Inc.

## INTRODUCTION

Injection moldings made from semicrystalline polymers possess a multilayer morphology. A distinct skin-core morphology is always present, visible in thin sections viewed in a polarizing microscope. A third intermediate layer is usually seen, while other techniques such as X-ray diffraction have revealed up to five layers in some examples.<sup>1-20</sup> The different layers have different crystallinity and/or crystal morphology and, as a consequence, have different properties. When fillers are present, there is further scope for stratification, and layers may form in which the filler concentration differs or, in the case of platelet or fibrous fillers, in which the filler orientation distribution differs.<sup>21-27</sup> The crystallinity and crystal orientation distribution may also differ from one layer to the next in a filled polymer mold-

ing. This is particularly likely if the filler particles act as nuclei for crystallization, especially if their action causes the crystals to grow in a directional manner. This does not necessarily require an epitaxial interaction but may result from geometric constraints, as is believed to be the cause of *trans-crystallinity* in some systems.<sup>28</sup> Preferred crystal orientation may also result from the preorientation of molecules in the melt when flowing into the mold, and this, in turn, may be influenced by the presence of fillers, especially if they have a high aspect ratio.<sup>29</sup> This has prompted two recent studies of crystal orientation in injection-molded talc-filled polypropylene.<sup>30,31</sup> Rybníkář deduced from crystallization rate measurements that the talc particles were indeed acting as nuclei for crystallization and found in addition that the preferred crystal orientation was re-established on melting and recrystallization.<sup>30</sup> This is further evidence for the influence of the filler particles, which retained their distribution through the melting experiment. Fujiyama and Wakino used wide-angle X-ray diffraction, in particular azimuthal scans of the (110) and (040) reflections from the  $\alpha$ -form crystals, to investigate the crystal orientation distribution.<sup>31</sup> Their measurements indicated that the polypropylene crystal *b*-axis was oriented pref-

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erentially parallel to the normal to the molding surface. Since the talc particles tended to lie with their flat faces parallel to the molding surface, this is consistent with the polypropylene crystal (010) planes lying parallel to the talc platelet surface. They found that the *b*-axis orientation was weaker near the surface and in the center than in the intermediate layer. They discovered further that the crystals with this common *b*-axis orientation showed a bimodal orientation with a preference for either the *c*-axis or the *a*\*-axis to lie parallel to the machine direction. Fujiyama et al. found a similar bimodal distribution in the skin of unfilled polypropylene moldings,<sup>19</sup> though it was not as strong as in the talc-filled moldings. In the core of the unfilled moldings, the *b*-axis was oriented preferentially in the transverse direction (TD), with the *c*-axis and the *a*\*-axis cylindrically distributed about the TD.<sup>19</sup> More recently, Fujiyama and Wakino extended their studies of both unfilled and particulate-filled polypropylene injection moldings, using different molding conditions and making a detailed structural examination of the material at different positions along the flow path as well as at different depths through the thickness.<sup>32,33</sup>

In the investigation reported here we have used wide-angle X-ray diffraction pole figures for a more complete representation of the crystal *b*-axis orientation distribution in injection moldings made from unfilled and talc-filled polypropylene. We have studied, in addition, polypropylene compounds containing chalk (with aspect ratio  $\approx 1$ ) or glass fibers or combinations of glass fibers and chalk and/or talc.

## EXPERIMENTAL

### Materials and Specimen Preparation

The materials used here were taken from a series prepared for a previous study of aging of polypropylene compounds by Crosby and White<sup>34</sup> plus a talc-filled compound made for a study by Morales and White.<sup>35</sup> The compositions are given in Table I. Each is based on the same polymer, supplied either in the form of granules (as ICI GWM 22) or powder (as GWM 522). Compound A is unmodified GWM 22. Compounds B and J both contain 20% glass fibers by weight. J is the only material containing GWM 522 and contains in addition 0.5% by weight of a nucleating agent. Compound C contains chalk and no other filler. Compound K contains talc and no other filler. The other materials all contain glass

