The Effect of Cooling Processing Conditions on the Crystallinity and Mechanical Performance of Pigmented Polypropylene Extruded Film

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The mechanical properties of semi-crystalline polymers will be dependant to a great extent on the overall crystalline morphology of these materials. These morphological structures are developed during cooling of the polymer melt during plastic fabrication processes such as extrusion. Control of this crystalline development is therefore a very important processing requirement in order to ensure optimum mechanical performance of products manufactured by extrusion processes. The nucleating effect of phthalocyanine-based pigments on the processing and properties of semi-crystalline polymers has also been a challenge to polymer processors for many years. These effects are ever more pronounced during in-line, post extrusion processes such as elevated temperature drawing of polypropylene slit film tapes, for rope and twine applications. A range of polypropylene films containing levels of 2% phthalocyanine based pigments and inorganic iron (II) oxide based pigments were manufactured using the chill roll cast extrusion process, using a range of quench temperatures and die to chill roll gaps. Analysis of the tensile properties of the films showed significant increase in modulus for the phthalocyanine pigmented films by up to 25% in comparison to the iron (II) oxide pigmented and non-pigmented films. DSC analysis showed the crystallinity of phthalocyanine-pigmented films to be less affected by quench roll temperatures than the iron (II) oxide pigmented and non-pigmented films. However polarized light microscopy analysis of the films showed the spherulite sizes for the phthalocyanine pigmented films to be significantly smaller than the iron (II) oxide pigmented films and non-pigmented films.

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Introduction

The growth in worldwide use of isotactic polypropylene (iPP) continues. Consumption for fiber application being 40% including face pile carpet yarns, secondary and primary carpet backing tapes, non-wovens, and slit tape production for rope and cordage. The increase usage is due to its low density, relatively low price, good thermal insulation, and inherent stain resistance. One of the drawbacks in the early development of polypropylene was its inability to be coloured by conventional dyeing systems. However, pigments were soon developed with suitable light stability and color fastness, to enable polypropylene fiber products to be manufactured in a wide range of colors.

Polypropylene ropes and cordage products manufactured from extruded tapes, continue to be an expanding market with the growing leisure marine industry, and its increasing use as reinforced netting products for geotextile applications. Polypropylene cordage has now virtually completely replaced twines made from sisal for agricultural applications in hay, straw and silage baling operations worldwide. It’s expansion in use in these applications is because of its low (almost zero) moisture uptake and its resistance to microbial attack. Many of these products are manufactured by the slit film extrusion process where the method of melt quenching will affect the properties of the extrudate film which in turn will influence post extrusion processing parameters such as oven drawing at elevated temperatures, fibrillation and winding as well as post manufacturing aging processes. The main methods used by the industry to cool the polymer melt on exiting the die are either chill roll or water bath quenching. However during production considerable alternations to chill roll temperatures, air gap settings, draw ratios and oven temperatures are always required after color changes in order to achieve good runnability and product quality. To date, these processing parameter changes have been laboriously carried out by experienced technicians, and there is now an urgent need to investigate the effect of pigmentation on extrusion and post-extrusion processes.

The effect of cooling rates on the crystallization of isotactic polypropylene has been well documented over the years [1-4]. However much of this work concentrates on crystallization thermodynamics and kinetic studies under isothermal conditions, and without consideration of the crystallization effects occurring during molecular orientation. The nucleating effects of pigments have been reported however these studies have concentrated on the crystallization kinetics and associated mechanical performance of injection-moulded products [5-8]. Therefore this work reports on the affect of film extrusion processing parameters such as air gap and chill roll temperature on the crystallinity and mechanical performance of a range of pigmented and unpigmented iPP films.

Experimental Details

(a) Materials

Commercial iPP was used throughout the experimental work. This is a homopolymer extrusion grade which is heat stabilized and has a MFI 2.8 (230°C /2.16 kg). The two
pigments studied were commercial pigment masterbatches supplied by Schluman containing iron oxide (Pigment red 101 No.77491) and copper phthalocyanine pigment blue (74160.3). Both pigment masterbatches were 30% w/w dilutions in low-density polyethylene carrier.

(b) Manufacture of films

A series of 48 films were manufactured during this investigation using a Killion cast film unit. This unit comprised a Killion 38 mm, 25:1 L:D, extruder fitted with a 600 mm wide flexilip die, and a single chill roll and haul off unit with sheet winding facility. The die lip opening was set at 1.0mm throughout the experimental trials. The chrome plated (2.0 mirror finish) casting roll was 600 mm wide and 300 mm diameter with internal double shell, spiral baffle design for improved heat transfer. The roll temperature was set using a Sterlco temperature control unit, which maintained the roll temperature to within ±2°C. The pigment masterbatch and polymer were table mixed prior to extrusion.

A range of pigmented and unpigmented films of constant thickness were manufactured using different chill roll temperatures and air gaps (i.e. the air gap being the distance between die lip and chill roll contact). The extruder output and chill roll speed were kept constant throughout the series of runs in order to manufacture films of 150 µm thick. The chill roll conditions for the various films are shown in Table 1.

