The effect of crystallinity on the properties of injection moulded polypropylene and polyacetal

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The effect of the degree of crystallinity on properties has been studied for two injection moulded semicrystalline engineering thermoplastic materials, polypropylene and polyacetal. The differences in the degree of crystallinity were obtained initially by altering the mould temperature and hence the polymer cooling rate. The effects of (1) annealing and (2) small changes in the melt temperature were also studied. The degree of crystallinity was evaluated by X-ray diffraction and differential scanning calorimetry (d.s.c.). Only small changes in the degree of crystallinity were recorded but considerable differences in microstructure were induced for both polypropylene and polyacetal. Tensile and tract properties were measured and are discussed in terms of the microstructural changes in the mouldings.

(Keywords: degree of crystallinity; thermoplastics; polypropylene; polyacetal)

INTRODUCTION

Semicrystalline thermoplastics are used for the fabrication of a wide range of moulded items. The performance of these materials is affected by the relative contributions of the amorphous and crystalline phases, which are themselves dependent on the processing history of the material. If mouldings of a consistent predetermined quality are to be produced then an acceptable level of control has to be established over the critical parameters of the moulding process. To achieve this it is necessary to understand the behaviour of semicrystalline materials and in particular the effects of processing variables on crystallinity and of crystalline microstructure on mechanical properties.

The microstructure of injection moulded semicrystalline polymers has been investigated by Katti and Schultz[1]. They reported that the structure and properties of the materials are dependent on the flow patterns within the mould during filling and packing, and the rate of heat loss to the mould walls.

In general, contact with the mould walls (a heat sink) promotes a high density of crystallite nucleation and corresponding growth centres. Simultaneously, very high shear gradients at the walls produce chain alignment in the flow direction and profuse fibrillar growth. Whether the chill or the shear induced effect predominates at the surface depends on details of each specific case.

Kantz *et al.*[2] has studied the morphology of polypropylene and has identified three distinct layers in a moulding, all of which are highly crystalline. At the surface is a skin which is non-spherulitic but with a high degree of orientation. Below this is a shear zone of oriented row structures, and then there is a spherulitic core having essentially no preferred orientation. The morphology of polyacetal has been studied by Clark[3], and shown to be similar to that of polypropylene with, again, three distinct regions. The microstructural features of semicrystalline polymers have recently been reviewed by Schultz[4] who considered the roles of chain properties and thermal history in their development. He also related mechanical properties to microstructural detail.

The objective of this programme was to examine the crystalline structures and mechanical properties of injection moulded semicrystalline thermoplastic test pieces prepared using 'normal' moulding conditions. The work also included a study of the effect of annealing on crystalline structure and mechanical properties.

The crystalline structure was characterized by optical microscopy, differential scanning calorimetry (d.s.c.) and X-ray diffraction. Mechanical testing included tensile, impact and torsion pendulum.

EXPERIMENTAL

Injection moulded tensile and disc test pieces were produced using two semicrystalline materials, polypropylene GWM 22 homopolymer (ex ICI Ltd) and polyacetal Delrin 500 NC 10 (ex Du Pont Ltd).

Different degrees of crystallinity were first produced by significantly changing the mould temperature while keeping the other moulding parameters essentially constant. Subsequently further work was carried out by slightly varying the melt temperature. The effect of annealing was investigated using samples of the lowest degree of crystallinity for each material. The morphology, crystallinity and mechanical properties were monitored.

The moulding conditions are summarized in *Tables 1* and *2*. Initially polypropylene mouldings were produced

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Table 1 Moulding conditions for polypropylene

Batch number	1	2	3	4	5	6
Melt temperature (°C)	230	230	230	230	191	191
Measured mould (°C) temperature	12	45	105	12 Annealed	105	22

Table 2 Moulding conditions for polyacetal

Batch number	7	8	9	10	11	12
Melt temperature (°C)	210	200	188	210	210	198
Measured mould (°C) temperature	65	96	130	65 Annealed	96	130

using a melt temperature of 230°C and mould temperatures of 12, 45 and 105°C. Some of the mouldings produced using the lowest mould temperature were later annealed at 150°C for 22 h. Further mouldings were produced at mould temperatures of 22 and 105°C using a lower melt temperature of 191°C.

The polyacetal mouldings were produced using melt temperatures in the range 188–210°C and mould temperatures of 65, 96 and 130°C. Some of the mouldings produced at the lowest mould temperature were later annealed at 160°C for 1 h. Additional mouldings were subsequently produced at mould temperatures of 96 and 130°C using melt temperatures 10°C higher than those used in the initial runs.

TESTING

The following physical and mechanical properties of the mouldings were measured on the samples from the initial moulding runs; crystallinity, morphology, tensile, impact and dynamic properties. On samples moulded subsequently, only the morphology was studied.

