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Effect of nucleating agents and cooling rate on the microstructure and properties of a rotational moulding grade of polypropylene

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Rotational moulding consists of coating the inside surface of a metal mould with a layer of plastic by rotating the mould, firstly in an oven and then in a cooling bay to induce solidification to the desired part shape. As the rotational speeds are slow (typically about 10 rev/min), the resulting hollow articles are practically stress free. The primary material used for rotationally moulded parts is polyethylene but there is an increasing interest in using polypropylene to provide stiffer, higher temperature products. Unfortunately the slow cooling combined with the slow crystallisation rate of polypropylene results in brittle mouldings with coarse spherulites. Since the inner surface of the plastic is in contact with air during moulding, degradation is also likely to occur. In order to improve the mechanical properties of the rotationally moulded polypropylene, α and β nucleating additives were added. The effect of using faster cooling rates was also studied. It was found that heterogeneous nucleation, both of β and α spherulites, did not improve the ductility of the samples. However, when fast cooling was used, the impact strength of the polypropylene improved markedly, independent of the presence of nucleating additives. In the rotationally moulded polypropylene parts, the fast cooling could only be applied to the outer surface of the mould, which led to asymmetric cooling. This resulted in severe warpage, and uneven morphology. This problem should be overcome by using fast cooling on both the inside and outside surfaces of the plastic. *© 2001 Kluwer Academic Publishers*

1. Introduction

Rotational moulding is used to manufacture one-piece hollow articles [1]. The process consists of covering the inside surface of a metal mould with a layer of plastic. To do this, the mould is charged with plastic, generally in the powder form, and rotated inside an oven to melt the plastic and coat the mould. Then, it is moved into a cooling bay where, with the mould still rotating, the plastic cools. The low shear on the melt, the slow rates of heating and cooling and the presence of air inside the mould are characteristic features of this process that lead to the formation of unique morphologies in the mouldings. Previous work with polyethylene [2] showed how the correct control of the peak internal air temperature (PIAT) reached by the air inside the mould is crucial to avoid polymer degradation or incomplete sintering of the powder. Further work [3] showed how combining the polymer with nucleating pigments using different methods affects the morphology and the mechanical properties of the mouldings.

Rotational moulding is currently one of the fastest growing sectors of the plastics industry with annual growth rates in the range of 10–12%. Polyethylene accounts for approximately 90% of the world market for rotational moulding materials but there is a growing interest in the use of polypropylene (PP) parts, mainly because of its higher stiffness and better performance at high temperatures.

The crystalline architecture of PP is complex and multifaceted. Three different crystal structures are known to exist: α (monoclinic), β (trigonal) and γ (orthorombic) [4]. These crystal forms are incorporated into spherulites of different types. Padden and Keith [5] identified four distinct types of spherulites and also some mixed forms. Types I and II, known as the α-modification, are distinguished by their low birefringence, being positive for the first and negative for the second. The low value of birefringence results from the type of branching of the lamellae in the spherulite that causes both radial and nearly tangential orientation of the crystals. The spherulites of types III and IV are composed of β crystals. The regular lamellar structure of these spherulites accounts for their highly negative birefringence.

The crystallization of polypropylene from unstressed melts leads usually to a predominance of type I or mixed sign spherulites, with a minority of type III. However, crystallisation of this latter type may be induced by the addition of specific nucleating agents [6, 7] or by shearing of the melt [8].

It is well known that the size, type and perfection of the crystalline structure of polymers are influenced by the crystallization temperature. In polymers with a low crystallization rate, as is the case of polypropylene, this effect is more pronounced and great variations in the size of the spherulites and degree of crystallinity can be observed. It has been shown that these microstructural features are related to the mechanical properties [9–12]. For example, Friedrich [10, 11] showed that PP mouldings with a coarse spherulitic morphology, produced by slow cooling from the melt, exhibit the lowest values in respect to yield stress and fracture toughness.

As was mentioned earlier, in rotational moulding the cooling of the melt is relatively slow (typically about 10°C/min). In the case of polypropylene, this causes the morphology to be very coarse, which generally explains the low impact strength observed in parts that are rotationally moulded with this material [13]. In this work, a complete study was carried out to investigate the influence of the processing temperature on the microstructure and mechanical properties of rotationally moulded PP. Furthermore, in an attempt to modify the microstructure of PP so as to improve its mechanical properties, the effects of compounding the polymer with nucleating additives and of using different rates of cooling were also investigated.

2. Experimental

2.1. Materials

The material used in this work was a rotational moulding grade of polypropylene, Borealis BE 182B. In the investigation of the effect of rotational moulding conditions, the material was used as supplied by the manufacturer. In order to analyse the effects of nucleating additives, the material was compounded with a variety of nucleating substances: a red pigment (azo condensation cromophtal scarlet, HC 7761 supplied by Hampton Colours Ltd.), sodium benzoate, and a mixture of equal parts of pimelic acid and calcium stearate (a β nucleator). All additives were used in the amount of 0.15% by weight.

2.2. Compounding of the additives

The three types of additives were compounded using a Leistritz twin screw co-rotating extruder fitted with a pelletizer. The extrusion temperature was 230°C and the screw speed was 50 rev/min.

Before rotational moulding, the compounded granules were ground into powder using a Wedco grinder. To avoid excessive heating during the grinding stage, the granules were cooled with liquid nitrogen. A batch of virgin material was similarly extruded and ground for use as a reference.

2.3. Moulding

2.3.1. Rotational moulding

The rotational moulding trials were done using a Ferry-Rotospeed 1600 three-arm machine and an oven set at 300°C. The parts, produced with a shot weight of 1.6 kg, had approximately a cubic shape of about 300 mm side and 3 mm thickness.

To quantify the effect of the processing temperature, the mouldings were heated in the oven until the peak inner air temperature (PIAT) reached a predefined value in the range from 190°C to 270°C. Table I shows the identification numbers and the PIAT of the samples.

The mouldings used to study the effects of compounding with the nucleating additives are shown in Table II. The PIAT of these samples was 230 °C.

To obtain mouldings with a finer crystalline texture, water cooling was also used. The sample code numbers and the moulding conditions are given in Table III. The PIAT of these samples was 225 °C.

TABLE I Identification of rotationally moulded samples

Sample Identification	PIAT (°C)
PP-190	190
PP-210	210
PP-220	220
PP-230	230
PP-240	240
PP-250	250
PP-270	270

TABLE II Samples used for studying the effect of cooling rate and of compounding with nucleating additives

Sample Identification	Type of additive	Moulding method	Cooling rate
PPvirRM	none	rot. moulding	slow
PPvirCMs	none	compr. moulding	slow
PPextCMs	none	compr. moulding	slow
PPvirCMf	none	compr. moulding	fast
PPextCMf	none	compr. moulding	fast
PPredRM	red pigment	rot. moulding	slow
PPredCMs	red pigment	compr. moulding	slow
PPβCMs	β-nucleator[a)]	compr. moulding	slow
PPsbCMs	sodium benzoate	compr. moulding	slow
PPredCMf	red pigment	compr. moulding	fast
PPβCMf	β-nucleator[a)]	compr. moulding	fast
PPsbCMf	sodium benzoate	compr. moulding	fast

[a)] Equal parts of pimelic acid and calcium stearate.

