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Studying Microstructure and Crystallinity of Polypropylene in an Injection Moulded Medical Bin Lid

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Abstract: Properties of injection moulded parts such as crystallinity and size of spherulite are strongly influenced by processing parameters. A polypropylene (PP) sharps bin lid manufactured via injection moulding shows a variable distribution of temperature along the surface on ejecting at the end of the moulding cycle. This discrepancy subsequently necessitates the characterization of crystallinity and spherulite size for the bin lid at its face and corners. DSC, polarized optical microscopy and scanning electron microscopy were used for this analysis. Results of DSC analysis reveal that crystallinity does not change throughout the bin lid and its average value for corner and face is approximately 30 %. Use of the etchant to reveal spherulites in PP and low voltage SEM analysis has proven to be an efficient method for microstructural analysis in polymers and does not require gold coat to be applied on the polymer. POM images of slow cooled PP thin films (2 °C/mins approximately) reveal comparatively larger spherulites (order of 50 µm) compared to fast cooled (3 °C/sec approximately) thin films (a few microns). This shows that microstructure can be tailored by changing the cooling rate in injection moulding to achieve an optimum set of properties. In corner samples, the relative fraction of larger spherulites is higher than in face samples, which is attributed to the relatively slow cooling in this region. Spherulites are bigger (1.5-3 µm) at the top surface and there is a slight inclination towards a decrease in size of spherulites through the sections

1. Background

Injection moulding is one of the most widely used manufacturing processes for the production of thermoplastic parts with almost a third of all polypropylene (PP) processed using this method [1]. Final properties of PP moulded parts do not only depend on its chemical makeup but also on the processing parameters of the injection moulding used in its manufacture. Cooling rate is one of the more important processing parameters with a strong influence on the size of spherulites and hence crystallinity in the structure of moulded PP. Effect of spherulite size on fracture morphology and mechanical properties in isotactic PP has already been studied by Way et al [2]. Their results show that the nature of fracture changes from ductile to brittle when the diameter of spherulites is changed from 92 µm to 252 µm; whereas, for 174 µm diameter spherulites fracture was intermediate. Hence, studying the morphology of spherulitie to achieve optimum mechanical properties in moulded articles is vital.

Considering the lid of a “Sharps bin” (Figure 3a) manufactured from PP using the injection moulding process, which is designed to survive in a cryogenic environment, with the possibility of being exposed to high strain rates due to being dropped in real life applications. It is observed that when the bin lid is ejected from the tooling at the end of its moulding cycle, the corners are hotter (90-110 °C) than the face (65-80 °C), as shown in Figure 1. This discrepancy subsequently necessitates the characterization of crystallinity and spherulite size for the bin lid at its face and corners.

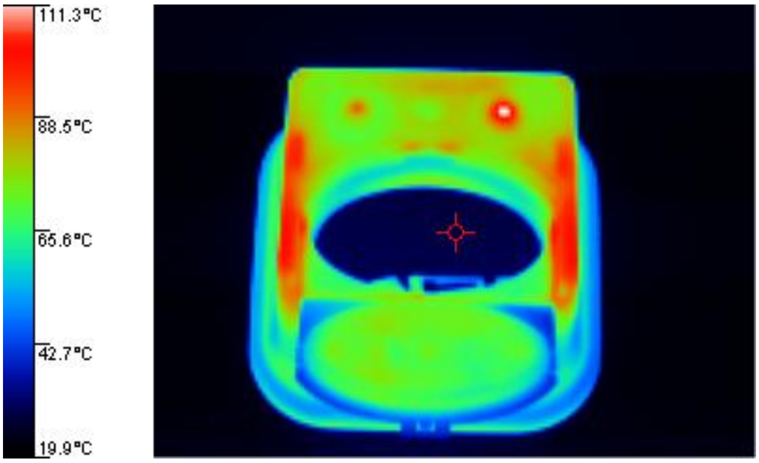


Figure 1: Thermal imaging map showing temperature distribution on the lid

2. Materials and methods

2.1. Material

The bin lid was injection moulded using PP block copolymer with high impact strength and stiffness even at low temperatures [3].