<table>
<thead>
<tr>
<th>Air Gap (mm)</th>
<th>Chill Roll Temperatures (°C)</th>
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<tbody>
<tr>
<td>10</td>
<td>37  43  62  69</td>
</tr>
<tr>
<td>50</td>
<td>37  43  62  69</td>
</tr>
<tr>
<td>100</td>
<td>37  43  62  69</td>
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</table>

Table 1. The chill roll settings for the manufacture of films.

Films containing, 100% virgin iPP, 98% virgin iPP and 2% phthalocyanine (blue), and 98% virgin iPP and 2% iron (II) oxide (orange) were manufactured at a die temperature of 240°C. The films were wound and stored under room temperature conditions for analysis.

(c) Tensile analysis

Tensile modulus, elongation and break strength, of the films were determined using an Instron 4411 universal tensile tester according to BS 2782, using crosshead speed of 100 mm/min and an initial gauge length of 50 mm. An average of at least twenty samples was recorded for each film.
(d) **Crystallinity**

The effect of cooling conditions, pigment type and concentration, on the crystallinity of these films was studied using differential scanning calorimetry techniques. The percentage crystallinity of the film samples was determined using a Perkin Elmer DSC-6. Samples of the films were heated at 10°C/min to 230°C and crystallinity was determined from the enthalpy (ΔH) values of the melt endotherms, using the ΔH value 164 J/g [9] for 100% crystalline polypropylene. Controlled cooling studies were also performed in situ using the DSC in order to determine the effect of controlled cooling rate on the solidification temperature and crystallinity of the pigmented films.

(e) **Polarized light microscopy**

The nucleating effect of pigments on the crystallization of polypropylene film was studied using an Olympus BH2 hot stage polarizing microscope system with controlled heating and cooling system and with photomicrograph facilities. Samples were prepared for polarizing microscopy studies, by melting film samples mounted between two glass microscope slides, on a hot plate and gently pressing both plates together. These samples were cooled to room temperature and then placed on the optical hot stage of the microscope system and heated to 230°C for 2 minutes to ensure complete melting. The samples were then cooled at a controlled rate of 50°C/min and the resultant spherulitic structures were recorded using the photomicroscopy facilities.

Results and Discussion

(i) **Tensile properties**

1. **Air gap of 10 mm**

The effect of chill roll temperature on the Young's modulus of films manufactured using an air gap of 10mm is shown in Figure 1. These results show that the modulus of all film types show an increase, with increase in chill roll temperature. The results also show that the modulus for the films containing phthalocyanine based pigment were all markedly higher than the other two film types. A maximum Young's modulus of 1540 MPa being recorded for phthalocyanine based film using a chill roll temperature of 38°C.

The results in Figures 2 and 3 show that chill roll temperature and pigment type had only a marginal affect on the overall percentage elongation and break strength of the films, with average elongations for all films being in the range of 900% – 1000%, with break modulii in the range of 38–40 MPa, being recorded for most of the films. However, it is noticeable that the elongation and break modulus for the phthalocyanine based films quenched at the higher chill roll temperature of 68°C had notably lower elongation (620%) and lower break modulus (37 MPa) than other films.
2. Air gap of 50 mm

The effect of chill roll temperature on the Young’s modulus of films manufactured with a larger air gap of 50 mm is shown in Figure 4. The results show that the effect of increasing chill roll temperature from 36°C to 68°C had a much more marked effect on the modulus of the non-pigmented and iron II oxide pigmented film, than the phthalocyanine based film, using this larger air gap of 50mm. Increase in modulus from 830 MPa to 1100 MPa and 860 MPa to 1120 MPa were recorded for the iron (II) oxide and non-pigmented films respectively over the chill roll temperature range 36°C to 68°C.
The modulus for the phthalocyanine pigmented film was shown to increase only marginally over those recorded for the smaller air gap of 10 mm (see Figure 1). The results in Figures 5 and 6 show very little change in elongation and break modulus with changes in chill roll temperature, however much lower elongations and break modulii were recorded for the phthalocyanine based film, especially at higher chill roll temperatures.

3. Air gap of 100 mm

The effect of chill roll temperature on the tensile properties of the films manufactured with a air gap of 100 mm are shown in Figures 7, 8 and 9.
Crystallinity and Mechanical Performance of Polypropylene

**Figure 7.** The effect of chill roll temperatures on tensile modulus of films manufactured with an air gap of 100 mm.

**Figure 8.** The effect of chill roll temperatures on elongation of films manufactured with air gap of 100 mm.

Once again, increase in modulus, of the unpigmented and iron (II) oxide pigmented film, with increasing chill roll temperature was recorded, with unpigmented film showing slightly higher moduli than the iron (II) oxide film. Only slight decrease in elongation and break modulus was recorded over the chill roll temperature range. However the modulus of the phthalocyanine pigmented film was shown to be much higher than the other two films and much less sensitive to increase in chill roll temperature. Figures 7 and 8 also show that the recorded elongations of these phthalocyanine films was much smaller, especially at the higher chill roll temperatures.