Measurement of the degree of crystallinity by d.s.c. was carried out using a Perkin–Elmer DSC 2 operated at a heating rate of 10°C $\min^{-1}$. A section 10 × 3 × 1 mm was taken from the centre of one moulding and cut into four pieces each weighing approximately 10 mg. The d.s.c. results for the four pieces were then averaged. Values of melting point (T_m) were measured by d.s.c. at the maximum endotherm.

The degree of crystallinity was also determined by the application of X-ray diffraction to thin sections cut from the centre of the dumb-bells. The method employed was essentially that of Hermans and Weidinger[5]. In this work, however, a 57.3 mm radius powder camera was used with the specimen stationary and its plane normal to the beam. Microdensitometer traces were compared for each material and empirical values for the crystallinity were determined as compared with an amorphous sample. Although in principle a difference in techniques might imply differences in results due to absorption effects, in practice, because of the thin specimens used, the low mass absorption coefficient of carbon and the restricted range of 2θ, these were considered to be insignificant.

The morphological structures of the mouldings were studied by optical microscopy on microtomed sections taken from the centre of the tensile test piece. The sections were viewed perpendicular to the direction of flow.

Tensile properties were measured on 10 as-moulded dumb-bells from each batch and the elongation was monitored using a contact extensometer. For dynamic testing, tensile mouldings were examined using a torsion pendulum technique to obtain data for shear modulus and tan δ.

Impact properties were determined using an instrumented falling weight machine on 10 moulded discs from each batch. Computer analysis of the force transducer output gave values of yield force and total energy.

RESULTS AND DISCUSSION

The results of d.s.c. and X-ray diffraction showed that increasing the mould temperature for both materials produced only slight increases in the degree of crystallinity (*Tables 3* and *4*). Annealing the samples produced at the lowest mould temperature also produced slight increases in the degree of crystallinity. The morphological structures in the various mouldings, however, showed significant differences in spherulitic growth with both changes in mould temperature and between materials, although no visible change was detected in the annealed samples.

For polypropylene, *Figures 1* and *2* show that under the initial moulding conditions, the highest mould temperature (105°C) produced the largest diameter spherulites (60 μm), while mould temperatures of 12 and 45°C yielded spherulites of diameter 10 and 30 μm, respectively. It was also noted that the skin thickness increased from 290 to 325 μm on lowering the mould temperature.

In the subsequent work, where the melt temperature used (191°C) was only 25°C above the melting point of the material as measured by d.s.c., the effect was to greatly reduce the spherulite diameter. Also, at this lower melt temperature there were no differences in spherulite size for the mouldings at the two mould temperatures used (22 and 105°C).

For polyacetal, *Figures 3* and *4* show that under the initial moulding conditions, the highest mould temperature (130°C) produced the smallest spherulites (20 μm) and mould temperatures of 65 and 96°C yielded spherulites having diameters of 160 and 60 μm, respectively. The skin region of polyacetal was not as well defined as had been observed with polypropylene, but estimated skin thickness did decrease from 80 to 40 μm with increasing mould temperature.

Table 3 D.s.c. and crystallinity results for polypropylene

Batch number	1	2	3	4	5	6
D.s.c. ΔHf (cal g^{-1})	18.6	19.7	20.8	21.9	–	–
Crystallinity by d.s.c. (%)	43	46	48	51	–	–
Crystallinity by X-ray diffraction (%)	43	47	48	50	–	–
Spherulite size (μm)	10	30	60	10	10	10
Skin thickness (μm)	325	310	290	325	575	600

Table 4 D.s.c. and crystallinity results for polyacetal

Batch number	7	8	9	10	11	12
Crystallinity by d.s.c. (%)	63	66	67	66	–	–
Crystallinity by X-ray diffraction (%)	68	75	78	78	–	–
Spherulite size (μm)	160	60	20	160	140	100
Skin thickness (μm)	80	60	40	80	80	80

