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# Relaxation Patterns in Powder Injection Mouldings Made with Repeated Flow Reversals

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***Abstract***

*Injection moulding suspensions based on both high and low molecular weight organic vehicles and incorporating both spherical and anisotropically shaped particles were prepared. A double end-gated rectangular bar cavity was used for injection moulding. Conventional mouldings were made by injection from one gate followed by static hold pressure. Modulated pressure mouldings were made in the same way but reciprocating flow was induced between the gates during solidification. The mouldings were sectioned, polished and heat treated whereupon a pattern of rings emerged in relief preserving the history of flow reversals as the solid-liquid interface advanced from the mould walls.*
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## 1 Introduction

Although there is much interest in the injection moulding of metal and ceramic powders, the injection moulding of composites thereof is somewhat troublesome. The orientation of anisotropically shaped particles or fibres, added for reinforcement, results in a complex orientation pattern in conventional mouldings so that the resulting powder assembly sinters non-uniformly giving rise to distortion.[1,2]

The orientation of short fibres in polymer matrices can be controlled by imposing reciprocating flows during the solidification stage. The liquid contents of the cavity are subjected to shear as the solid-liquid boundary advances and this aligns fibres in the region of high velocity gradient which are then occluded by the solid phase.[3–5] This technique has been used successfully for the alignment of fibres in metal [6,7] and ceramic [8] matrices.

Any anisotropically-shaped objects can be aligned by this operation including polymer molecules. Indeed this method has been used for property enhancement in unfilled polymers.[9,10] The presence of 'frozen in' molecular orientation in powder injection moulding is of interest because such mouldings are reheated to remove the organic vehicle. At this stage, relaxation process may take place which rearrange the particle assembly.

In conventional powder injection moulding, there is evidence that an orientation pattern develops in the organic vehicle which indeed influences the relaxation strains which occur on reheating. Thus anomalous thermal expansion coefficients are recorded in samples cut from mouldings.[11] Such samples must be fully annealed after cutting if the true thermal expansion is to be recorded. Depending on the moulding conditions, swelling or depressions appear in polished sections of mouldings on annealing which are indicative of heterogenous relaxation strains.[12]

In the present work, the relaxation behaviour witnessed by the annealing patterns in polished sections is compared for conventional and reciprocating flow conditions. Since particle orientation might also be implicated in the development of these patterns, spherical carbonyl iron powder mouldings were compared with those containing relatively equiaxed and platy alumina powders.

## 2 Experimental Details

Details and sources of the materials are given in Table 1. The carbonyl iron is a spherical powder of average diameter 3 $\mu$m, while the RA6 alumina is irregular but equiaxed with average particle diameter 0·9 $\mu$m. The MA95, in contrast, is a coarse

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and platy powder. Wax-based and polypropylene-based organic vehicles were used and stearic acid was incorporated in all mixtures. The compositions are given in Table 2.

Mixing was carried out on a twin screw extruder (Model TS40, Betol Machinery, Luton, UK) using a procedure fully described elsewhere.[7,8] Injection moulding was carried out on a Demag D150 NC III K (Schwaig, Germany) machine fitted with a double valve assembly shown in Fig. 1 using the conditions shown in Table 3. The mould cavity was a double end-gated bar 10×15×70 mm shown complete with runners and sprue in Fig. 2

The bars were cut at least 15 mm away from the gates and polished. This section was then viewed in oblique illumination after heat treatment. The heat treatments of individual mouldings are given in the relevant figure captions. The rate of heating had no effect on the deformation pattern provided the heating rate was less than 5°C $h^{-1}$. The polymer-based mouldings retained sufficient strength for handling when cooled from an annealing temperature of 180–200°C. The wax-based ceramic samples were very fragile after annealing and were heated to higher temperatures to effect partial sintering. This treatment was not essential for the development of

**Table 1.** Details of materials

| | *Grade* | *Source* |
|---|---|---|
| Unfilled polypropylene | HW1925 | ICI, Welwyn, UK |
| Isotactic polypropylene | GY545M | ICI, Welwyn, UK |
| Atactic polypropylene | MF70 | APP Chemicals, Salop, UK |
| Microcrystalline wax | 1865 | Astor Chemicals, West Drayton, UK |
| Stearic acid | GPR | BDH-Merck, Lutterworth, Leicestershire, UK |
| Iron | OM | BASF, Cheadle Hulme, Cheshire, UK |
| Alumina | RA6 | Alcan Chemicals, Gerrards Cross, UK |
| Alumina | MA95 | Alcan Chemicals, Gerrards Cross, UK |