2.2. Differential Scanning Calorimetery (DSC) setting and heating cycle

A Differential scanning calorimetery (DSC) test was performed using PerkinElmer apparatus to measure the percentage of crystallinity. Four bin lids were studied and from each bin lid four samples were taken for the DSC tests; two from the corners of the bin lid (Figure 3a, region enclosed in red circle) and two from the face of the bin lid (Figure 3a, region enclosed in green ellipse). In total sixteen samples were tested. The mass of the samples was 28 ± 5 mg. During testing, the samples were heated from 30 °C to 210 °C at a rate of 10 °C/min under a nitrogen atmosphere to prevent oxidation [4, 5].

2.3. Crystallinity measurement

The percentage of crystallinity was determined using Equation 1 [4, 5].

$$\boldsymbol{Percentage\ of\ crystallinity} = \frac{\Delta H_m - \Delta H_c}{\Delta H_m^{\circ}} \times \mathbf{100} \qquad \text{Equation 1}$$

ΔH_m = Heat of melting (J/g),

ΔH_c = Heat of crystallisation (J/g).

ΔH_m°= Standard value of heat of melting for 100 % crystalline polymer; a value for PP from literature was found to be 207 J/g [4, 5].

For the calculation, ΔH_c was ignored, as a definitive crystalline peak was not observed during the DSC test. Absence of a crystallisation peak in a DSC thermogram, which plots heat flow versus temperature or time, is reported to be related to the thermal history to which the sample is exposed during its processing [4, 6]. The area under the melting peak (peak enclosed in green circle) in the DSC thermogram (Figure 2) was integrated and the resulting value was divided by the mass of the sample to attain ΔH_m.

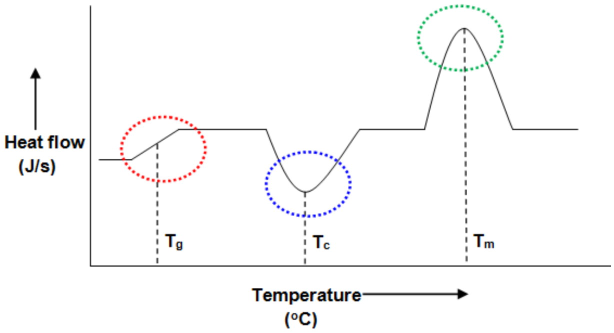


Figure 2: A standard DSC thermogram showing various thermal transitions in polymers including glass transition (endothermic), crystallisation (exothermic) and melting (endothermic).

2.4. Sample preparation for Scanning electron microscopy (SEM)

Three lids were studied under a Hitachi S4800 SEM, to observe for spherulites. From each lid two samples were taken, one from the corner of the lid and one from the face of the lid (Figure 3); in total six samples were observed.

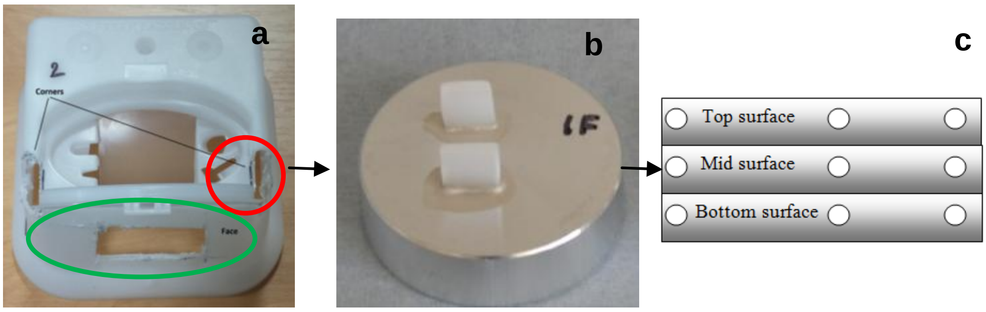


Figure 3: a) The bin lid with areas of investigation under SEM highlighted (green ellipse's area - face and red circle's area - corner); b) specimen stuck to the stub; c) circles represent locations on the specimen where SEM analyses was undertaken

The area considered for observation under SEM was taken through the cross-section of the bin lid to capture structural changes through this orientation. In general, the area in close contact with the mould should cool quicker ("Top surface" in Figure 3c) compared to the core region, due to variation in cooling rate through the cross-section.