**Table I** Compound Compositions

Code	Glass	Chalk	Talc	Young's Modulus (GN/m <sup>2</sup> )
A	0	0	0	2.3
B	20	0	0	5.3
C	0	20	0	3.1
E	15	20	0	6.35
G	15	0	20	4.7
H	15	10	10	5.0
J	20	0	0	5.8
K	0	0	25	

fibers plus, in addition, chalk and/or talc (Table I). The materials were injection-molded into ASTM D638 tensile test bars measuring approximately 190  $\times$  12.7  $\times$  3.1 mm using a mold with a single-ended cavity.<sup>34,35</sup> For the compounds A–J, the principal machine settings were as follows:

Barrel temperatures: zone 1, 236°C; zone 2, 231°C; nozzle, 207°C

Mold temperatures: fixed plate, 43°C; moving plate: 42°C

Injection pressure delivered: 93–106 MPa

Total cycle time: 55 s

For Compound K, containing talc only, the conditions were as follows:

Barrel temperatures: zone 1, 200°C; zone 2, 220°C; nozzle, 200°C

Mold temperatures: fixed plate, 35°C; moving plate: 35°C

Injection pressure delivered: 161 MPa

Total cycle time: 55 s

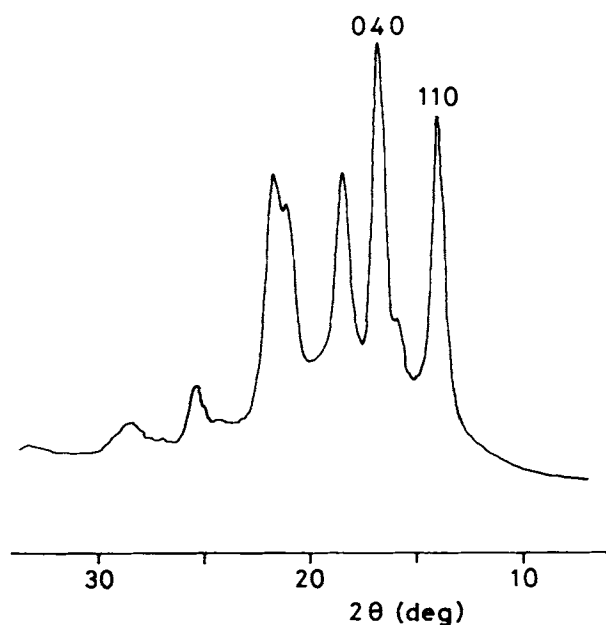
Samples in the form of thin strips approximately 0.2 mm thick were extracted from selected locations within these bars by milling away the material on either side using a single-point cutter with fly cutting action. This technique was chosen because of the extensive experience we have gained from using it for layer removal in the measurement of residual stress in molded thermoplastics and reinforced thermoplastics.<sup>34–38</sup> During these studies, we have conducted various tests to check that milling does not alter the remaining material, including inspection in the scanning electron microscope (in which we looked for, but did not find, evidence for melting) and molecular weight measurement of the swarf.

Pieces were cut from within the central gauge section of the thin strips for the measurement of density and shrinkage<sup>39</sup> as well as for crystal orientation characterization. Three locations were selected: The *skin* was represented by a surface layer 0.2 mm thick; the *intermediate* layer was taken at 0.6–0.8 mm from the surface; and the *core* sample was extracted from the center of the molding.