**Table 2.** Compositions of injection moulding suspensions

| *Code* | *Powder* | *Organic vehicle* | *Powder vol%* |
|---|---|---|---|
| UPP | — | HW1925 polypropylene | 0 |
| FPP | Iron | PP-based[a] | 60 |
| FW | Iron | wax-based[b] | 60 |
| APP | RA6 alumina | PP-based[a] | 60 |
| AW | RA6 alumina | wax-based[b] | 60 |
| AAP | RA6 alumina<br>MA95 alumina | PP-based[a] | 48/12 |

[a]Isotactic polypropylene; atactic polypropylene; stearic acid 4:4:1 by weight.
[b]1865 wax; stearic acid 9:1 by weight.

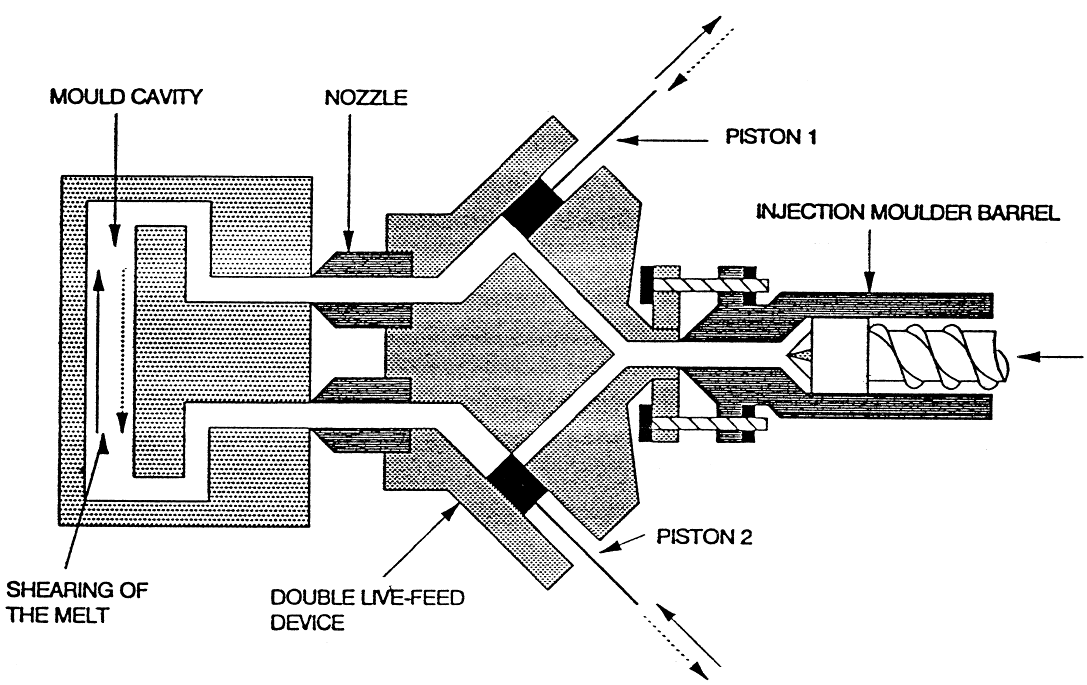



**Fig. 1.** The valve arrangement used to induce reciprocating flow after mould filling.

the surface profile and was used to confer handleability. On the other hand, the wax-based iron powder mouldings could be handled after removal of the wax.

## 3 Results and Discussion

During solidification under modulated pressure conditions the advance of the solid-liquid interface is accompanied by repeated flow reversals of the molten contents of the cavity. This causes heat to be generated in the melt by viscous dissipation and forced convective flow causes heat to be exchanged with the heated nozzle of the valve assembly. A preliminary model for this heat balance has been made.[13] It suggests that substantial temperature rises can occur in the flowing melt and that for low thermal conductivity materials reciprocation can be continued indefinitely.