TABLE III Cooling conditions of samples used for studying the effect of fast cooling in rotational moulding

Sample Identification	Cooling program
PPair	Air cooling from 225 °C until 80 °C
PPwater	Water cooling from 225 °C until 80 °C
PPw/a	Combined cooling: Water: 225 °C - 185 °C Air: 185 °C - 120 °C Water: 120 °C - 80 °C

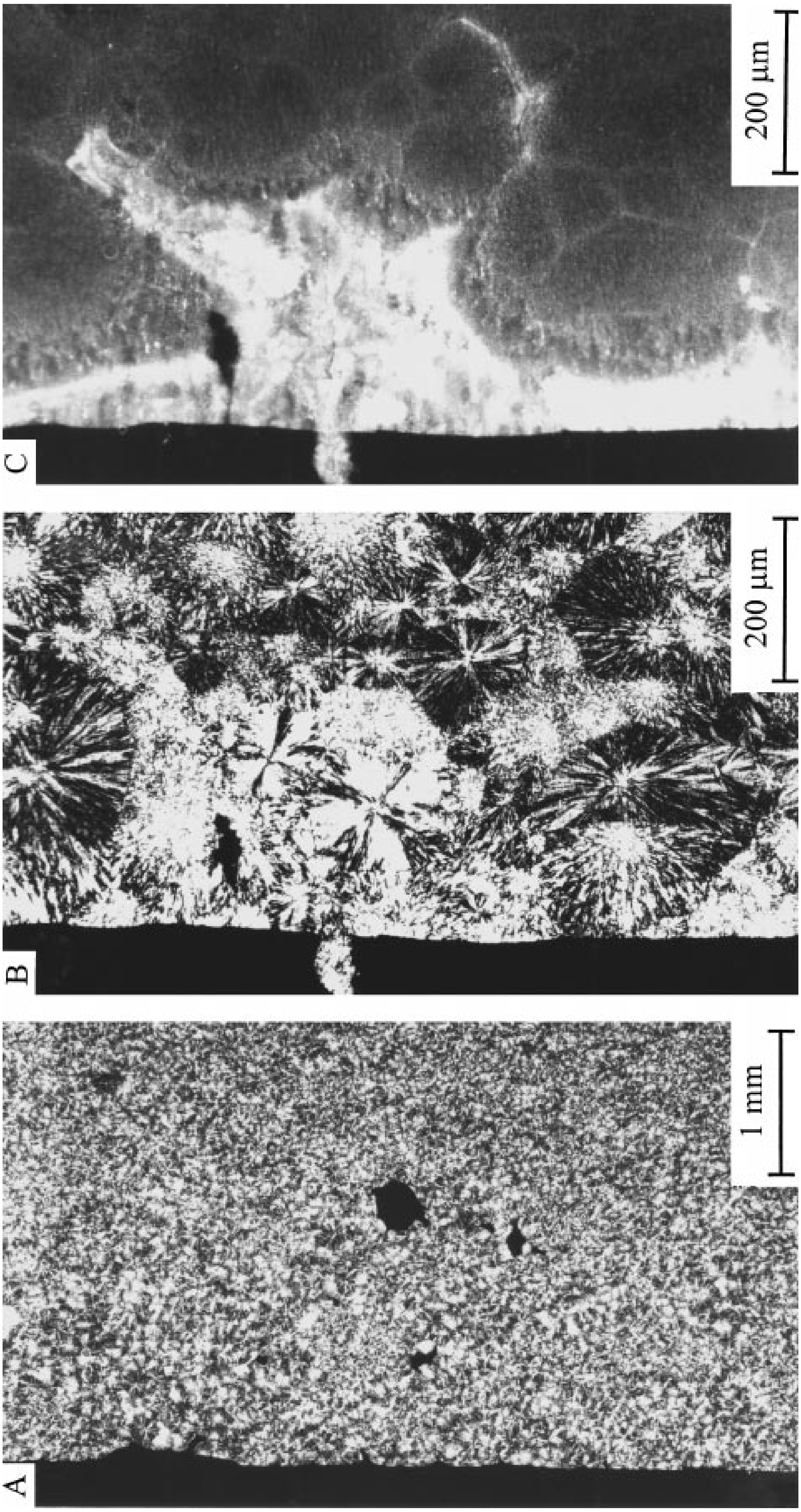

Figure 1 Microstructure of rotationally moulded samples. (A) Underheated sample (PIAT: 190°C)—polarised light microscopy (B) Overheated sample (PIAT: 270°C)—polarised light microscopy (C) Idem—fluorescence microscopy.

The temperature of the oven and of the air inside the mould was measured throughout the cycle using a Rotolog data logger [14].

2.3.2. Compression moulding

The main objective of this work was to investigate the properties of rotationally moulded PP. However, as these mouldings have a microstructure and properties very similar to those produced by compression moulding, and as this method allows better control of the rate of cooling and uses smaller amounts of material, some mouldings were also produced by this method.

The compression moulding was carried out using a 400 kN Moore & Son hot platen press and using a frame mould producing square plaques of 60 mm side and 2 mm thickness. In order to get mouldings with smooth surfaces, two PTFE sheets were placed between the plastic and the steel plates.

To mould the samples, the mould, filled with the plastic powder, was placed between the platens of the press and heated at 200 °C for 3 minutes. A pressure of 30 kg/cm^2 was then applied for 1 minute. After this period the moulding was cooled. Two different cooling methods were used. A slow cooling (ca. 10 °C/min.), identical to that used in rotational moulding and a fast cooling (ca. 200 °C/min).

Table II summarises the processing conditions of the compression moulded samples.

2.4. Characterisation of moulded parts

The morphology of the samples was analysed with an Olympus BH2 polarising microscope using 15 μm thick cross-sections embedded in Canada balsam. Two methods were used for detecting the occurrence of degradation: fluorescence microscopy and Fourier transform infrared spectroscopy (FTIR). The fluorescence technique was performed on 30 μm sections cut across the thickness of the mouldings and embedded in glycerol. For the FTIR analysis, 30 μm thick sections were cut from the inside wall of the mouldings, parallel to the surface. The rheological behaviour of the moulded materials was assessed using a parallel plate rheometer. The tests were done on 1mm thick discs cut from the internal surface of the mouldings. The tests were performed at 190°C, using a frequency sweep from 0.5 to 50 Hz. The strain amplitude was 0.001 rad.

Density measurements were done with a density gradient column prepared with a mixture of isopropanol and water. The results were used for the determination of the degree of crystallinity assuming that the density of the α crystalline and amorphous phases are 940 kg/m^3 and 850 kg/m^3, respectively [15].