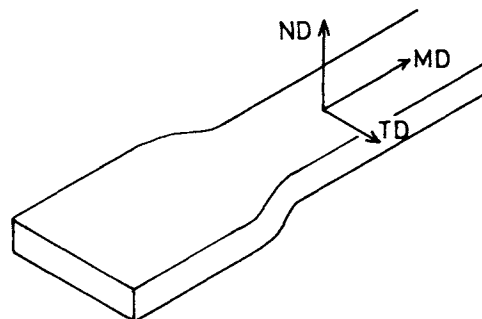
### Orientation Assessment

Wide-angle X-ray diffractometer scans were made and confirmed that the vast majority of the crystals were of the monoclinic ( $\alpha$ -) form, though weak reflections from hexagonal ( $\beta$ -) crystals were also present in some cases (Fig. 1). It is evident that the most intense X-ray reflections are the monoclinic (040) and (110) and these have been used to characterize orientation in many studies of textured polypropylene.<sup>5,19,31–33,40</sup> In the investigation reported here, we have used only the (040) (monoclinic) reflection. A detailed description of the conformation of the polypropylene molecule within the monoclinic crystal is given by Geil.<sup>41</sup>

The data for pole figure construction were obtained using a Philips PW1078 texture attachment on a standard PW1050 vertical X-ray goniometer. The thin samples were suitable for generating pole figures in both reflection and transmission. In this way, the orientation distribution pattern was deter-



**Figure 1** X-ray diffractometer trace from the core of a molding made from unfilled polypropylene.



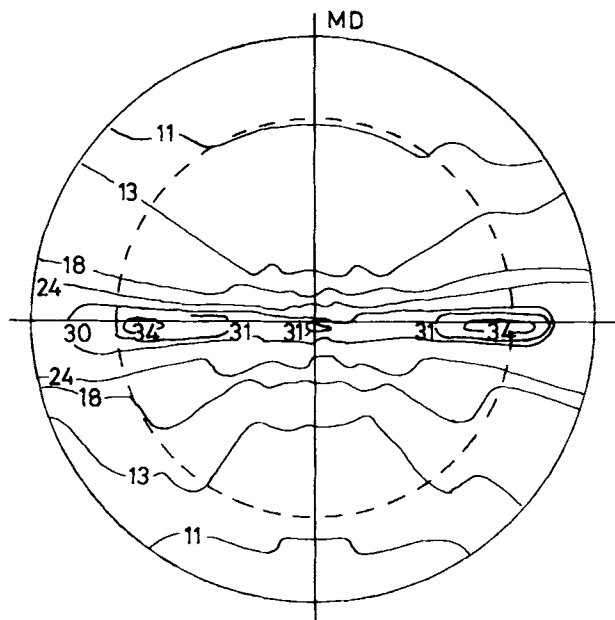
**Figure 2** Sketch of part of a bar showing the machine direction (MD), the transverse direction (TD), and the normal direction (ND).

mined over all possible angles. The main reference axis was chosen to be parallel to the bar axis, or the *machine direction* (MD in Fig. 2), and samples were normally mounted on the sample holder so that this axis coincided with the vertical axis in the analyzed pole figure. As a check on the trueness of the sample stage, some samples were mounted turned through  $90^\circ$  so that in the as-analyzed pole figure the transverse direction (TD) coincided with the vertical axis and the pole figure required rotation through  $90^\circ$  to restore the chosen presentation configuration. The direction parallel to the normal to the molding surface is labeled ND and the nomenclature used here is the same as that used by Fujiyama et al.<sup>19,31</sup> (Fig. 2). In the pole figures presented below, the reflection geometry was used to obtain the central region, out to the ring that corresponds to poles inclined at  $70^\circ$  to ND, represented by a dotted line. The transmission data were used in the construction of the regions at higher angles, but exact matching of the levels in reflection and transmission figures from the same specimen is rarely possible and the contour magnitudes in this region have been adjusted arbitrarily to coincide with the values taken from the reflection analysis. To determine background levels and to check that no spurious geometrical artifact was present, a polypropylene sample melt-crystallized from granules in an open mold, conditions unlikely to promote orientation, was tested and the resulting texture camera trace indeed confirmed that no detectable orientation was present.