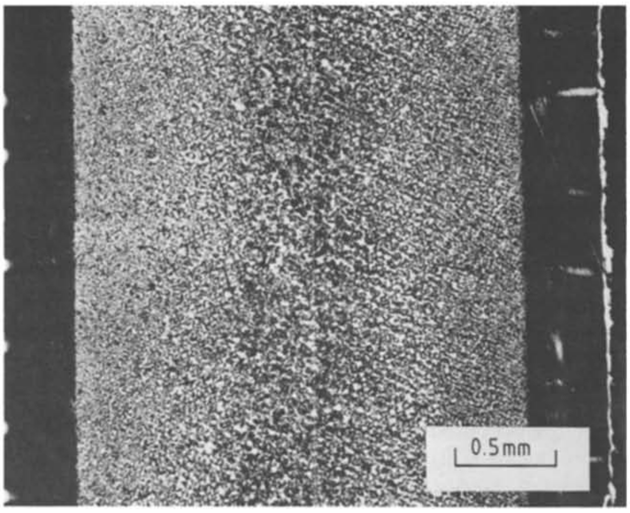

Figure 1 Morphology of polypropylene test piece. Mould temperature 105°C

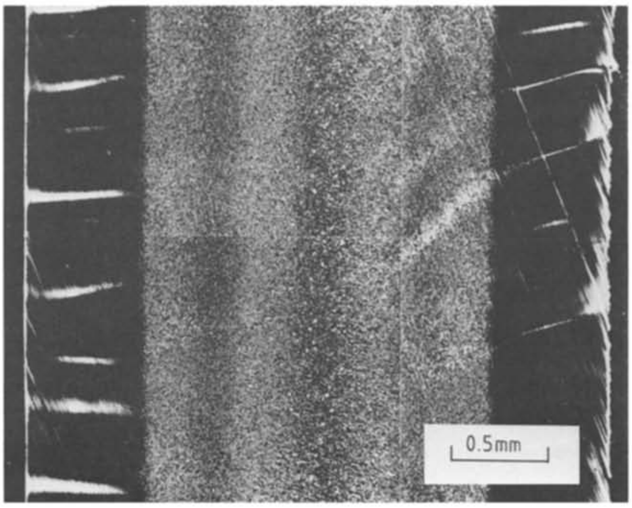

Figure 2 Morphology of polypropylene test piece. Mould temperature 12°C

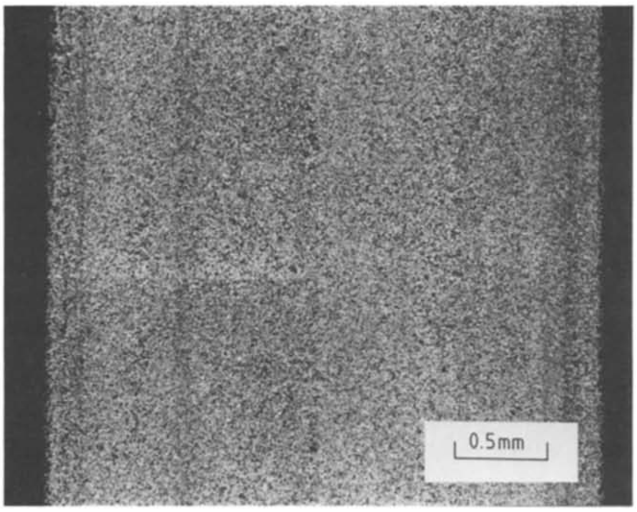

Figure 3 Morphology of polyacetal test piece. Mould temperature 130°C

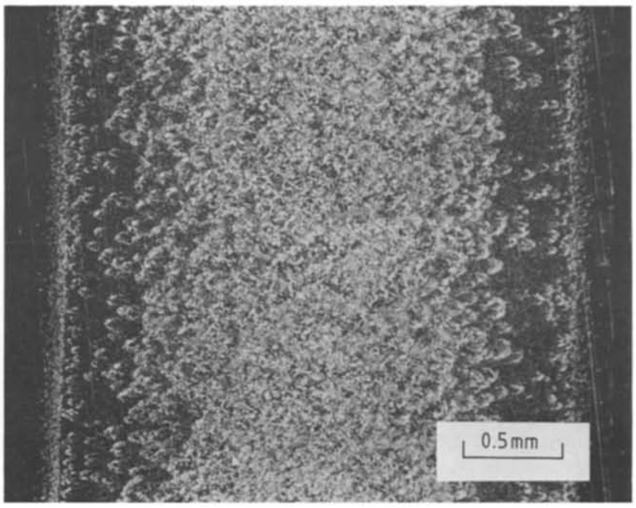

Figure 4 Morphology of polyacetal test piece. Mould temperature 65°C

In the subsequent work, where mouldings were produced using the two higher mould temperatures (96 and 130°C) and the melt temperatures were increased by 10°C, the effect was to significantly increase the spherulite size. The melt temperatures in this case were 34 and 22°C, respectively above T_m. Thus, while mould temperature is a dominant factor in determining the degree of crystallinity, a complex relationship exists between melt and mould temperatures and structure.

The small spherulites formed in both materials when a melt temperature only slightly above T_m was used (batches 5 and 9), suggest a high nucleation density leading to a profusion of small or immature spherulites. This is probably associated with the retention of local crystal memory in the polymeric melt at temperatures slightly above T_m.

At higher melt temperatures for both materials, the competition between rate of nucleation and rate of spherulite growth becomes more apparent.