Large samples were cut from the highlighted areas of interest using a grinding wheel, with a sharp blade used to cut the samples to size for microscopy; avoiding any kind of microstructural changes due to heating effects from the grinding wheel.

Flat surfaces of the cut samples were polished with Silicon Carbide (SiC) papers; size P 2500, for two minutes. With an alumina suspension on a chemomet cloth used to remove any scratches or cut marks. The samples were immersed for 24 hrs in an etchant, which was formulated by dissolving a mixture of 1.3 wt% potassium permanganate, 32.9 wt% concentrated phosphoric acid and 65.8 wt% concentrated sulphuric acid. The solvent was originally proposed by Olley and Basset [7, 8, 9] but is also reported by other researchers in the successful observation of spherulites in PP [7, 10, 11]. To improve the efficiency of the etchant, the samples were placed inside an etchant filled beaker placed into an ultrasonic bath. Continuous agitation is considered to enhance the etching reaction. Subsequently, samples were rinsed with distilled water to remove any debris and placed onto silver stubs using silver paste as an adhesive joint (Figure

4). This configuration also served to make the sample conductive. As a result of the described chemical treatment, amorphous regions of spherulite were preferentially etched and thus crystalline spherulitic portion was revealed under SEM.

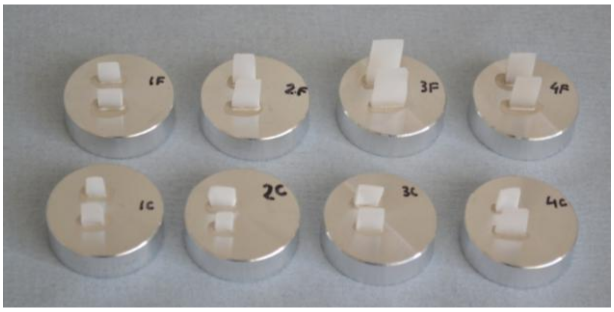


Figure 4: PP samples ready for SEM analysis

2.5. Spherulite size measurement

SEM images were analyzed using an in house image processing tool to measure the spherulite size (diameter). The data was normalized to calculate the percentage frequency distributions of spherulite size in the sampled bin lids, at corner and face locations as shown in Figure 8.

2.6. Sample preparation for Polarization microscopy (POM)

A small piece of PP was sliced from one of the faces of the bin and sandwiched in aluminum foil. The PP and aluminum foil was placed between the two hot plates of a hydraulic press, at a temperature of 210 °C and a pressure of 7 bar of pressure for approximately three minutes. This process resulted in the production of a very thin film of PP (Figure 5).

Figure 5: Thin films of PP

In order to understand the effect of cooling rate on the size of spherulites, a total of four samples were prepared using this technique. Two samples were taken out of the press and air cooled at the rate of 3 °C/sec approximately (Figure 5, left) and two samples were left inside the press allowing them to cool slowly (Figure 5, right) at the rate of 2 °C/mins approximately.

3. Results and discussions

3.1. Effect of cooling rate on crystallinity

Table 1 and Table 2 show the results of the DSC experiments for face and corner samples respectively. From these results it is clear that the onset of melting temperature for both face and corner samples is 132.05 °C and the melt peak is found at 172 °C. Melt end temperature for the two set of samples shows a slight scatter. A slight difference is observed in the height of the melting peaks for the two sets of samples; melting peaks in face samples are slightly higher than in corner samples (Figure 6). The bar chart for percentage crystallinity (Figure 7) shows that there is no obvious difference between the two sample sets and percentage crystallinity for both sets is around 30 %.