**Figure 9.** The effect of chill roll temperatures on break strength of films manufactured with an air gap of 100 mm.
(ii) **Crystallinity**

The tensile modulus results discussed in the preceding section would tend to indicate that both the pigment type and the quenching conditions had a significant effect on morphological development of the various films. In order to investigate the effect of pigment type and cooling rate on the crystallinity of iPP, a preliminary study on controlled cooling of films was performed "in situ" using DSC analysis. Samples of pigmented and non-pigmented films were heated in the DSC pans to 230°C and held at this temperature for 2 minutes to ensure complete melting had occurred. The samples were then cooled in the DSC at 5°C/min, 10°C/min, 20°C/min, 30°C/min and 50°C/min and the crystallisation temperatures for all the films at the various cooling rates were recorded as shown in Table 2. The samples were then reheated at a rate of 10°C/min and the percentage crystallinity was calculated. The results in Figure 13 clearly show an overall decrease in crystallinity for all the films with an increase in DSC cooling rate. The results also clearly show the nucleating effect of the pigments, resulting in increase in crystallinity for iron (II) oxide pigmented film and an even greater increase in overall crystallinity for the phthalocyanine pigmented films.

<table>
<thead>
<tr>
<th>Cooling Rate (^{0}{\text{C/min}})</th>
<th>Solidification Temperature of Film (^{0}{\text{C}})</th>
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<tbody>
<tr>
<td>No Pigment</td>
<td>2% iron (II) oxide (orange)</td>
</tr>
<tr>
<td>5</td>
<td>116</td>
</tr>
<tr>
<td>10</td>
<td>112</td>
</tr>
<tr>
<td>20</td>
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<td>30</td>
<td>108</td>
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<td>50</td>
<td>107</td>
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*Table 2. The effect of DSC cooling rate on solidification temperature.*

DSC analysis was also performed on the various films manufactured using different chill roll temperatures and air gap distances. The results in Figures 10 and 12 show that percentage crystallinity of the unpigmented and iron (II) oxide pigmented films was affected to a greater extent by chill roll temperature than the phthalocyanine pigmented films. Increase in air gap from 10 to 50 mm had little added affect on the crystallinity of the films, however there was a slight increase in overall crystallinity at these air gaps.
Figure 10. The effect of chill roll temperature and pigment type on percentage crystallinity of films manufactured with an air gap of 10 mm.

Figure 11. The effect of chill roll temperature and pigment type on percentage crystallinity of films manufactured with air gap of 50 mm.

Figure 12. The effects of chill roll temperature and pigment type on percentage crystallinity of films manufactured with an air gap of 100 mm.

(iii) Polarized light microscopy

Samples of unpigmented films and iron (II) oxide (2%) and phthalocyanine (2%) pigmented films were prepared for the polarized light microscopy analysis as described previously. All samples were individually heated to 230°C on the hot stage, held at this temperature for two minutes, and then cooled at 50°C/min to room temperature. The photomicrographs in Figures 14(a) and 14(d) show the classic large spherulitic structure associated with slow quenching of polypropylene.
Figures 14(b) and (c) show the different nucleating affects of the two pigment types, with the phthalocyanine based pigment having the greatest affect showing extremely fine spherulitic structure having been developed.
Conclusions

The optical microscopy studies have shown that the morphological development of iPP is greatly affected by both the iron (II) oxide and the phthalocyanine pigments. The presence of these pigments results in a much smaller spherulitic structure, with the phthalocyanine pigment having the most dramatic effect on the spherulite size, as shown in the photomicrographs in Figure 14(c). Differential scanning calorimetry analysis showed that increase in cooling rate resulted in a decrease in overall crystallinity. This analysis also showed that the latent heat of fusion of the pigmented films was greater than the unpigmented film and the cooling exotherms also showed that the crystallization temperature of the phthalocyanine pigmented films was up to 15°C higher than both the iron II oxide and unpigmented film types, for all cooling rates (see Table 2). This would tend to suggest that morphological development of the phthalocyanine films will be initiated at much higher temperatures, and the crystallization process may in fact be well developed in the cooling melt (130°C) even before contact with the chill roll. This is confirmed by the results showing the percentage crystallinity, and resultant modulus of these films to be less affected by chill roll temperature at the high air gap settings.

The tensile analysis shows that the modulus for the phthalocyanine pigmented films was much greater than the modulus of the other films. This high modulii would result in much higher stress being developed in the film during subsequent drawing processes and which would require higher draw oven temperatures in order to prevent the stretched film tapes “necking” outside the oven. The results also show considerable reduction in the percentage elongation of the phthalocyanine films especially at the higher chill roll temperatures and larger air gaps. This reduction in elongation would ultimately lead to film breaks during drawing and so would limit the maximum achievable draw ratio and so affect the mechanical properties of the stretch film tapes.

In summary, the results of this study would indicate that in order to overcome the problems associated with the extrusion of phthalocyanine pigmented isotactic polypropylene, these products should be quenched at much lower temperatures, with much smaller die lip to chill roll gaps, in order to develop optimum morphological structure for subsequent drawing operations.

Acknowledgments

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References