The mechanical properties were assessed both by impact and tensile tests. The impact tests were performed on squares of 60 mm side cut from the samples with a Rosand IFW instrumented falling dart machine. The testing was conducted at room temperature with speed of 1 ms^{-1} and mass of 25 kg. The tensile testing was done at room temperature with an Instron 4505 machine using dumbbell-shaped specimens cut from the moulded parts. The test speed was of 50 mm/min.

The thermal properties of the original and nucleated powders were studied using Differential Scanning Calorimetry (DSC). Samples weighing 8 mg were heated up to 190 °C, cooled down to 30 °C, and then heated up again above the melting point. The cooling and heating rates were set at 10°C/min.

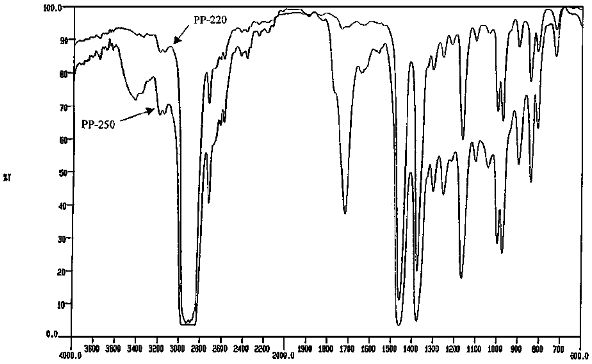

Figure 2 FT-IR spectra of sample PP-220 and sample PP-250 obtained with sections cut from the inside surface.

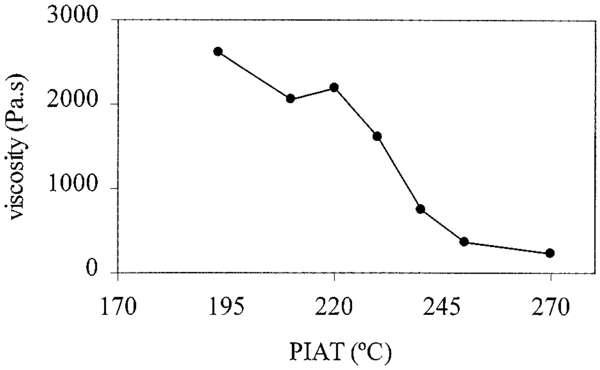

Figure 3 Variation of the viscosity of the rotationally moulded PP with the PIAT.

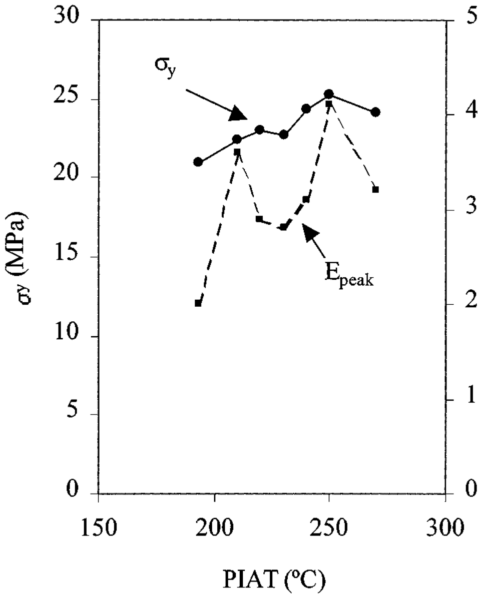

Figure 4 Effect of PIAT on the mechanical properties of rotationally moulded samples.

3. Result and discussion

3.1. Effect of processing temperature on rotationally moulded samples

The peak internal temperature reached by the air inside the mould (PIAT) affected the microstructure of the mouldings, in a similar manner to that observed in previous work [13]. The slow cooling rate, characteristic of this process, combined with the slow crystallisation rate of polypropylene, produced coarse low birefringence spherulites in all mouldings. The mouldings prepared using low temperatures showed voids in the bulk (see Fig. 1A). These resulted from air trapped between the powder particles that, due to insufficient heating of the material, could not diffuse out completely. The mouldings where the PIAT was higher than 230°C showed degradation of the polymer at a layer adjacent to the internal surface. The thermal oxidative degradation is revealed by the higher birefringence of the spherulites (Fig. 1B), by the fluorescence (Fig. 1C) of the material at that layer and by the presence of carbonyl (at $\sim$1725 cm^{-1}), and hydroperoxide (at $\sim$3500 cm^{-1}) groups in the FTIR spectra (Fig. 2). The occurrence of double bonds, namely C=O in the carbonyl groups, accounts for the fluorescence of the degraded material under the fluorescence microscope. The increase in birefringence of the spherulites formed from the degraded material suggests that the cross-hatching of the lamellae is lower in these spherulites. The reduction of cross-hatching is the result of the decrease of molecular weight caused by degradation, as was previously observed by Padden and Keith [16].

The decrease of molecular weight of the polymer with the processing temperature is confirmed by the rheological data. As Fig. 3 shows, the viscosity, which