Thus, for the initial work on polypropylene, where a melt temperature significantly above T_m was used, an increase in mould temperature produced both a decrease in nucleation density and an increase in radial growth rate leading to larger spherulites. The work on polyacetal showed that at a constant mould temperature, an increase in melt temperature produced an increase in spherulite size although the nature and shape of the spherulites made accurate measurements difficult.

Obviously the significance of the change in crystallinity and structure can only be assessed if their effects on mechanical properties are understood.

For both materials, increasing the mould temperature at a constant melt temperature slightly increased the tensile yield strength and tensile modulus, and in both cases, the effect of annealing was to also increase the tensile properties (*Tables 5* and *6*). This was consistent with the induced increase in the degree of crystallinity. Results from the dynamic testing of both materials by torsion pendulum were consistent with the tensile properties in that shear modulus increased with increasing crystallinity.

For polypropylene, the elongation at break decreased significantly for both the highest mould temperature and annealed samples. For the highest mould temperature it could be postulated that the large reduction in elongation was a property of the large spherulites formed. Schultz[4] suggests that large spherulite formation can result in an increased amount of less readily crystallized material

Table 5 Results of physical properties for polypropylene

Batch number	1	2	3	4	5	6
Tensile strength (MPa)	34.4	35.8	36.9	35.8	–	–
Elongation at break (%)	600	600	30	120	–	–
Tensile modulus (MPa)	1.88	1.89	1.92	2.41	–	–
Impact transition temperature (°C)	30	26	23	16.5	–	–

Table 6 Results of physical properties for polyacetal

Batch number	7	8	9	10	11	12
Tensile strength (MPa)	64	69	70	69	–	–
Tensile modulus (MPa)	3.07	3.48	3.54	3.40	–	–
Impact strength						
Yield force (N)	638	841	3270	761	–	–
Total energy (Nm)	2.70	2.91	17.3	3.32	–	

being deposited at the spherulite boundaries leading to weak boundary conditions and low elongation. The effect of intrinsic spherulite size and boundary properties also contribute to this effect. For the annealed sample, a large decrease in elongation was induced by increasing the degree of crystallinity but with no visual observation of change in spherulite size or structure. In the annealing, structural changes are thought to occur at the sub-spherulite level[6,7] in that crystallinity increases by both the development of new crystallites in the amorphous regions and boundary thickening of existing crystallites. Annealing is thought to reduce the number of tie chains emerging from each crystal face and hence the tie chain density which has important effect on properties.

The deleterious effect that large spherulite formation can have on mechanical properties is evident in the instrumented impact test results. For polyacetal (*Tables 4* and *6*), both yield force and total energy decreased with increasing spherulite size. For polypropylene (*Tables 3* and *5*) the overall picture was masked by the existence of an impact transition in the region of the selected test temperature (23°C). The results, however, did suggest a decrease in the transition temperature with increasing crystallinity and for the unannealed samples this could also be related to increasing spherulite size.

Semicrystalline polymers are microstructurally and mechanically complex systems and this work clearly demonstrates the problems of trying to establish a direct relationship between crystallinity, spherulite size and the mechanical properties. As suggested by Schultz[4], most, if not all practical investigations of these effects vary spherulite size by controlling the temperature of isothermal crystallization or the cooling rate. In both instances this also changes both the overall crystallinity and crystallite thickness and precludes the establishment of direct relationships.

It is also evident, however, that small changes in the processing conditions for semicrystalline polymers can cause pronounced changes in morphology while having numerically small effects on the degree of crystallinity. The importance of morphological structure is apparent in the impact test results where, in the case of polyacetal, specimens having a small, dense spherulitic structure had markedly higher impact strengths than those with a large spherulitic structure yet with similar degrees of crystallinity.

While annealing had no apparent effect on morphology as determined optically, small increases in crystallinity and changes in mechanical properties were measured.

In conclusion, it is apparent that for these semicrystalline materials a consistent quality of moulded item can only be achieved by establishing and maintaining adequate controls over the moulding process parameters. The moulding process needs to be controlled both during the injection and cooling phases of the production of a moulding if consistent levels of crystallinity, structure and hence performance are to be achieved.

REFERENCES

1 Katti, S. S. and Schulta, J. M. *Polym. Eng. Sci.* 1982, **22**(16), 1001
2 Kantz, M. R. *et al. J. Appl. Polym. Sci.* 1972, **16**, 1249
3 Clark, E. S. *SPEJ* 1967, **23**(7), 46
4 Schultz, J. M. *Polym. Eng. Sci.* 1984, **24**(10), 770
5 Hermans, D. and Weidinger, A. *Macromol. Chem.* 1961, **50**, 98
6 Dlugosz, J. *et al. Polymer* 1976, **17**, 471
7 Schultz, J. M. *et al. J. Polym. Sci., Polym. Phys. Edn.* 1976, **14**, 2291