## RESULTS

### Unfilled Polypropylene

Figure 3 shows the (040) pole figure obtained from the skin of unfilled polypropylene (A). The (040)

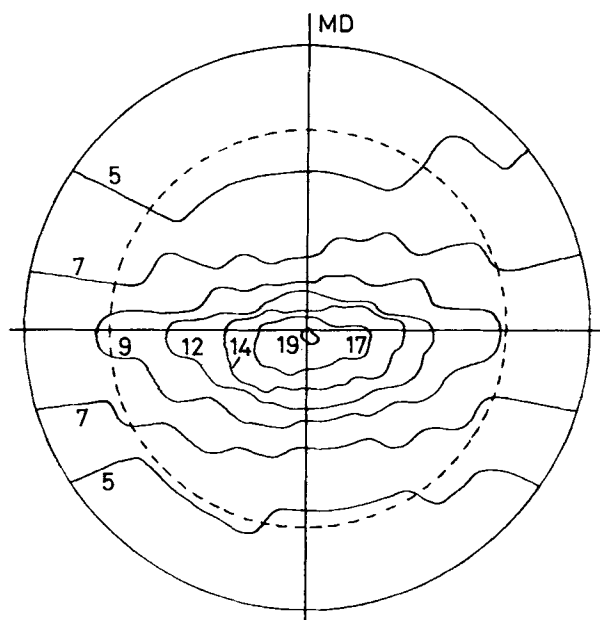


**Figure 3** (040) pole figure from the skin of unfilled polypropylene (A).

poles have a strong equatorial orientation and it is evident that the  $b$ -axes are arranged in a cylindrical manner about the bar axis (= machine direction, MD). The intermediate layer showed a similar orientation preference for the (040) (though somewhat weaker), whereas the core showed almost no preferred orientation for this pole.

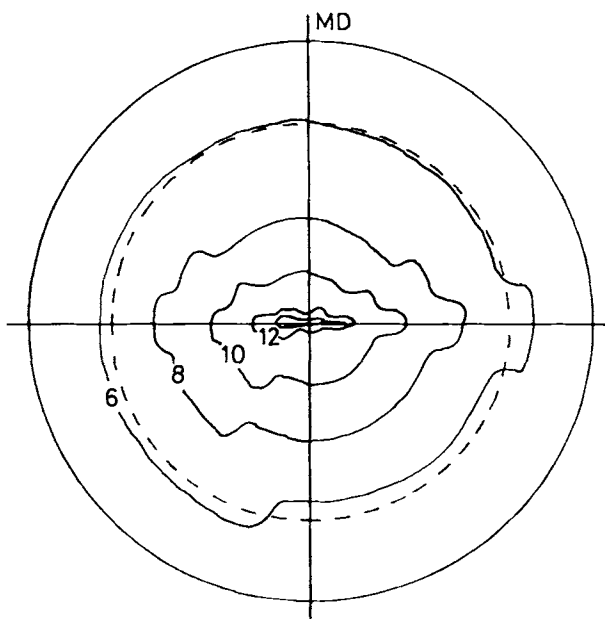
### Glass Fiber-filled Polypropylene

The (040) pole figure from the skin of glass fiber-filled polypropylene (B) indicated that the  $b$ -axis is again concentrated in a cylindrical manner about MD; furthermore, within this, there is a preference for the direction normal to the mold face (ND), as shown by closed contours in the center of the pole figure (Fig. 4). Although the  $b$ -axis orientation in the intermediate layer was not quite as pronounced as that in the skin, the difference was less than that found in the unfilled polymer. The contours in the (040) pole figure given in Figure 5 become almost circular at large angles, however, whereas in the pole figure for the skin (Fig. 4), the cylindrical distribution is maintained almost throughout, much as in Figure 3 for the skin in unfilled polypropylene. To account for their observations on the skin of unfilled polypropylene moldings, Fujiyama et al. proposed a bimodal crystallization scheme in which crystals showed a preference to have either the  $c$ -



**Figure 4** (040) pole figure from the skin of glass fiber-reinforced polypropylene (B).

axis or the  $a^*$ -axis parallel to MD.<sup>19</sup> Fujiyama and Wakino claimed that the same description applies at all depths in their talc-filled moldings.<sup>31</sup> In the current work, the  $c$ -axis orientation cannot be deduced. The core from glass fiber-filled polypropylene (B) moldings showed very weak orientation with



**Figure 5** (040) pole figure from the intermediate layer of glass fiber-reinforced polypropylene (B).

the core (040) pole figure, indicating a slight preference for orientation parallel to ND.

