Influence of the β-Nucleator on the Thermal and Sagging Behaviours of Polypropylene*

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ABSTRACT

According to the crystallization conditions, polypropylene (PP) can be crystallized into three forms: α-monoclinic, β-hexagonal, and γ-form. The major problem with thermoforming of PP is its narrow processing window. Due to broadening the melting region, β-crystal form has a significant effect on the thermoformability of PP. In this study γ-quinacridone (Q-dye) was used as a β-nucleator agent. Three different concentrations of Q-dye (5, 10, and 50 ppm) were mixed separately with PP by a laboratory twin screw extruder. X-ray graphs confirmed the β-nucleating effect of Q-dye obviously. Differential scanning calorimetry (DSC) was used for evaluating the crystallization behaviour. Both melting points of α- and β-crystals were seen in the samples containing Q-dye. Crystallization temperature and the rate and degree of crystallinity increase with β-nucleator concentration. Sagging tests were carried out at 170°C and it was observed that sag distance and sagging rate decreased with increasing Q-dye content.

INTRODUCTION

Thermoforming is a process for shaping the plastic sheets which they have been heated until it soften, and then it is stretched into a mould with the assistance of pressure, vacuum, a mechanically operated plug, or a combination of these methods to give the shape of the formed part. This process is widely used to produce several types of industrial articles. In comparison with other thermoplastics, polypropylene (PP) shows very good properties. It has high melting point, chemical inertness, low density, excellent chemical and thermal resistance and low cost. Therefore, PP is a very desirable polymer for thermoforming applications from food packaging to large industrial parts [1]. The main thermoforming problems of PP are: excessive sagging of the heated sheet,

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narrow processing window, long cycle time and poor thickness distribution in the final part [2]. Due to semi-crystalline structure, PP has a fairly sharp melting region and changes rather abruptly from a solid to the melt at the melting point, unlike amorphous polymers such as polystyrene, poly vinyl chloride, and acrylonitrile butadiene styrene which gradually soften above their transition temperatures. This phase transition behaviour of PP makes thermoforming difficult [3]. In recent years, many researches have been devoted to improve the thermoformability of PP. Some of these approaches are:

1. Molecular architecting of PP: formation of long chain branching [4-6] and improvement of molecular weight and molecular weight distribution [7,8].
2. Blending with other polymers, especially polyolefins [9-11].
3. Using mineral fillers such as talc and calcium carbonate [12-15].
4. Changing of the crystalline structure by nucleators adding [16-19].

In addition to the material modification, machine manufacturers also tried to find the suitable way of PP thermoforming. The method which has been developed by Shell Co. is solid phase pressure forming known as SPPF. This process allows a hot but not molten sheet to be thermoformed just below its melting point under high pressure. Disadvantages of the SPPF method are: expensive thermoforming equipment, restricted dept of draw, and high levels of residual stresses [3].

An effective factor on the thermoformability of PP is its crystalline structure which controls melting behaviour. PP crystallizes into three forms: the most stable monoclinic α-form, the hexagonal β-form and the less stable triclinic γ-form [15,20]. The conventional PP grades crystallize into the α-form, while β-crystals form in the presence of β-nucleator and special quenching conditions and γ-form is found only in the low molecular iPP by crystallization under high pressure and slower cooling rate [21]. Melting temperature of β-form is lower than α-form therefore, a good combination of these two types cause broader melting region. However, it should be noted that the melted β-crystals can be recrystallized into the α-form [22].

For changing the PP crystalline structure it is need to incorporate the nucleator in small amounts into the polymer before or during processing [23]. PP Nucleating agents divided into the two main groups: α-nucleators and β-nucleators. Some of the effective α-nucleators are: sodium tertiary butylbenzoate, sodium benzoate, colloidal silver, phosphoric acid, phosphorous acid, derivatives of sorbitol, tcalc, and air bubbles, and the β-nucleators are: 2-mercapto benzimidazole, anthracene, phenothiazine, triphenodithiazine, phenanthrene, isophtalic acid, and terephthalic acid [3,20,23,24]. The γ-quinaclidone dye which has been reported as the most effective β-nucleating agent [25] is known as the permanent red and here in after refers to as "Q-dye". Q-dye is a commercial red pigment of high tintorial strength and outstanding resistance to light, heat, and chemicals often uses in automobile finishes and coloring plastics.