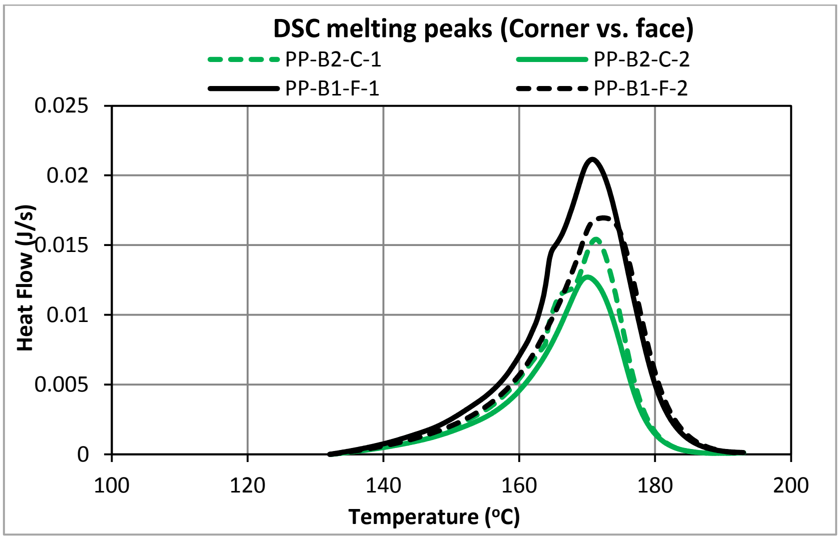


Figure 6: DSC thermograms showing the melting peaks for corner (green lines) and face (black lines) samples; black F-face, C-corner and B- bin lid

Table 1: DSC characterisation of PP samples taken from face of sampled bin lids,

Sample	Melt onset temperature	Melt peak temperature	Melt end temperature	Energy	mass	Enthalpy	Crystallinity
	^{o}C	*^{o}C*	*^{o}C*	*J*	*g*	*J/g*	*%*
PP-B1-F-1	132.063	170.720	192.970	2.172	0.033	65.621	31.686
PP-B1-F-2	132.103	172.254	193.012	1.854	0.033	56.187	27.131
PP-B2-F-1	132.063	170.256	192.982	1.935	0.033	59.548	28.753
PP-B2-F-2	132.025	172.142	189.854	2.296	0.033	68.960	33.298
PP-B3-F-1	132.065	173.346	192.977	2.054	0.034	61.312	29.605
PP-B3-F-2	132.025	175.560	192.915	2.546	0.032	78.835	38.066
PP-B4-F-1	132.064	172.687	191.314	2.065	0.034	60.028	28.985
PP-B4-F-2	132.062	171.273	192.981	1.986	0.034	58.927	28.453
Average	132.059	172.280	192.376	2.114	0.033	63.677	30.747
Std dv	0.025	1.674	1.173	0.222	0.001	7.330	3.539

Table 2: DSC characterisation of PP samples taken from corner of sampled bin lids

Sample	Melt onset temperature	Melt peak temperature	Melt end temperature	Energy	mass	Enthalpy	Crystallinity
	^{o}C	*^{o}C*	*^{o}C*	*J*	*g*	*J/g*	*%*
PP-B1-C-1	132.108	170.783	188.688	1.694	0.028	60.506	29.216
PP-B1-C-2	132.150	170.347	193.058	1.326	0.019	69.041	33.337
PP-B2-C-1	132.143	171.345	193.061	1.441	0.023	64.056	30.930
PP-B2-C-2	132.154	170.150	193.062	1.220	0.021	56.998	27.522
PP-B3-C-1	132.090	172.836	192.988	2.012	0.029	69.131	33.380
PP-B3-C-2	132.238	173.145	189.898	0.847	0.020	42.357	20.452
PP-B4-C-1	132.130	171.441	185.210	1.395	0.021	66.412	32.067
PP-B4-C-2	132.106	172.613	186.776	1.518	0.028	55.187	26.647
Average	132.140	171.583	190.343	1.431	0.024	60.461	29.194
Std dv	0.046	1.157	3.188	0.341	0.004	8.982	4.337