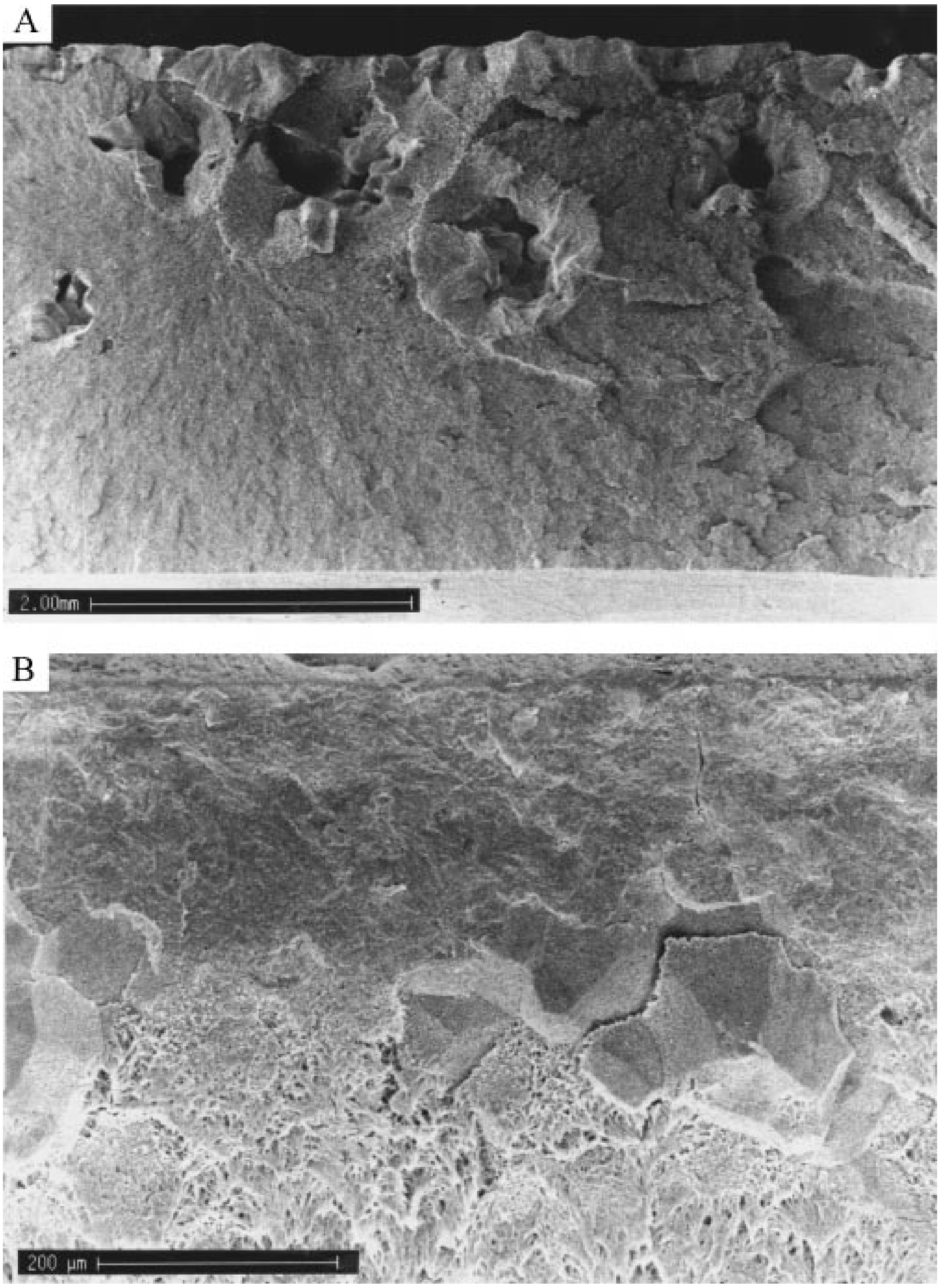

Figure 5 SEM micrographs of rotationally moulded samples fractured under tensile testing. (A) PP-210; (B) PP-270.

TABLE IV Effect of PIAT on the yield stress (σ_y) and peak energy (E_p) of rotational moulded samples

Sample Identification	σ_y (MPa)	E_p (J/mm)
PP-190	21.0 (0.3)	2.0 (1.1)
PP-210	22.4 (0.4)	3.6 (1.0)
PP-220	23.0 (0.3)	2.9 (0.2)
PP-230	23.7 (0.5)	2.8 (0.7)
PP-240	24.3 (0.7)	3.1 (0.7)
PP-250	25.3 (0.3)	4.11 (0.4)
PP-270	24.1 (0.6)	3.2 (0.5)

In brackets—standard deviation.

decreases with the molecular weight, decreases from 230°C onwards and indicates that the degradation of the PP causes chain scission predominantly. This behavior of PP, also reported for multiple extrusions [17], is in clear contrast with what was observed in a previous study [2] with rotationally moulded PE. This showed an increase of molecular weight above a certain processing temperature, due to degradation occurring mainly through a cross-linking mechanism.

As is shown in Table IV and Fig. 4, the mechanical properties did not reveal clear changes with the processing temperature and only a slight increase of the yield strength and impact strength were observed for the samples processed at 250°C. In the case of the samples with voids (underheated) or with a layer of degraded material (overheated) the fracture was initiated by these features (see Fig. 5) confirming their detrimental effect on the material strength. However, it was observed that independent of the occurrence of these defects, all the samples broke in a brittle manner during tensile and impact testing. This behaviour is due to the coarseness of the spherulitic structure in all the samples. The increase of the size of the spherulites is accompanied by a reduction of the interspherulitic boundary links, which allows transmission of energy through the material, and this causes a decrease of the ductility [18–21]. The effect of reducing the size of the spherulites, with the aim of improving the ductility of the mouldings, by incorporating nucleating additives and by using a faster rate of cooling of the mouldings will be analysed in the following sections.

3.2. Effect of nucleating additives and cooling rate

It was observed that the samples made both by rotational moulding and by compression moulding under identical cooling rates show identical morphologies. This is illustrated in Fig. 6 with samples that were made from virgin powder and from material nucleated with the red pigment by both moulding methods. The mechanical properties of samples moulded by the two methods also follow a similar trend (see Table V). These observations validate the use of compression moulding for studying the behaviour of the material when it is mixed with nucleating additives or has its structure modified by cooling rate. This is therefore a convenient way to reduce the expenditure of material and time in the rotational moulding experiments. It was also observed that the extrusion and grinding processes did not impart significant modifications to the morphology and mechanical properties of the virgin material.

As can be seen from Figs 6 and 7, the mixing of the material with nucleating additives has a strong influence on the morphology of the mouldings. When the

TABLE V Properties of samples used for studying the effect of cooling rate and of compounding with nucleating additives

Sample	Density (g/cm^3)	χ_c (%)	E (GPa)	σ_y (MPa)	ε_y (%)	σ_b (MPa)	ε_b (%)	E_{peak} (J/mm)	E_{total} (J/mm)
PPvirRM	0.9092	65.8	1.54	25.43	3.27	24.20	6.50	2.65	5.90
	(0.0001)		(0.06)	(0.47)	(0.14)	(0.48)	(0.48)	(0.40)	(0.80)
PPvirCMs	0.9080	64.4	1.55	26.12	3.89	21.38	18.0	2.35	2.45
	(0.0001)		(0.07)	(0.45)	(0.32)	(0.50)	(3.4)	(0.60)	(0.65)
PPextCMs	0.9077	64.1	1.55	26.42	4.43	24.05	12.6	1.50	1.55
	(0.0001)		(0.10)	(0.25)	(0.29)	(0.46)	(2.2)	(0.80)	(1.0)
PPvirCMf	0.9010	56.7	1.32	25.64	3.92	17.7	17.2	3.05	5.95
	(0.0001)		(0.14)	(1.23)	(0.32)	(1.7)	(2.1)	(0.45)	(0.60)
PPextCMf	0.9008	56.4	1.58	26.19	3.58	21.32	18.3	3.20	5.85
	(0.0001)		(0.02)	(0.47)	(0.09)	(0.97)	(5.2)	(0.10)	(0.15)
PPredRM	0.9110	67.8	2.02	25.92	2.52	25.22	3.57	2.55	4.45
	(0.0001)		(0.03)	(0.23)	(0.03)	(0.26)	(0.34)	(0.40)	(0.90)
PPredCMs	0.9090	65.6	1.59	25.00	3.72	24.02	9.3	2.40	2.55
	(0.0001)		(0.08)	(1.15)	(0.41)	(0.68)	(4.1)	(0.50)	(0.65)
PPβCMs	0.904	—	1.49	25.18	4.45	23.20	14.7	1.45	1.45
	(0.001)		(0.10)	(0.53)	(0.29)	(0.66)	(5.9)	(0.35)	(0.35)
PPsbCMs	0.9095	66.1	1.58	25.81	4.14	24.4	8.8	0.63	0.63
	(0.0001)		(0.06)	(0.95)	(0.27)	(1.1)	(2.4)	(0.23)	(0.23)
PPredCMf	0.9028	58.7	1.74	25.13	3.06	22.23	16.9	3.20	5.70
	(0.0001)		(0.08)	(0.62)	(0.04)	(0.23)	(6.6)	(0.15)	(0.35)
PPβCMf	0.9008	—	1.48	23.33	4.07	19.17	29.4	2.95	5.05
	(0.0001)		(0.06)	(0.75)	(0.23)	(0.18)	(11.6)	(0.35)	(0.40)
PPsbCMf	0.9028	58.7	1.20	26.27	4.77	20.7	12.3	2.50	4.23
	(0.0001)		(0.04)	(0.50)	(0.38)	(1.0)	(2.5)	(0.38)	(0.42)