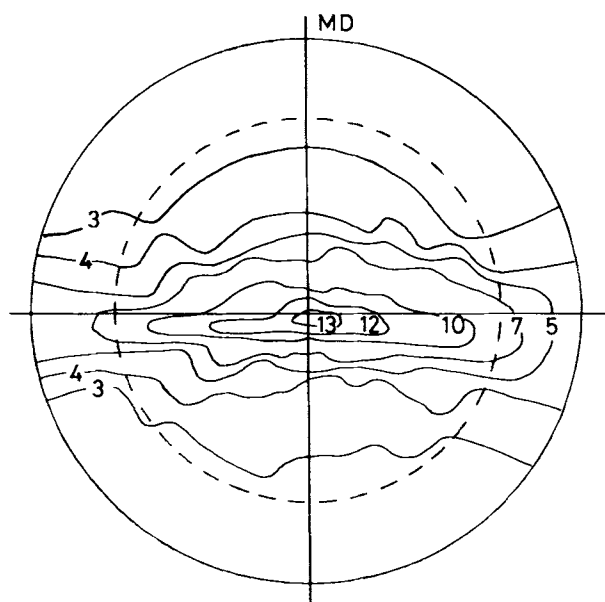
The results obtained with the skin from moldings made with glass fiber-filled polypropylene containing a nucleating agent (J) were rather similar to those for compound B. In the intermediate layer of compound J, the (040) pole figure again showed a predominantly cylindrical distribution, with a possible preference for ND. The core showed a slight tendency for the *b*-axis to favor ND.

### Chalk-filled Polypropylene

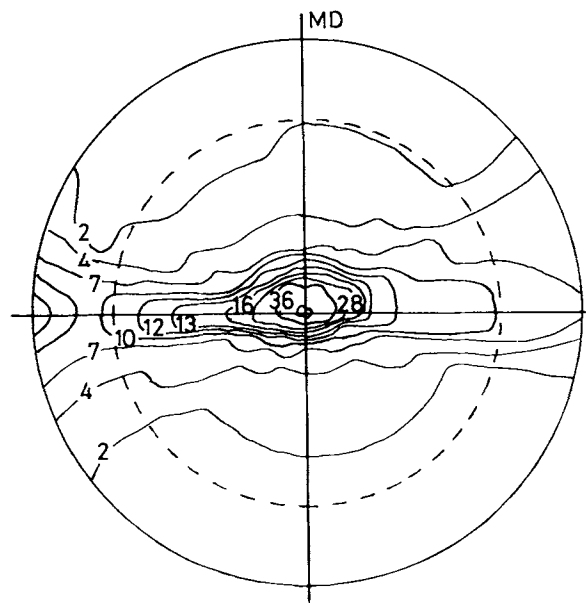
The (040) pole figure for the skin from moldings of chalk-filled polypropylene (C) again shows a strong preference for equatorial directions within which there is a slight preference for ND (Fig. 6). The (040) pole figures for both the intermediate layer and the core were almost identical and indicated very little *b*-axis orientation was present, with a slight preference for ND.

### Talc-filled Polypropylene

The (040) pole figure for the skin taken from a talc-filled polypropylene molding (K) is given in Figure 7. Equatorial directions are again favored, but this time the preference for ND is very strong. The intermediate layer shows a similar preference for *b*-axis orientation parallel to ND but no pronounced *b*-axis orientation was present in the core.