Figure 3 shows a microtomed section of an unfilled polypropylene bar (UPP) in which reciprocation had been continued for 600 s. Polarized light reveals the effect of residual orientation and the rings can be studied to deduce the history of flow reversals rather in the way that dendrochronologists access climatic conditions of the past. The moulding has been subjected to 86 oscillation cycles (i.e. 172 flow reversals) but only about 30 rings can be detected. Thus steady state was reached after about 105 s at a set pressure amplitude of 150 MPa and thereafter the heat input due to shear flow and heat convected from the nozzle exactly balanced the heat lost to the mould walls as predicted by the model.[13]

After 600 s the moulding operation was terminated and the contents of the cavity allowed to cool. The elliptical central region of the section represents the melt which cooled passively, retaining little preferred orientation. Signs of shrinkage voids, exacerbated by microtomy, can be seen at the centre because this molten region solidified without an imposed pressure when reciprocation ceased. The rings arise because only the material which was subject to a high velocity gradient adjacent to the solidified wall shows strong preferred orientation. During the short stationary period before flow reversal, the solidification front continued to advance, occluding molecules with less preferred orientation.

Figure 4 is a polished section of an unfilled polypropylene moulding (UPP) prepared under similar conditions. It has been annealed and is viewed in oblique illumination. Close inspection of the profile shows that the same rings are made visible as a result of deformation caused by molecular relaxation. The elliptical rings at the surface and the depression at the centre correspond to

**Table 3.** Injection moulding conditions

| | *AW/FW* | *UPP* | *APP* | *FPP* | *AAP* |
|---|---|---|---|---|---|
| Barrel temps (°C) | 80, 90, 100, 100 | 170, 200, 210, 210 | 180, 200, 210, 210 | 180, 190, 190, 190 | 180, 190, 200, 210 |
| Mould temp (°C) | 30 | 40 | 80 | 80 | 80 |
| Injection speed ($m^3/s$) | $15\times10^{-6}$ | $15\times10^{-6}$ | $15\times10^{-6}$ | $15\times10^{-6}$ | $15\times10^{-6}$ |
| Injection pressure (MPa) | 84 | 30 | 84 | 84 | 84 |
| Hold pressure[a] (MPa) | 28 | 28 | 28 | 28 | 28 |
| Background pressure[b] | 14 | 14 | 14 | 14 | 14 |
| Osc. pressure (MPa) | 100 | 100–150 | 150 | 100–150 | 100–150 |
| Osc. cycle time (s) | 4 | 6–8 | 4 | 4 | 4 |

[a]For conventional moulding.
[b]For modulated pressure moulding.

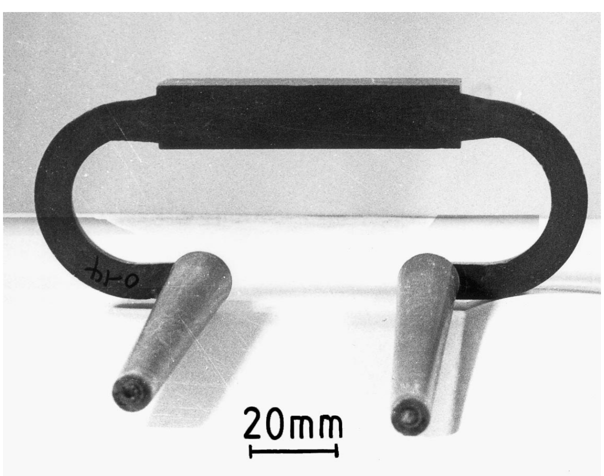



**Fig. 2.** The rectangular bar cavity and runner system.

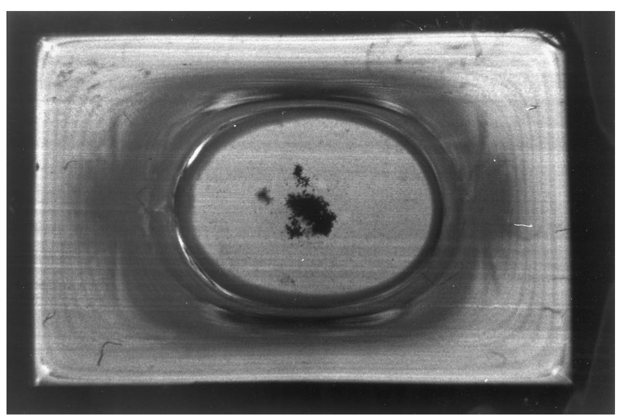


**Fig. 3.** Unfilled polypropylene (UPP) moulded with 600 s of modulated pressure (mould temperature 40°C, oscillating cycle time 7 s). Microtomed section viewed between cross polars.

