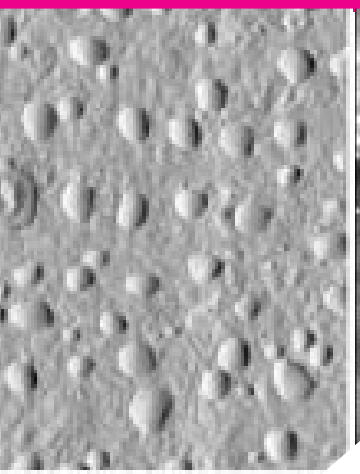

Thermal analysis of BOPP resins

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MORPHOLOGY development during processing of sheet is very critical for thermoforming and also during biaxial stretching of polypropylene films.

Lot of additives such as pigments, lubricants, nucleating agents, functional resins are added to achieve esthetic or functional properties in the final product. Such additives affect the processing parameters which need to be adjusted to get desired line speeds and productivity, especially in high speed BOPP lines.

Measurement of thermal properties by Differential Scanning Calorimeter (DSC) equipment gives important indications towards the changes that can be done for process optimisation. In plastics processing industry it is observed that every production line behaves in different manner to given batch of resin supplied by raw material manufacturer. Since raw material manufacturer is also running a complex process there are always variations arising due to minimum and maximum process tolerances. Such variations though within the specifications of ISO norms do pass on the variation to the processor.

It is necessary for the processor to understand the fundamentals of morphology that gets developed with the help of sophisticated instrumentations. Processors who are keen to develop new products due to reducing margins in commodity BOPP films, due to new large players coming in the field, have felt the need for understanding this science. These players are now investing in sophisticated instrumentation and in developing people who are able to interpret the data.

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Polypropylene

Polypropylene is a thermoplastic polymer of considerable commercial interest. There are two main products homopolymer of propylene and ethylene/propylene copolymers where propylene is a major constituent.

Commercially available isotatic polypropylene (iPP) is capable of crystallizing in three polymorphic forms.

α - Monoclinic form
β - Pseudohexagonal form
γ - Triclinic form.

α-form is the most common form and in the major part.

β-form occurs if

1) Crystallisation has occurred in temperature gradient, or

2) in presence of shearing forces

3) β-nucleators are present..

γ-form is observed in low molecular weight fractions have been crystallized at elevated processors or in degraded, low molecular wt PP.

Characteristics of α & β crystals

Crystal Form	Unit cell volume A^3	Melting Point °C	Density g/Co
α	905	160	0.936
β	3150	148	0.921

B- crystals have large cell volume. Such crystals have potential of causing web breakages on BOPP lines.

The present article aims to elaborate practical use of Differential Scanning Calorimetry in the day to day operations of plastics processing industry especially during manufacture of BOPP films. In order to explain the subject the data was taken from the cited reference. The original reference does not mention BOPP application but it is a scientific investigation on the performance of Milad 3988 in Polypropylene resin.

Individual BOPP manufacturers can however generate their own data based on the resins used by them and the films produced on their various lines. To understand behavior of one resin on different lines it is necessary to understand the morphology getting developed on the given line during the entire process from resin to cast film, film at the MDO and TDO stages and the final film. The additional knowledge of influence of various additives, hydrocarbon resins, organic and inorganic antiblocks will help if generated as in the present example.

This kind of knowledge if developed in house reinforces the confidence among the people which helps in reducing wastages

due to web breakages, winding, rewinding slitting issues as well as customer complaints and returns.

Thermal Analysis

Following are few experiments carried out using DSC on Polypropylene homopolymer with MFI 3.

For Isothermal tests:

1. Sample was loaded into the DSC at 30°C and heated at 40 K/min to 200°C and maintained at this temperature for 3 mins to erase thermal history.
2. The sample was then cooled at 100K/min to the required crystallisation temperature. On completion of crystallization sample was cooled to 30°C.
3. Heating scan at 10K/min was then run from 30°C to 200°C to obtain final sample enthalpy of fusion.

For non-Isothermal tests,

1. Sample was loaded at 30°C heated at 40K/min to 200 °C and held for 3 mins to erase thermal history.
2. Sample was then cooled at the required rate (1, 5, 10, 30 and 100K/min) to 30°C.
3. Heating scan was then carried out at 10K/min from 30°C to 200°C to obtain enthalpy of fusion.

DSC Measurements - Un-nucleated PP homopolymer

Figure 1 shows heating thermograms of isothermally crystallized unnucleated iPP (Fina 4060S).

For sample crystallized below 135°C
The first peak at 148 - 155°C corresponds to β crystals
The second peak at 163 - 167°C corresponds to α-crystals.