**Figure 6** (040) pole figure from the skin of chalk-filled polypropylene (C).



**Figure 7** (040) pole figure for talc-filled polypropylene skin (K).

### Polypropylene Filled with Glass Fibers plus Chalk

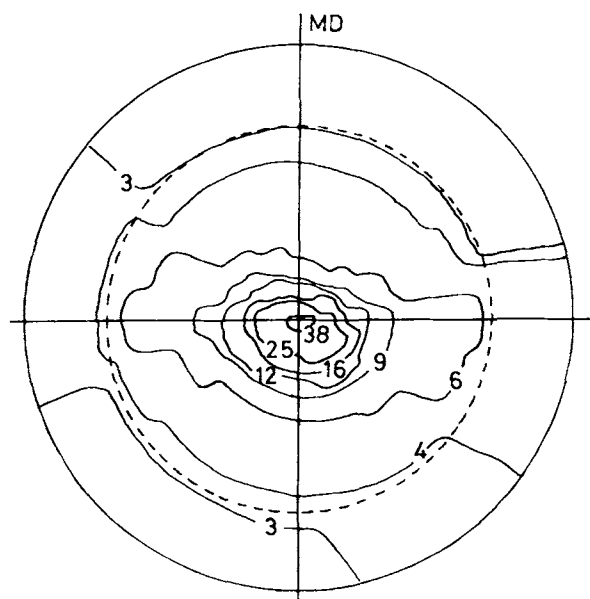
The (040) pole figure for the skin from a molding containing glass fibers and chalk (E) was very similar to that obtained with the sample containing glass alone (B). The (040) pole figure from the intermediate layer showed a preference for the *b*-axis to orient parallel to ND, similar to that with the compound filled with chalk only (C) and possibly slightly sharper. A similar but much weaker *b*-axis orientation was indicated to be present in the core.

### Polypropylene Filled with Glass Fibers plus Talc

The (040) pole figure for the skin from the sample having glass fibers plus talc as fillers (G) shows that the *b*-axis has a pronounced tendency to lie parallel to ND, superimposed on a general preference for equatorial directions (Fig. 8). The *b*-axis orientation in the intermediate layer is also strongly parallel to ND, but the general equatorial orientation is less than that observed in the skin, a similar result to that found with the compound containing only talc as filler. A very weak preference for *b*-axis orientation parallel to ND was found in the core.

### Polypropylene Filled with Glass Fibers, Chalk, and Talc

The sample molded from the compound containing glass fibers, chalk, and talc (H) again showed strong



**Figure 8** (040) pole figure from the skin of polypropylene filled with glass fibers plus talc (G).

orientation of the  $b$ -axis parallel to ND in both the skin and the core with a secondary general preference for equatorial directions. In the core, there was a slight tendency for the  $b$ -axis to align to ND.