Fig. 3. Such deformation has also been seen in ceramic mouldings made by various methods.[12]

Since, in filled systems, such deformation could reasonably be attributed to some aspect of particle orientation rather than to polymer relaxation, the choice of powder in such experiments is critical. Carbonyl iron, like several metal powders, can be reliably obtained in spherical form. Figure 5 shows the iron powder before mixing. Although there is a proportion of particle pairs, the majority of particles are isotropic in shape. Figure 6 shows the polished sections of a moulding made under oscillating pressure conditions which consisted of 60 vol% carbonyl iron in the polypropylene-based organic vehicle (FPP). In this cross section one can detect seven rings corresponding to 3·5 cycles of 4 s each. The higher thermal conductivity of the suspension means that heat is rapidly lost to the mould wall and a heat balance corresponding to indefinite reciprocation cannot be achieved. The central core in which rings are absent corresponds to the region that solidified after the runners and therefore without reciprocating flow. The larger spacing of the rings compared with Figs 3 and 4 corresponds to the higher velocity with which the solid–liquid interface advanced resulting from increased thermal diffusivity. The sections of conventionally moulded bars of this material, like those of unfilled polypropylene, were featureless. However, concentric rings can sometimes be detected in the sprues used to feed conventional mouldings and this can also be attributed to an unsteady flow caused by stick–slip behaviour of the machine which is often audible, especially during the packing stage.

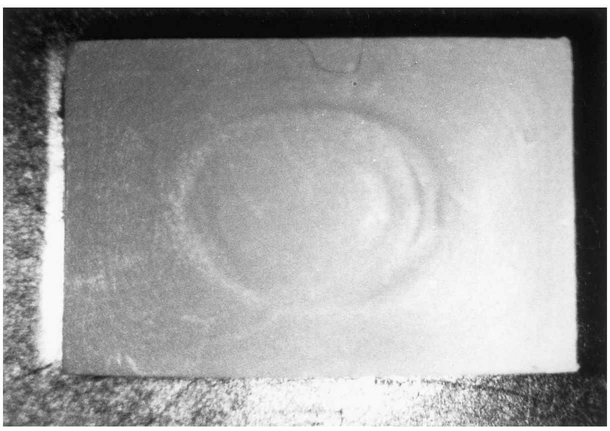


**Fig. 4.** Polished section of unfilled polypropylene (UPP) moulded as for Fig. 1 viewed in oblique illumination after annealing at 180°C for 24 h.

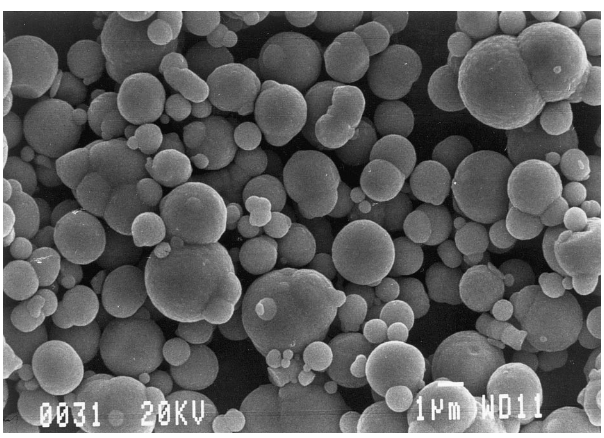



**Fig. 5.** Scanning electron micrograph of carbonyl iron powder, as-received.

Figure 7 shows RA6 alumina suspensions in the polypropylene-based vehicle (APP). In conventional mouldings the pattern of rings is absent. In the modulated pressure moulding it is possible to detect six rings corresponding to three oscillation cycles or 12 s. The central region solidified without reciprocating flow or static hold pressure and a crack, associated with shrinkage of this region, is visible. Although this alumina consists of particles which appear equiaxed in the electron microscope, there is some debate about the existence of preferred orientation in particles which display imperceptible shape anisotropy.[14] Such orientation cannot apparently be detected by X-ray methods for reasonably equiaxed particles but manifests itself in optical microscopy of thin sections of the particle assembly immersed in a liquid of similar refractive index to the powder and viewed between crossed polars. The role of particle orientation in generating the relaxation patterns seen in this work appears to be small in view of the results gained with spherical powder and unfilled polymer.