In brackets—std. deviation χ_c—degree of crystallinity (std.dev. = 0.1%) E—Young modulus σ_y, σ_b—yield and break stress, respectively ε_y, ε_b—elongation at yield and at break, respectively E_{peak}, E_{total}—peak and total impact energy, respectively.

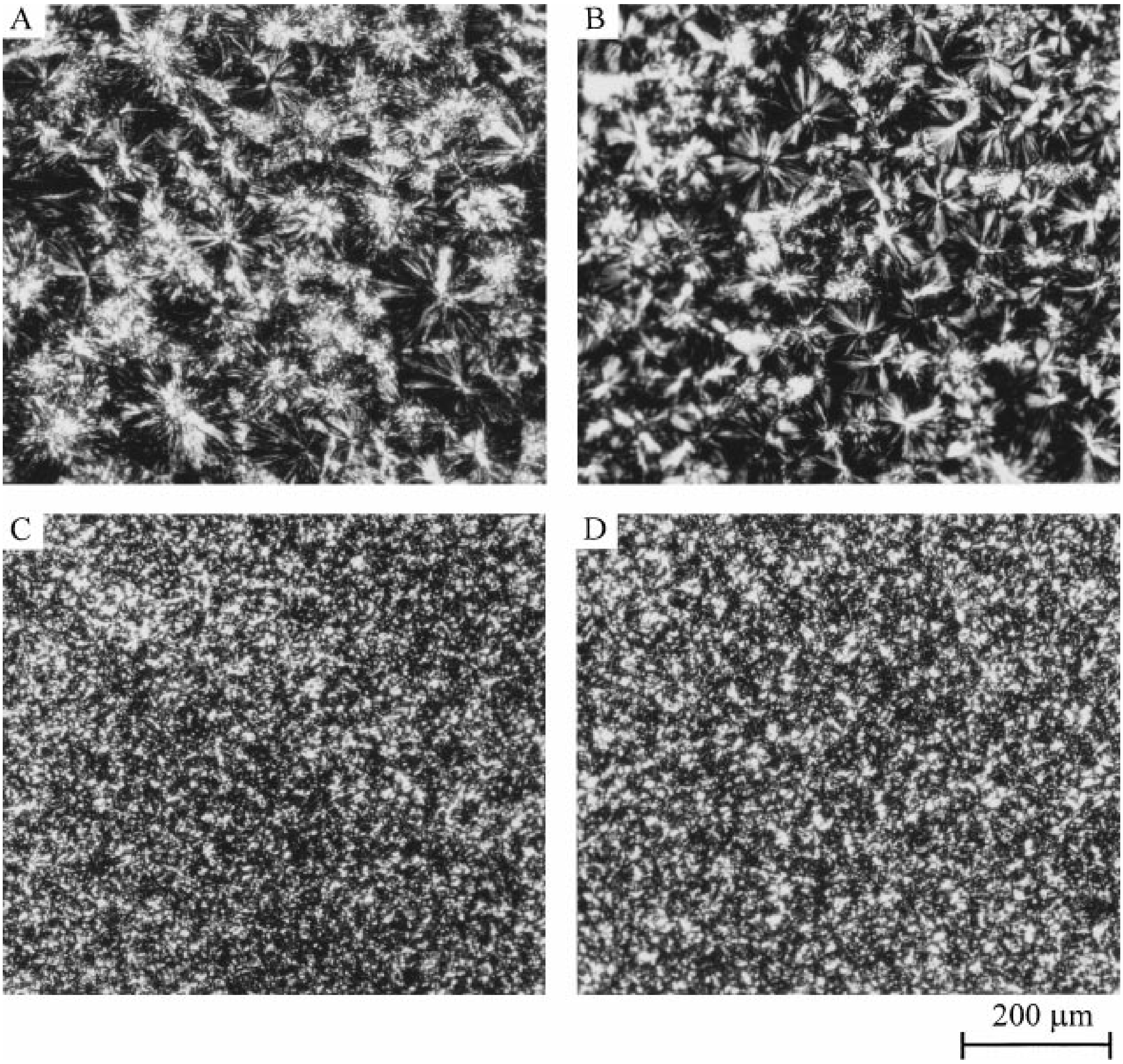

Figure 6 Microstructure of samples moulded with identical cooling rates (10°C/min) (A) PPvirRM; (B) PPvirCMs; (C) PPredRM; (D) PPredCMs.

polymer was compounded with the red nucleating pigment or with the sodium benzoate, the mouldings presented a very fine microstructure in clear contrast with the very coarse one formed with the virgin polymer. In agreement with previous reports [3, 22] this shows that extrusion mixing is very effective to disperse nucleating additives, increasing enormously the nucleating sites. The spherulites formed in the presence of these nucleating agents are of the low birefringent type and this shows that not only sodium benzoate [23] but also the red pigment used in this work are effective α—form nucleators of PP.

The compounding of the polymer with the β-nucleator produced a large number of high birefringence type III spherulites. These are easily recognised under the polarised light microscope by their higher brightness compared to the less birefringent α-form spherulites (Fig. 7C).

As shown by the DSC results (Table VI) the addition of nucleating pigment modifies its thermal behaviour. The β-nucleated polymer showed multiple endothermic peaks, typical of polypropylene with α and β-forms [24]. The compounding with a nucleating pigment caused a clear increase of the crystallization and melting temperatures and of the melting enthalpy. The mixing with sodium benzoate had a similar effect although less pronounced. The increase in the crystallisation temperature is often used in industrial practice to judge the effectiveness of nucleating agents [24]. These modifications certainly have an effect on the moulding behaviour of the material by increasing the amount of heat necessary for the polymer to melt, and the solidification temperature, which may have consequences on the optimum processing conditions.