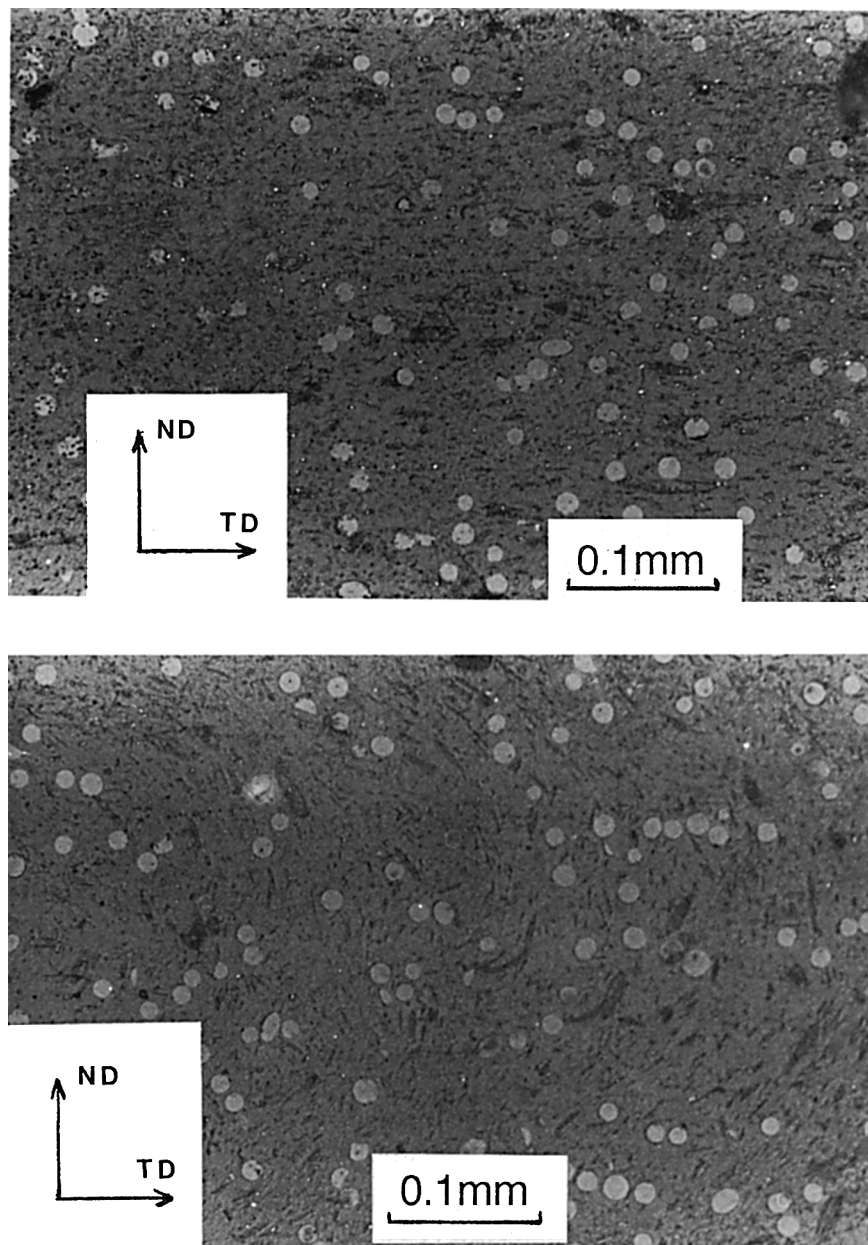
## DISCUSSION

In all the injection-molded polypropylene compounds studied, the skin possessed a pronounced orientation with the  $b$ -axis showing a strong preference for directions transverse to the machine direction (MD). In some cases, the  $b$ -axis tended to be almost randomly oriented about MD, but in others there was a strong preference to align parallel to the normal to the mold face (ND). The samples containing talc all showed strong ND orientation of the  $b$ -axis, much stronger than that displayed by any of the other materials. It is concluded that this is the direct result of interaction between the filler and the polymer. In previous studies of these compounds, it was observed that the talc particles in moldings made from the material with talc as the only filler (K) and those containing talc in combination with other fillers lie predominantly parallel to the mold surface down to considerable depths from the surface.<sup>34,42</sup> It was confirmed by scanning electron microscopy of fracture surfaces<sup>34</sup> and by optical microscopy of polished sections that in the samples used here the talc particles show a very strong alignment through and beyond the inter-

mediate layer (0.6–0.8 mm from the surface) but that they show a quasi-random orientation in the core (Fig. 9). A similar observation was made by Fujiyama and Wakino<sup>31</sup> and our results support their view that the preferential crystallization habit for the polypropylene is with the (010) plane parallel to the flat talc surfaces. In the compounds containing talc, the  $b$ -axis orientation in the intermediate layer was similar to that in the skin, as was the orientation of the talc particles but little or no  $b$ -axis orientation was present in the core.