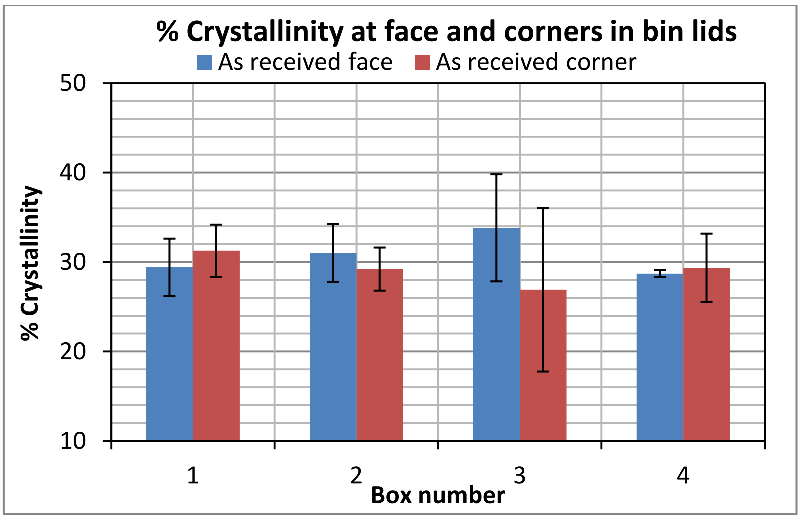
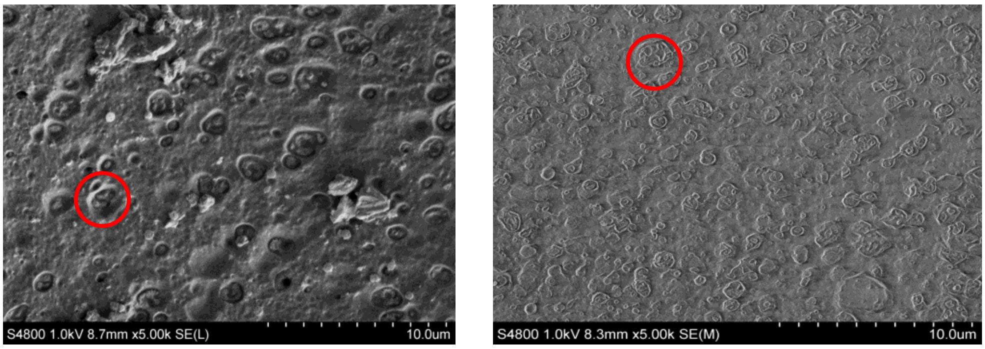


Figure 7: Percentage Crystallinity for face and corner samples of the bin lid

3.2. Effect of cooling rate on size of spherulites – SEM

Figure 8 shows spherulites in the PP when examined under SEM. Figure 8 left and right show spherulites in a corner sample from bin lid 2 and a face sample from bin lid 1 respectively. For the left SEM image a lower detector was used and for the right image a mixed detector was used. Owing to the fact that polymers charge under an electron beam with high voltage, a lower voltage of 1 KV and lower detector were used for all the analyses. It is likely that regions enclosed inside red circles (Figure 8) are spherulites due to their dimensions i.e. of the order of a few microns [12].



Corner (bin lid 2) *Face (bin lid 1)*

Figure 8: SEM images showing spherulites in PP samples taken from corner (left) and face (right) and of a sampled bin lid.

The results of the image analyses conducted at face and corner samples for three different locations (Top, mid and bottom), in bin lid 1 and bin lid 2, are shown graphically in Figure 9.