TABLE VI Thermal properties of virgin and nucleated materials

Material	Tcryst (°C)[a]	Tmelt (°C)[a]	ΔHmelt (J/g)[b]
virgin	117.8	156.9	76.7
virgin extruded	119.7	157.0	79.7
pigmented	125.5	158.9	83.0
β-nucleated	120.4	157.5(α) 144.2(β)	79.7
sb-nucleated	122.6	158.0	80.9

[a] standard deviation 0.2 °C.
[b] standard deviation 1.0 J/g.

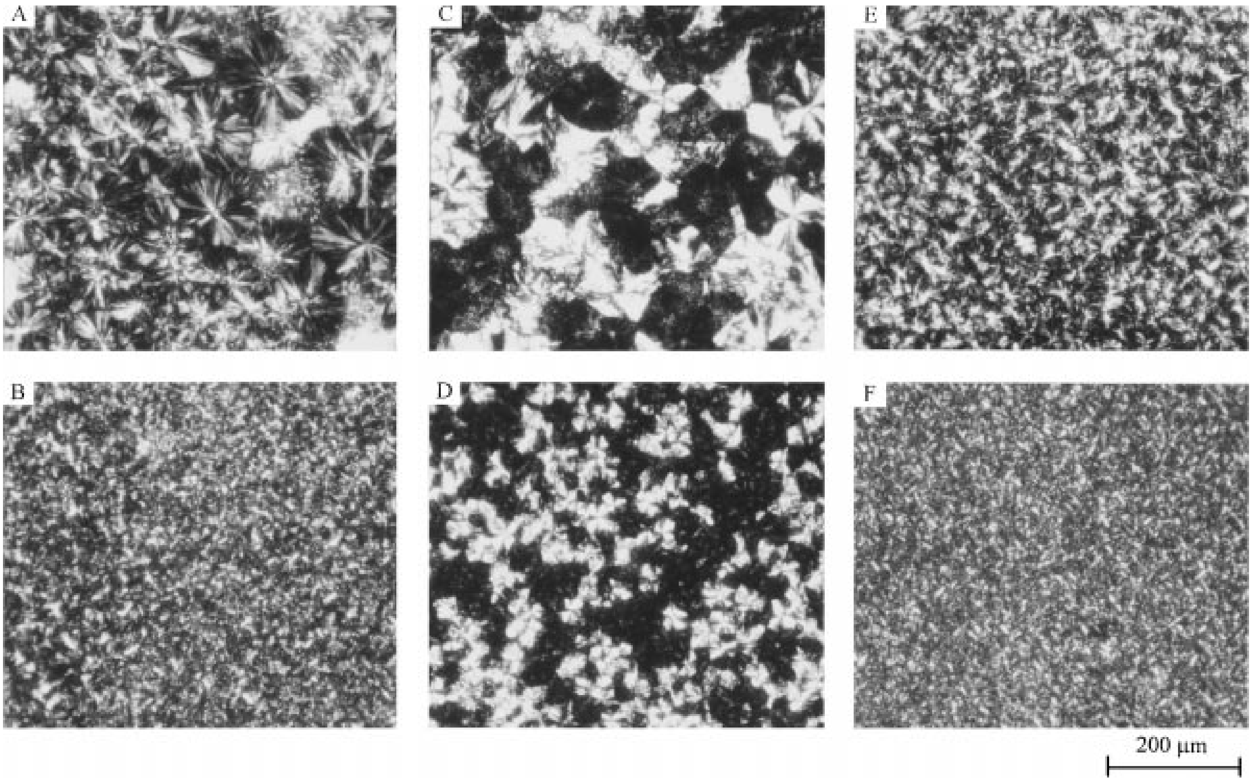

Figure 7 Effect of the nucleating additives and cooling rate on the morphology of PP. (A) PPvirCMs; (B) PPvirCMf; (C) PPβCMs; (D) PPβCMf; (E) PPsbCMs; (F) PPsbCMf.

The use of a faster cooling rate (ca. 200 °C/min) showed that the nucleation of polypropylene spherulites is dependent on the rate of cooling. This is apparent from the decrease in the size of the spherulites not only in the virgin but also in the nucleated materials (Fig. 7).

The crystallinity, determined from the density results, was affected by the nucleating additives and by the cooling rate (Table V). In agreement with what was expected from the DSC results, the samples moulded with the α-nucleating agents showed a higher degree of crystallinity. This is due to the increase of the crystallization temperature, which allows the crystallization to occur at higher temperature and for a longer time. It is known that these conditions promote an increase in the perfection and size of the crystalline lamellae.

The rate of cooling had a very strong effect on the density of the samples (Fig. 8) and consequently on the crystallinity (Table V). Independent of the addition of nucleating agents, the crystallinity decreased by about 8% when the rate of cooling changed from 10 °C/min to 200 °C/min. Irrespective of the cooling rate used, the presence of β-spherulites caused a decrease in the density. This is due to the lower density of this type of spherulites [25].

For the samples moulded using the slow cooling rate, the decrease in the size of the spherulites caused by the presence of the α-nucleating agents did not change the brittle behaviour of the samples in both the tensile and impact tests. The values of the mechanical properties remained similar to those obtained for the virgin material, except for the modulus, which showed an increase due to the higher degree of crystallinity of the nucleated samples (Table V). The improvement in ductility, usually associated with the presence of β-form spherulites [6–9] was only apparent in the increase in the deformation at yield.

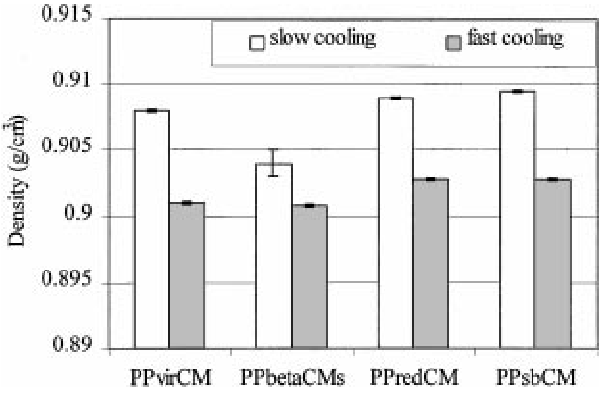

Figure 8 Effect of the rate of cooling on the density of the PP samples.

Independent of the composition, a clear improvement in the ductility was observed when the samples were cooled using the faster rate. This is apparent from the higher values of the impact energy (Fig. 9), which were accompanied by a change in the type of failure from brittle to ductile (Fig. 10). These results are explained by the decrease in crystallinity when a fast rate of cooling is used. Under these conditions the crystallization of the polymer occurs at lower temperatures and is partially hindered, resulting in a lower amount of a less perfect crystalline phase. Thus, the resulting morphology has a higher amorphous (flexible) content and consequently a higher number of interlamellar and interspherulitic tie-molecules acting as stress transducers, which improves the ductility. These results are in

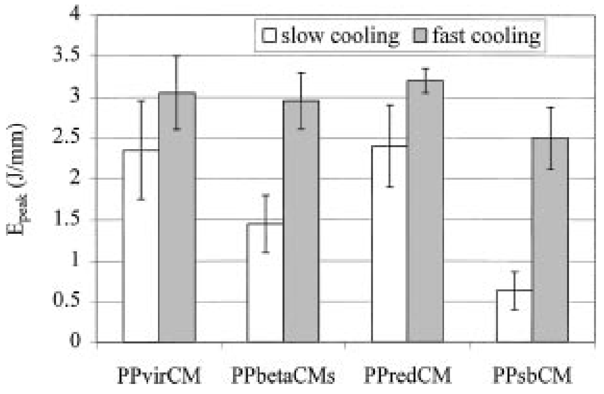

Figure 9 Effect of the cooling rate on the impact strength of PP samples.