The amount of β-crystals in the β-nucleated PP is dependent on the nucleator efficiency, its concentration, and cooling conditions [20]. Q-dye is an efficient β-nucleator at low concentrations and low cooling rates, but depends on processing conditions, it can posses as α-nucleator role too. By increasing nucleating content in the resin and increasing cooling rate, the β-nucleating effect of Q-dye decreases and its action as an α-nucleator increases [28]. The influence of Q-dye on the injection moulding process was investigated [29]. It is reported that impact resistance of injected product increases, resulting especially in a much higher ductility of iPP [27]. Furthermore, nucleated iPP has the same rheological properties as the origin resin, thus the extrusion efficiency is not compromised [16]. In order to reduce cycle time and make uniform material distribution in the final part, α- nucleators have been used in thermoforming process [17,18].

The purpose of our work is to study the influence of β-nucleator on the thermoformability of iPP. Thermal

![Scheme I. Chemical structure of Q-dye.](image)
and sagging behaviours of samples containing various concentrations of nucleator was investigated to predict the effect of Q-dye on the thermoformability of iPP. Crystallinity of nucleated PP was studied using DSC and XRD (X Ray Diffraction) techniques. Some results of this study was reported in ISPST 2005 congress [30].

EXPERIMENTAL

Material
A commercial isotactic homopolymer of PP produced by Bandar Imam Petrochemical Co. was used in this study (PI0800, MFI=8 dg/min at 230°C/2.16 Kg). Hostaperm E3B (Q-dye) supplied by Clariant Co. was used as a β-nucleator of chemical structure as shown in Scheme I and its properties listed in Table 1.

Compounding
Compounding of Q-dye in PP was carried out in two steps. At first, 5 wt% master batch of Q-dye in PP matrix was prepared through the internal mixer (Haake sys 90) at temperature of 190°C and rotor speed of 60 rpm. Samples containing 5, 10, and 50 ppm of Q-dye, named as 1Q5, 1Q10, and 1Q50, respectively were prepared by compounding the aforesaid master batch with the original PP in a laboratory corotating twin screw extruder (ZSK 25). The temperature zones were set as 170, 175, 180, 190, 200, and 210°C. Screw rotation speed was 200 rpm. The extrudate was water-cooled and granulated.

Analysis
Crystalline structure of samples were studied by wide-angle X-ray scattering (WAXS) method, using CuKα radiation (λ=1.5418 Å). The instrument was X’Pert from Philips (Netherland). β-phase content and degree of crystallinity were analyzed. Circular specimens (diameter = 20 mm, thickness = 1 mm) were prepared through the compression moulding at 210°C and pressure of 25 MPa by mini test press of Toyoseiki Co. (Japan).

Crystallization and melting behaviour of samples were studied using a PL differential scanning calorimetric (DSC). 9-10 mg of each sample heated to 200°C, kept for 5 min, cooled to room temperature

Table 1. Properties of Q-dye.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>1.48</td>
</tr>
<tr>
<td>Specific surface (m²/g)</td>
<td>41</td>
</tr>
<tr>
<td>Average particle size (nm)</td>
<td>195</td>
</tr>
<tr>
<td>Heat stability</td>
<td></td>
</tr>
<tr>
<td>10 min at 220°C</td>
<td></td>
</tr>
<tr>
<td>30 min at 200°C</td>
<td></td>
</tr>
<tr>
<td>Sublimation temperature(°C)</td>
<td>425</td>
</tr>
</tbody>
</table>

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Figure 1. Sagging test scheme.
with 10°C/min rate and reheated up to 200°C, with a rate of 10°C/min.