To confirm this, an alumina suspension was made up with 48 vol% RA6 and 12 vol% of a platey alumina, MA95 (AAP). Figure 8(a) shows that the annealed section of the conventional moulding is featureless as in Fig. 7(a). In Fig. 8(b), the pattern of rings is similar to that in Fig. 7(b). The pattern does not appear to be enhanced or reduced by the presence of anisotropically shaped particles which confirms the view expressed in this and previous

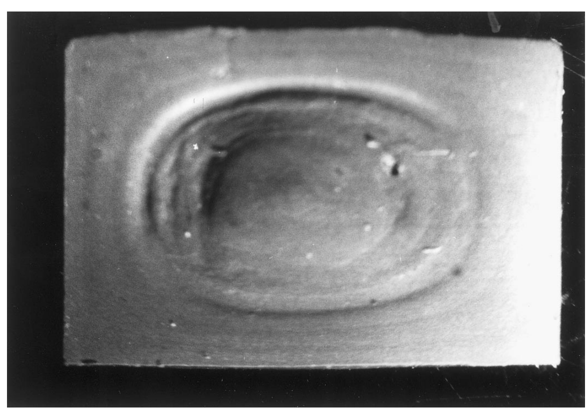


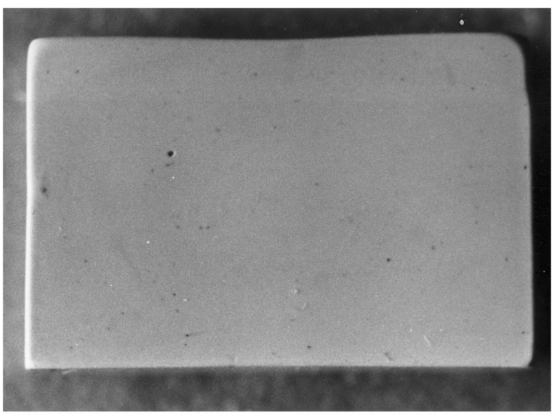
**Fig. 6.** Polished section of a moulding of carbonyl iron in the polypropylene-based vehicle (FPP) made using reciprocating flow and viewed after annealing the transverse section at 180°C for 24 h.

work that such deformations are the result of the relaxation of chain extended molecules. The platy alumina particles are, unsurprisingly, aligned preferentially by the reciprocating flow process.

It could also reasonably be argued that since it is known [15] that particles migrate away from regions of high shear rate, local non-uniform volume fraction could be responsible for the deformation. Thus reciprocating flow would cause bands of powder depletion when solidification occluded flowing material, interspersed with regions of powder excess occluded during stasis. Such rearrangement may take place to some extent but Fig. 4 clearly shows the development of relaxation patterns in an *unfilled* polymer moulding. Furthermore, the rings in Fig. 4 correspond to those in the microtomed section viewed between crossed polars (Fig. 3). This clearly identifies the pattern with molecular orientation effects which are independent of the presence of powder. As confirmation, the annealing schedules used for samples in Figs 6 and 7 were capable of removing only a few percent of organic vehicle. Since the total shrinkage due to removal of all the binder from a 60 vol% powder loading is only 1–2% linear,[16] there is insufficient scope for differential shrinkage. Thus for the fine RA6 alumina, the powder volume fraction is close to the maximum that can be injection moulded.

Large deformations are well known in relaxation studies of high polymers and this could be cited as a reason to avoid the use of high polymers in powder injection moulding; such large strains may lead to defects during binder removal. However, the results obtained with low molecular weight organic vehicles and described below show that the occurrence of large relaxation strains is not restricted to high molecular weight vehicles.