The orientation distribution of fibrous fillers has been discussed by Folkes and Russell<sup>23,25</sup> in terms of *fountain flow*,<sup>43,44</sup> but the orientation distribution of platelet fillers has received less attention. Folkes cited work by Schmidt<sup>45</sup> as indicating that the addition of fillers does not alter significantly the flow pattern of thermoplastic melts. Schmidt<sup>45</sup> used colored tracers and viewed flow in a mold with a glass plate, but the filler particles used in these studies were glass spheres and would not be expected to modify flow as much as fibers or platelets. Nevertheless, the general pattern of fountain flow known to exist with unfilled thermoplastics has been used fairly successfully to account for the fiber orientation distribution in fiber-reinforced moldings at least qualitatively. This may well apply equally to platelets. The change in orientation of the reinforcing particles from longitudinal to transverse found with 1-dimensional fibers does not apply to 2-dimensional platelets, and the presence of preferred orientation of the platelet surface to the mold cavity surface can be expected in regions showing both longitudinal and transverse fiber orientation, reducing the number of strata visible in platelet-filled materials.

In the compounds containing glass fibers but no talc, the  $b$ -axis in the skin showed a strong equatorial orientation with a slight preference for ND; in the compound containing chalk only as filler, a  $b$ -axis preference for ND was still detectable but was even smaller. The equatorial orientation would be produced if the molecular chains retained flow-direction orientation and the slight preference for ND could be caused by directional crystallization close to the mold wall. The exception is the compound containing a nucleating additive (J) in which the equatorial  $b$ -axis orientation in the intermediate layer was similar to that in the skin. Compared with a similar compound without the nucleating additive, crystal growth can be expected to commence earlier in compound J at any chosen location and we speculate that the intermediate layer began to crystallize before molecular recoil was too far advanced in the surrounding region. In the core in all these com-



**Figure 9** Section of a bar made from compound G taken perpendicular to the bar axis (MD): (a) near the surface, showing the glass fibers lying predominately parallel to MD, as indicated by their circular cross sections, and the dark talc platelets lying predominately parallel to the MD-TD plane; (b) near the center, showing that the talc particles are no longer parallel to the MD-TD plane.

pounds, the *b*-axis showed a slight preference for ND. The source of this preference is not immediately obvious but we speculate that it is related to the advance of the solidification front, which is parallel to the mold face during the (relatively) slow cooling of the molding and that it may be related to the developing thermal stresses. We believe that this

has a strong influence on the molecular conformation frozen-in when polystyrene moldings cool<sup>46</sup> and it would not be surprising if a similar effect is present with a crystallizing polymer. This idea was proposed by Misra and co-workers,<sup>47</sup> and although in an earlier paper<sup>29</sup> one of the present authors suggested alternative explanations for the observations of

Misra et al., it does seem that there may be a stress (or stress gradient) effect that dominates in certain circumstances. This is essentially the same process as that discussed by Greener and co-workers.<sup>48</sup> It is interesting to note that in the intermediate layer from compound J the *b*-axis showed an equatorial orientation with no preference for ND; this can again be explained if the presence of the nucleating agent caused crystallization to occur before significant thermal stresses developed, unlike the case with the other compounds, leaving no mechanism for the promotion of preferential ND orientation.

It is worth considering the effect that directional crystallization of the kind observed here has on the overall properties of the moldings. It is well known that injection moldings made from unfilled thermoplastics are anisotropic. In the case of semicrystalline polymers, this is partly (perhaps largely) due to the anisotropy of the crystals coupled with preferred crystal orientation. In fiber-reinforced polymers, the anisotropy is generally attributed to the filler orientation distribution and the anisotropy of the polymer matrix is often disregarded. Recent studies of reinforced nylon 6.6 have shown that variations in the properties of the crystalline matrix can produce significant variations in property through the depth of injection moldings even when the filler content is fairly high (33% by weight).<sup>49,50</sup> The various effects produced by fillers such as talc that promote directional crystallization and by nucleating agents that cause crystallization to occur at an earlier stage of the cooling process can thus produce significant changes in property.

## CONCLUSIONS

When injection moldings are made from polypropylene-containing fillers, the crystal orientation distribution depends on the nature of the filler. Talc is found to have a particularly strong effect, because the talc particles themselves become strongly oriented during molding and the polypropylene crystals seem to form with their (010) plane parallel to the flat face of the talc particles. Polymer crystals are highly anisotropic and a molding that has strong preferred orientation in the crystal phase is itself anisotropic.

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