Sagging test carried out to measure the amount and the rate of sagging. This experiment was done in an air circulating oven with a front glass door as shown in Figure 1 at the temperature of 170°C. For this test, polymer sheets with an average thickness of 1 mm and area of 160×160 mm² were prepared by compression moulding under 25 MPa pressure at 210°C. The sag distance at the center of the supported sheet, where the maximum amount of sagging occurs, recorded as a function of time using a camera. Due to thermal expanding of the polymer sheet at the first step of the test, data considered after 3 min at 10 minutes in 30 s intervals. Sagging rate was calculated by determining the slope of the sagging-time curves obtained by this test. Each test was carried out three times and the average of results was reported.

RESULTS AND DISCUSSION

X-ray test is a desirable method to evaluate the crystalline structure of PP. The main peaks of α crystals can be seen in 2θ = 14, 16.9, and 18.5° and β-crystals show a sharp intensity at 2θ = 16° [20, 23, 24]. The amount of β-form (K) in samples was determined using the equation (1) proposed by Turner-Jones [21].

\[ K = \frac{H_{(300)}}{H_{(300)} + H_{(110)} + H_{(040)} + H_{(130)}} \]  

Where, the \( H_{(300)} \) is the maximum diffraction intensity of the β-form and \( H_{(110)}, H_{(040)}, \) and \( H_{(130)} \) are the intensities of the α-form.

Figure 2 shows the X-ray diffraction results of samples. It is clearly observed that by increasing Q-dye content in samples, all of the intensity amounts increase briefly. There is no peak at 2θ = 16° for original PP; hence no β-crystal forms. In samples containing Q-dye, the β-form intensity can be observed, which becomes higher as Q-dye concentration increases. Presence of a peak at 2θ = 16° confirms the formation of β-crystals with the increasing of Q-dye content.

Influence of Q-dye on K value is shown in Figure 3. Due to β-nucleating effect of Q-dye on PP, K values (amount of β-form) of samples increase with the increasing of the Q-dye concentration.

Figure 4 illustrates area under XRD curves versus Q-dye content, which has a close relation to the degree of crystallinity [3]. Increase of this area means that there is the higher degree of crystallinity in nucleated PP.

Figure 5 shows the typical crystallization and
melting thermograms of DSC. As can be seen, obtained parameters are: onset crystallization temperature ($T_o$), initial slope of the crystallization ($S_i$), width at the half height of the crystallization peak ($W_h$), area under the crystallization peak per unit of the sample ($A_f$), exotherm peak temperature ($T_c$), melting point ($T_m$) and area of the melting peak per unit of the sample ($A_m$).

$T_o$ is the onset temperature of the crystallization. At this temperature the first deviation from the baseline is observed. $S_i$ indicates the rate of the crystallization. The greater amount of $S_i$ means the faster crystallization; $W_h$ is proportional to the spherulite size distribution and the smaller $W_h$ reflects the narrower distribution [18].

According to the crystalline structure, different melting points can be observed. In this paper $T_m^\beta$ and $T_m^\alpha$ are related to $\beta$- and $\alpha$-crystals. Both $A_f$ and $A_m$ relate to the degree of crystallinity. The increase of these values denotes the higher degree of crystallinity.

The variation of melting and crystallization behaviour of the original PP and the samples with increasing of the Q-dye content at various levels are shown in Figures 6 and 7, respectively. Data obtained from DSC tests are summarized in Table 2.

The effect of Q-dye on the melting trend is clear from Figure 6. Samples contain Q-dye were showed two melting temperatures. Lower and higher $T_m$ is related to $T_m^\beta$ and $T_m^\alpha$, respectively. By increasing the Q-dye content in the samples, $T_m^\beta$ shifts to the lower temperatures but the variations was not considerable. Formation of $\beta$-crystals causes broadening the melting region. $T_m^\alpha$ did not change by adding Q-dye. $A_m$ increases with increasing Q-dye concentration.