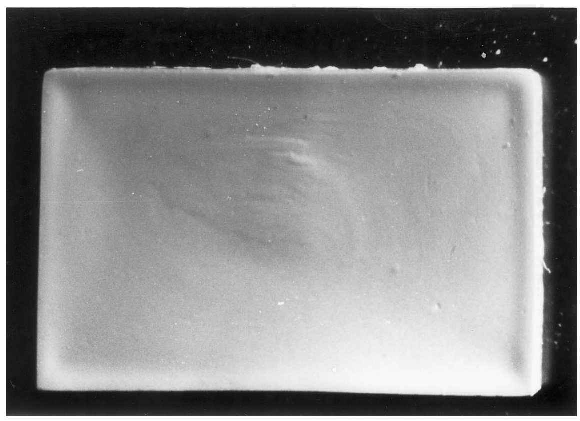
Figure 9 shows the relaxation pattern in alumina-wax mouldings (AW). In this case it was also possible to detect a relaxation pattern in conventional mouldings [Fig. 9(a)]. Although the multiple rings are not present in conventional moulding, there are three zones; a central depressed region associated with thermal contraction after the runners had solidified, an outer subskin region which is well known to be associated with high orientation in conventional mouldings [17] and an intermediate region where orientation due to mould filling is limited but where solidification occurred



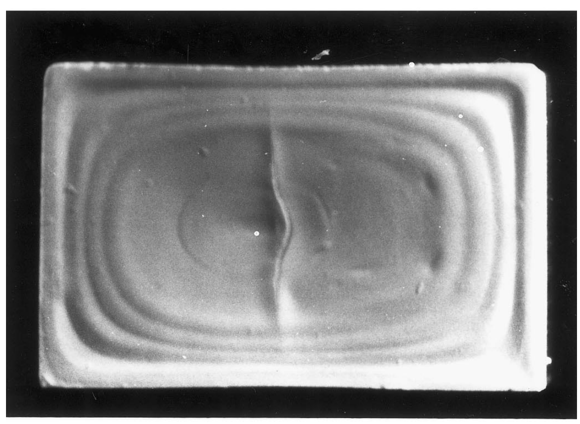
(a)

(b)

**Fig. 7.** Polished section of (a) conventional and (b) modulated pressure mouldings of 60 vol% RA6 alurnina in a polypropylene-based (APP) vehicle after annealing at 200°C for 24 h thermolysis at 1°C/h$^{-1}$ from 140–350° under nitrogen and partial sintering in air.



(a)



(b)

**Fig. 8.** Polished section of (a) conventional and (b) modulated pressure mouldings of 48 vol% RA6 alumina/ 12 vol% MA95 platey alumina in the polypropylene based vehicle (AAP) after thermolysis at 1°C h$^{-1}$ from 140 to 350°C and partial sintering at 1400°C for 30 min in air.

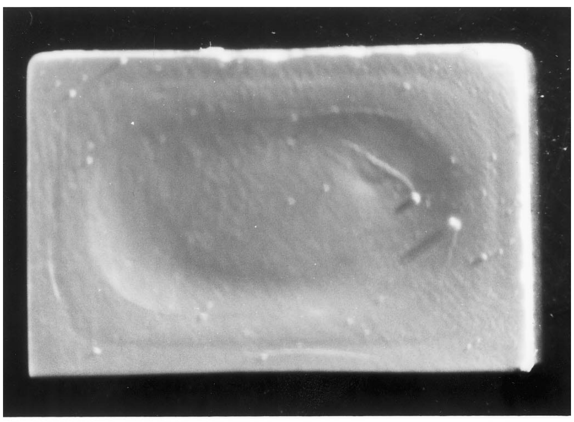
while a static packing pressure was still applied. The relaxation pattern for the modulated pressure moulding is shown in Fig. 9(b) and is similar to the pattern in Figs 7(b) and 8(b). The relaxation pattern is thus found in an organic vehicle with a radius of gyration, Rg, of 2–3 nm as well as a high polymer with Rg $\approx$ 20–30 nm.

In contrast, the sections of oscillating pressure mouldings made with spherical iron powder in a wax-based system (FW) did not show extensive deformation on annealing. The pattern of rings could be detected and is shown in Fig. 10 but it does not stand in relief. There are reasons to suspect that the relaxation time of oriented wax molecules in the case of the iron powder suspensions is shorter. The specific surface area of the iron powder is one order of magnitude lower than that of the alumina powder and therefore a smaller fraction of the organic vehicle experiences the immobilizing effect of adsorption on a high energy surface. Furthermore, the viscosity of the wax-based suspension incorporating iron powder was nearly two orders of magnitude lower than that of the corresponding alumina suspension. [18] Thus, the relaxation process may already have taken place during cooling in the mould or subsequent storage.