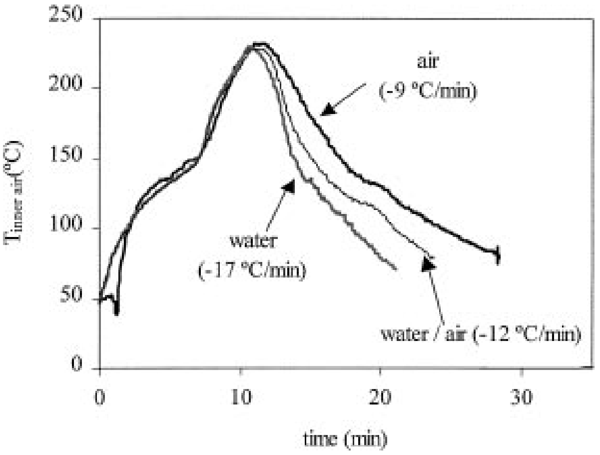

Figure 11 Rotolog traces of samples fast cooled according to Table III.

agreement with those reported by Friedrich for PP samples that showed a better fracture toughness when the rate of cooling was fast [10] or when the atactic component was higher [11].

3.3. Effect of fast cooling in rotational moulding

The above results indicate that the use of a fast cooling rate is the more effective way to improve the ductility of the PP material. Following these findings, water-cooling was used in rotational moulding to prepare samples as indicated in Table III.

The Rotolog traces in Fig. 11 show the internal air temperature of the mouldings and quantify the difference in the cooling rates of the samples.

The samples that experienced the fastest cooling show an uneven morphology (see Fig. 12). Close to the mould, where the water was applied, the spherulites are small while away from the mould they are bigger. This difference is accentuated when air was used in the range of temperatures where crystallisation occurs (Fig. 12C and D). This is the result of a non-uniform cooling rate through the thickness. As the cooling is done only through the mould wall, the plastic close to it solidifies earlier and at a faster rate, resulting in a finer texture and eventually in an early release of the moulding (detachment of the part from the mould surface). This solid layer acts as an insulator and causes the cooling of the bulk to be much slower, resulting in bigger spherulites. This uneven cooling also causes differences through the thickness in crystallinity, and consequently in shrinkage. This led to severe warpage in all the samples that were water-cooled. Warpage is a common problem with rotationally moulded products [26], especially when they have large flat parts, and is affected by factors like part thickness, cooling medium and mould material [27].

The failure behaviour of the samples cooled with water remained brittle. Nevertheless, it can be seen that the zone with a finer texture has a higher resistance to impact than the one with coarser texture (inner zone). This is illustrated in Fig. 13, which shows the fracture surface of sample PP_{water} impacted at the inner surface. It can be seen that the fracture started at the inner surface, where the spherulites are bigger, despite the fact that the high tensile stress was concentrated at the mould (outer) surface.

These results lead to the conclusion that the improvement of the ductility of the PP rotational mouldings can

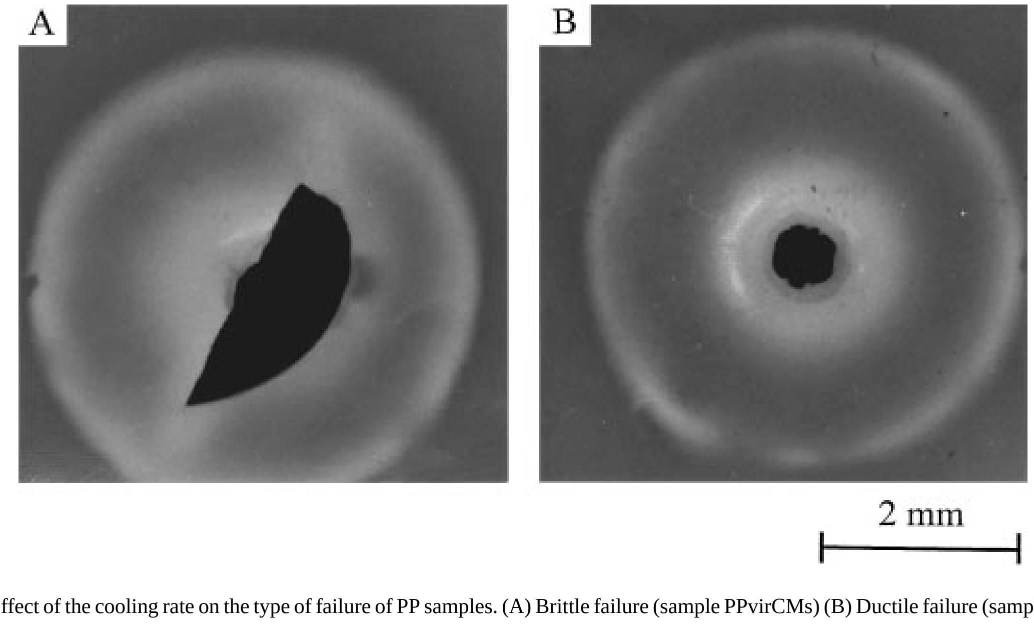

Figure 10 Effect of the cooling rate on the type of failure of PP samples. (A) Brittle failure (sample PPvirCMs) (B) Ductile failure (sample PPvirCMf).