<table>
<thead>
<tr>
<th>Properties</th>
<th>PI0800</th>
<th>1Q5</th>
<th>1Q10</th>
<th>1Q50</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_m^\beta$ (°C)</td>
<td>-</td>
<td>158.4</td>
<td>156.43</td>
<td>153.9</td>
</tr>
<tr>
<td>$T_m^\alpha$ (°C)</td>
<td>170.06</td>
<td>170.81</td>
<td>170.88</td>
<td>170.41</td>
</tr>
<tr>
<td>$A_m$ (cal/g)</td>
<td>11.1</td>
<td>12.13</td>
<td>15.11</td>
<td>15.85</td>
</tr>
<tr>
<td>$T_c$ (°C)</td>
<td>125.77</td>
<td>127.81</td>
<td>132.12</td>
<td>133.33</td>
</tr>
<tr>
<td>$T_m$ (°C)</td>
<td>114.6</td>
<td>123.4</td>
<td>128.2</td>
<td>129.5</td>
</tr>
<tr>
<td>$S_i$</td>
<td>1.7</td>
<td>3.3</td>
<td>4.8</td>
<td>7.2</td>
</tr>
<tr>
<td>$A_f$ (cal/g)</td>
<td>12.69</td>
<td>13.72</td>
<td>17.72</td>
<td>18.32</td>
</tr>
<tr>
<td>$W_h$ (°C)</td>
<td>7.02</td>
<td>5.94</td>
<td>4.36</td>
<td>4.13</td>
</tr>
</tbody>
</table>

Table 2. Data obtained from DSC tests.

Figure 4. Area of XRD curves vs. Q-dye content.

Figure 5. Typical crystallization and melting thermograms of DSC.

Figure 6. Melting curves of sample.
(Table 2). Changing the melting behaviour by Q-dye can affect the thermoformability of PP. During the thermoforming process, when the processing temperature is between $T_{m}^{β}$ and $T_{m}^{α}$, β-crystals melt and the unmelted α-crystals reinforce the sheet against sagging, while the polymer sheet is softening enough to thermoform. Therefore, in the presence of β-crystals, PP can be thermoformed at lower temperatures.

Refer to Figure 7 and Table 2, $T_o$, $T_c$, $S_i$, $A_f$, increase and $W_h$ decreases by the addition of Q-dye content. In contrast to melting curves, crystallization curves show only a single exothermic peak. This observation implies that α- and β-structures crystallize simultaneously on the nucleating agent surface. Increasing of crystallization temperatures allow the β-nucleated PP to thermoform in a shorter cycle time, relative to the conventional PP. Due to increasing of $S_i$, nucleation and growth of crystals are faster and homogeneous therefore, the size of crystals is more uniform (narrower distribution of crystal size) and consequently $W_h$ decreases. Reduction in $W_h$ leads to a greater uniformity of heating and improves final thickness distribution in the thermoformed product. The increment in $A_m$ and $A_r$ indicates the higher degree of crystallinity.

Figures 8 and 9 illustrate the influence of Q-dye on the sag distance and sagging rate, respectively. It is clearly observed that by increasing the Q-dye content in samples, the amount and the rate of sagging reduce. It can be explained by considering the higher degree of crystallinity which promotes the modulus, stiffness, and the required softening heat. Therefore, sagging resistance of the polymer sheet is enhanced during thermoforming. Figure 10 shows the relation...
between the ultimate sag amount (after 10 min) and $A_\alpha$ (crystallinity), that confirms the aforesaid behaviour.

**CONCLUSION**

To improve thermoformability of PP, its crystalline structure was changed by adding a $\beta$-nucleator named Q-dye. Q-dye incorporated into PP by a laboratory corotating twin screw extruder. The DSC and sagging tests were carried out to predict thermoforming behaviour of samples. Q-dye at very low concentrations affects PP crystalline structure as a $\beta$-nucleator. The combination of $\beta$-form and $\alpha$-form crystals has a good effect on the thermoformability of PP. The PP sheet containing Q-dye, can be thermoformed at lower temperatures, shorter cycle times, wider processing window, and less sagging in comparison with the conventional PP.

**REFERENCES**

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