It can be seen from Figure 9 that the size of spherulites lies in the range 0.1-3.0 µm. A large fraction of spherulites lie in the size range 0.5-1.3 µm irrespective of the location (bottom, mid and top) or type of the samples (Face or corner). An increased fraction of large spherulites (1.5-3 µm) are found in corner samples as compared to face samples. Additionally, a greater fraction of large spherulites are found at the top location in the corner samples decreasing in the mid and bottom locations. This could be caused by a considerable difference in temperature at the top surface of the corner compared to the face when the bin lid is removed from the mould (Figure 1). The temperature at the corners lies in the range 90-110 ^{o}C; whilst, the temperature at the face lies in the range 65-80 ^{o}C. However, this temperature difference may diminish through the thickness.

3.3. Effect of cooling rate on size of spherulites - POM

POM images of the thin PP films exposed to different cooling rates are shown in Figure 10. A higher cooling rate allows less time for chains to orient themselves, resulting in smaller spherulite sizes [2] in the range of a few microns (Figure 10b). Allowing material to cool slowly provides enough time for orientation of the chain [2] and subsequently larger spherulites are seen of up to 50 µm size (Figure 10a).

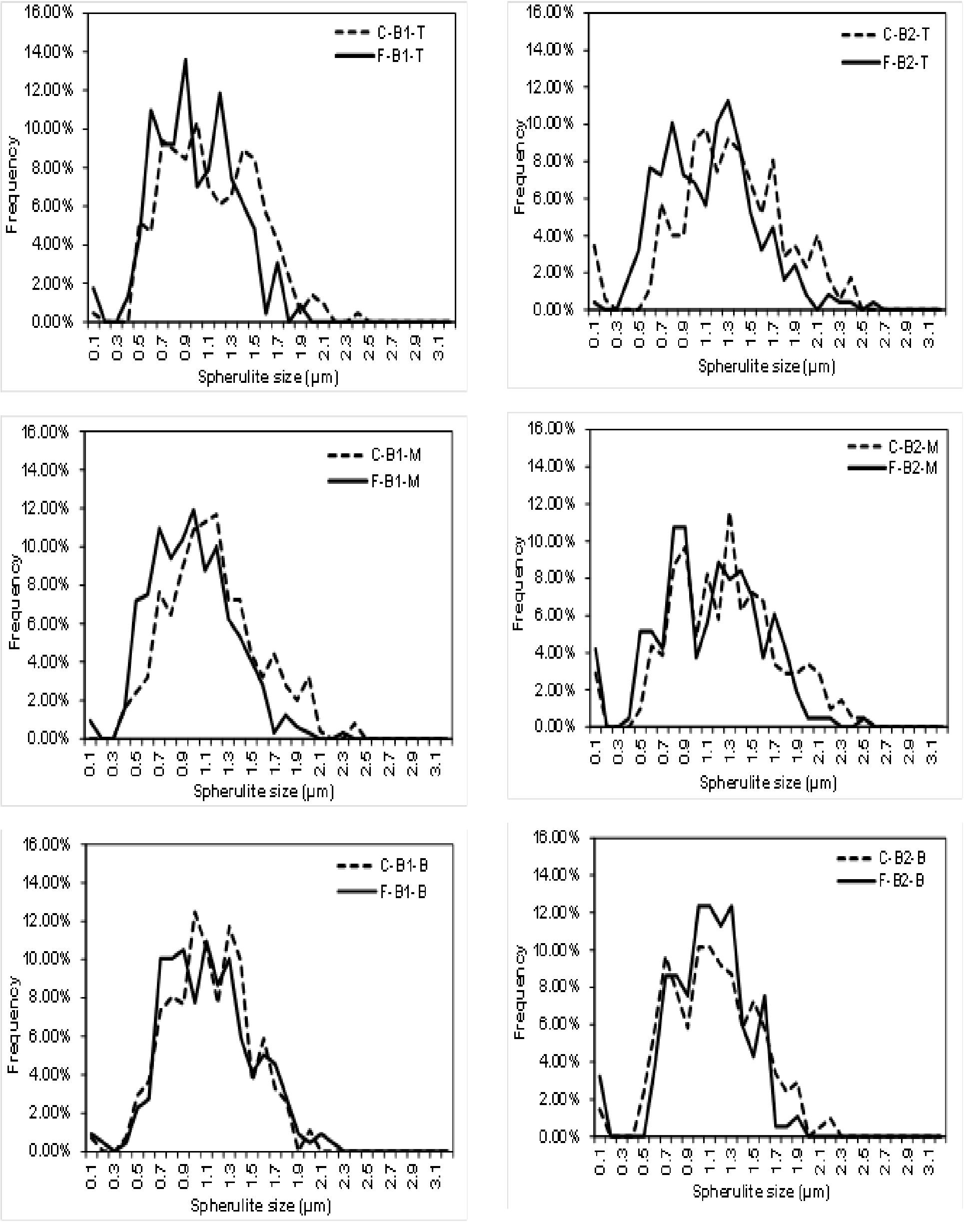
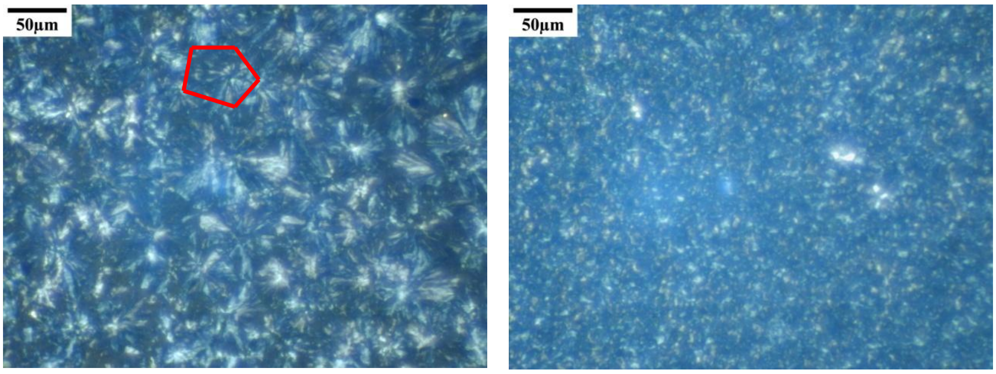