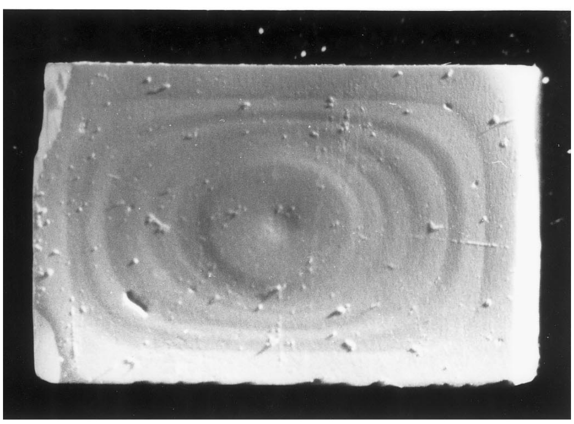
The implications of this study are that in any powder injection moulding, whether it contains spherical or anisotropically-shaped powder and whether it contains high or low molecular weight organic molecules, molecular orientation may be present to some extent after solidification.

The complications introduced by inorganic fillers for the measured residual stresses in polymer mouldings before and after annealing of whole mouldings have been discussed by White and coworkers [19] in terms of the inhibition to molecular relaxation. Their material was polypropylene with up to only 20 vol% talc and the residual stress distributions changed significantly, and sometimes unpredictably, on ageing.

The problem that remains for ceramic processing where much higher loadings are encountered is that it has not been possible to connect the known existence of relaxation strains in the organic vehicle, which necessarily displace particles in a heterogeneous way, directly with the aetiology of moulding defects which occur when whole, uncut mouldings are heat treated to remove the organic vehicle. This is principally because the pattern of defects often seen in large mouldings on binder removal does not consistently reflect the pattern of relaxation strain as shown for example in Figs 7 and 8(b). The existence of residual stress derived from transient cooling is present in all solidification processes to some extent and can equally be identified as a cause of cracking, notably because it is usually found in the centre of mouldings where tensile stresses prevail.[20,21,22] It remains difficult to devise an unambiguous experiment which distinguishes these effects. This is also true in the context of filled polymer moulding but the problem there is mainly one of dimensional reproducibility. For ceramic mouldings these problems are more severe, possibly resulting in large moulding defects.



(a)



(b)

**Fig. 9.** Polished sections of (a) conventional and (b) modulated pressure moulding of RA6 alumina in a wax-based vehicle (AW) after removing the wax by thermolysis under nitrogen at 1°C $h^{-1}$ from 40°C to 350°C and partial sintering at 1400°C for 30 min in air.

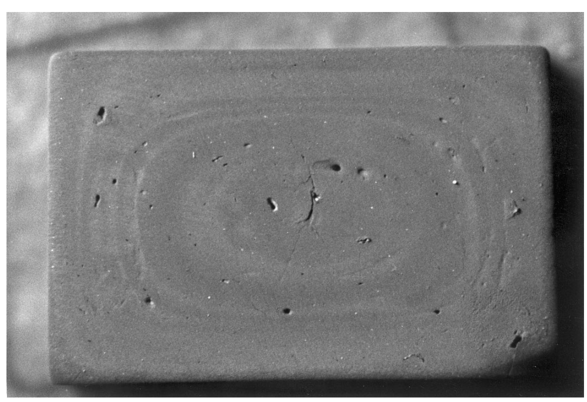


**Fig. 10.** Polished section of modulated pressure moulding of spherical iron powder in the waxbased vehicle (FW) after heating at 1°C $h^{-1}$ from 40°C to 350°C under nitrogen.

## 4 Conclusions

Ceramic and metal powder injection moulded bars made with repeated flow reversals during solidification in the cavity contain, in addition to orientation of anisotropic shaped particles or fibres, a pattern of molecular orientation which presents itself during annealing of polished sections. The appearance of concentric rings arises from the concurrent changes in melt velocity in the flow direction and the monotonically decelerating advance of the solid-liquid interface perpendicular to flow. The effect is observed in mouldings of unfilled polymer and in mouldings with spherical powder and is therefore not attributed to orientation of anisotropically shaped particles. It is also observed with wax-based organic vehicles indicating that the use of high molecular weight of polymers in powder injection moulding is not a necessary condition for retained molecular orientation.

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