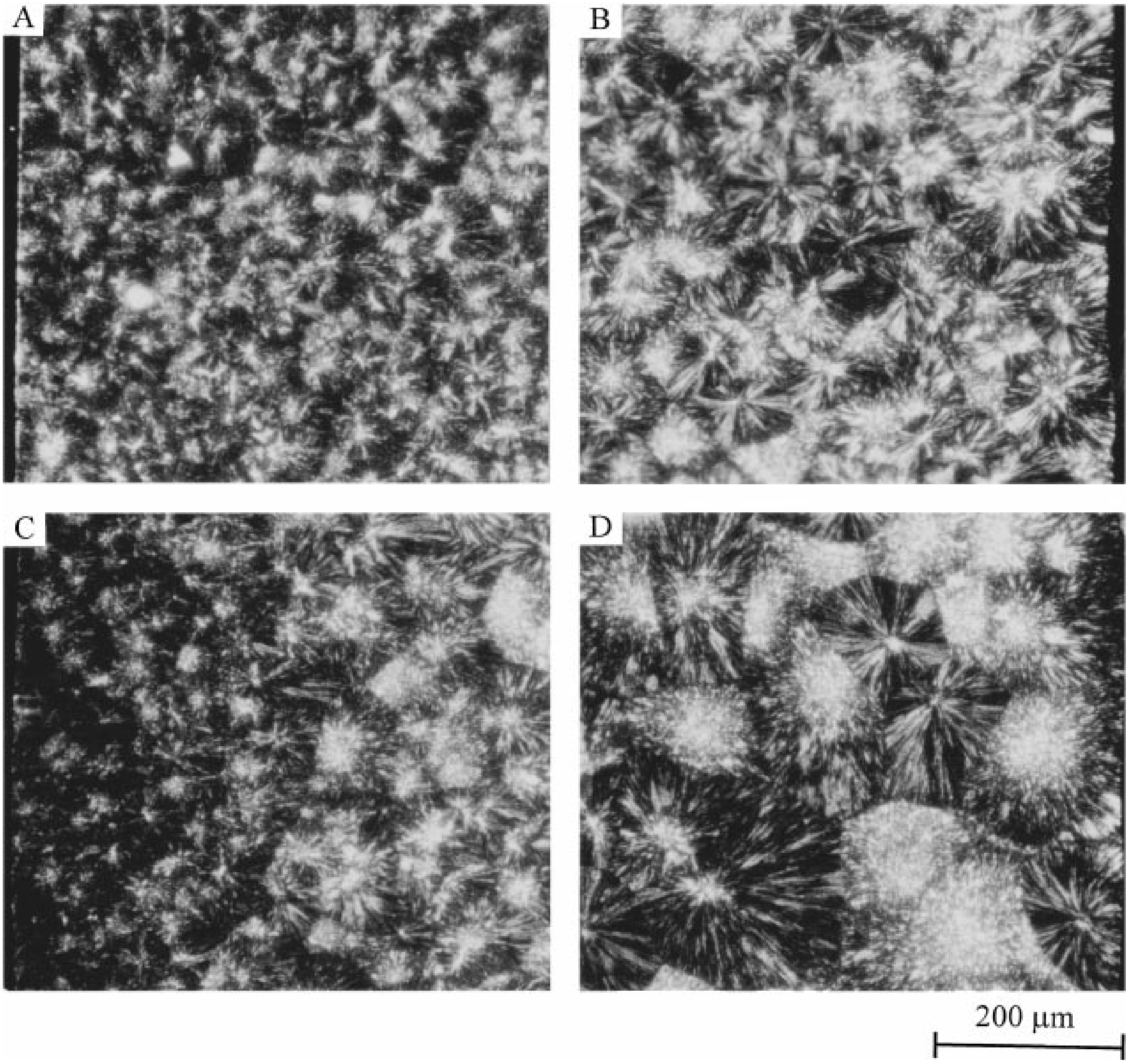

Figure 12 Microstructure of fast-cooled rotationally moulded samples. (A) PPwater—mould side; (B) PPwater—inner side; (C) PPw/a—mould side; (D) PPw/a—inner side.

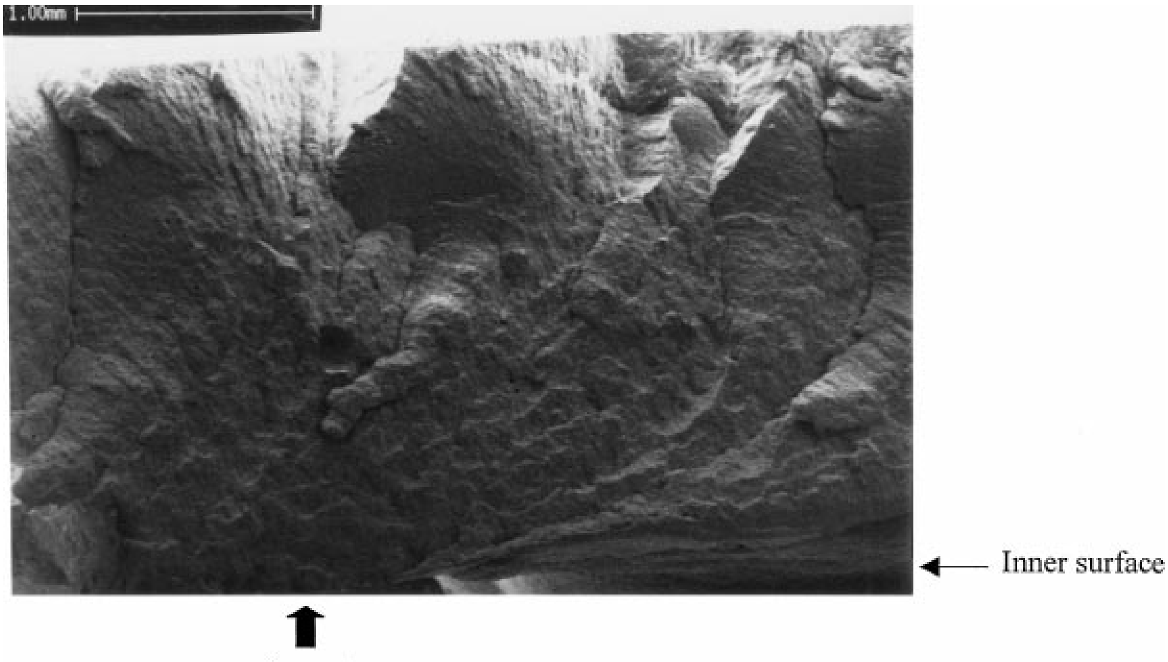

Figure 13 Fracture surface of sample PPwater, submitted to impact on the inner surface.

only be achieved through the application of fast cooling on both sides of the parts. One possibility is to cool the inner surface by blowing refrigerated air into the mould during the cooling stage, as is done frequently in the blow moulding industry.

4. Conclusions

In this work the relationships between the morphology and the properties of rotationally moulded polypropylene were studied and related to the processing conditions and to the effects of nucleating additives. The influence of the cooling rate was also studied. The main conclusions are:

1. In rotational moulding the polymer crystallises in the absence of shear and at low cooling rates. For polypropylene, these conditions favour the formation of a coarse and brittle spherulitic morphology.
2. The morphology of rotationally moulded PP is affected in a unique way by the processing temperature. Underheating causes voids in the bulk while overheating causes degradation at the inner surface. At the degraded layer the spherulites have higher birefringence and fluoresce when irradiated with UV light.
3. The rheological results showed that above an internal temperature of 230 °C the polymer suffers chain scission.
4. The compounding of the polymer with nucleating additives results in mouldings with finer microstructure.
5. Under slow cooling, the nucleating additives do not improve the impact strength of the mouldings, probably due to an increase in crystallinity.
6. The impact properties of rotationally moulded PP improve markedly when the cooling is fast, but steps must be taken to cool both surfaces of the plastic equally in order to fully realise the benefits in properties and avoid warpage in the end-product.

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