Figure 9: % Frequency distribution of spherulite sizes in faces (solid line) and corners (dashed line) at three different locations (T-top, M-Mid and B-bottom) for bin lid 1 (Left hand graphs) and bin lid 2 (Right hand graphs).



a) Cooled inside mould (Slow cooled) *b) Air cooled (Fast cooled)*

Figure 10: POM images of thin films of PP

The results from the POM suggest that PP is significantly affected by the cooling rate during the moulding process used for the bin lid's production. In order to achieve either smaller or larger spherulites inside the structure, material should be exposed to very fast or very slow cooling rates (section 2.6).

4. Conclusions

In this study, corner and face locations on a PP injection moulded bin lid were analysed for microstructure and percentage crystallinity. A systematic characterisation of the bin lid showed a number of findings:

- Percentage crystallinity does not change throughout the bin lid and its average value for corner and face is approximately 30 %, despite the fact that melting peaks in face samples are slightly higher than corner samples.
- Use of etchant to reveal spherulites in PP and low voltage SEM analysis has proven to be an efficient method for microstructural analysis in polymers. Eliminating the need to gold coat polymer samples which makes analysis more cost effective.
- POM images of slow cooled PP thin films reveal comparatively larger spherulites (order of 50 µm) compared to fast cooled thin films (a few microns). This shows that microstructure can be tailored by changing the cooling rate in injection moulding to achieve an optimum set of properties.
- In corner samples, the relative fraction of larger spherulites is higher than in face samples, which is attributed to the relatively slow cooling in this region.
- Spherulites are bigger (1.5-3 µm) at the top surface and there is a slight inclination towards a decrease in size of spherulites through the sections.

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