For samples crystallized at 140°C
A double peak is observed
The first peak occurring at 163°C and
The second peak is occurring at 171°C

Both these peaks correspond to α-Crystals and second peak being due to melting of crystals generated by recrystallisation during scan.

DSC measurement
- Nucleated PP (proprietory)
- Nucleated PP using Milad 3988

Figure 2 show heating thermograms of Fina 4042S which has proprietary nucleating agent and of iPP with 5000 ppm of Milad 3988.

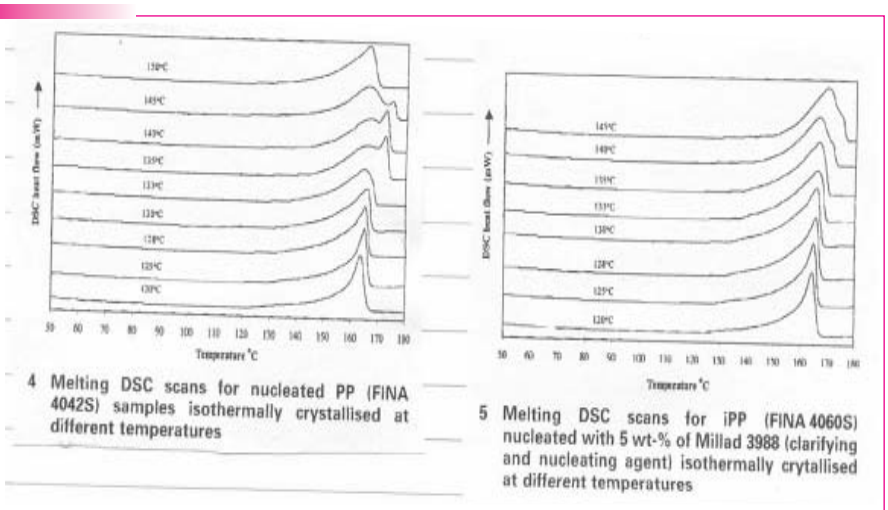
In Fina 4042S and with Milad 3988 there is no evidence of β Crystals.

Co-relation with Thermoforming process:

Shift in the peak upto 175°C helps in PP Thermoforming processing.

Co-relation with BOPP Process

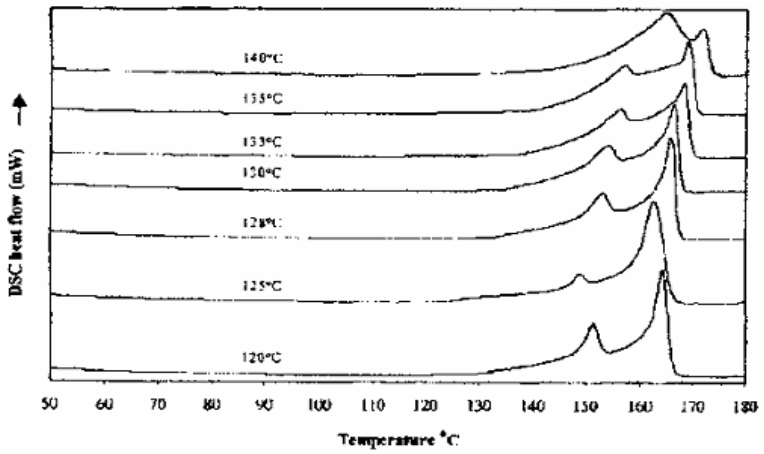
Shift in peak indicates that stretching TDO should be done at higher temperature. This is further reinforced by enthalpy of fusion.



4 Melting DSC scans for nucleated PP (FINA 4042S) samples isothermally crystallised at different temperatures

5 Melting DSC scans for iPP (FINA 4060S) nucleated with 5 wt-% of Millad 3988 (clarifying and nucleating agent) isothermally crytallised at different temperatures

Fig.2



2 DSC melting scans for un-nucleated iPP (FINA 4060S) samples isothermally crystallised at different temperatures

Fig. 1

Enthalpy of Fusion at Cooling rate 5 K/min

Polymer	TC OC	ΔH J/g
1) Fina 4060S (unnucleated)	112	85.5
2) Fina 40425 (nucleated)	125.3	90.3
3) Fina 4060 with Milad 3988	128.5	92.0

Enthalpy of Fusion at Cooling rate 100 K/min

Polymer	TC OC	▲H J/g
1) Fina 4060S (unnucleated)	80.2	80.5
2) Fina 40425 (nucleated)	101.9	84.7
3) Fina 4060 with Milad 3988	106.9	85.6

Higher melting point and higher enthalpy helps in reducing the sag in thermoforming.

Higher melting point and higher enthalpy requires higher TDO temperatures in BOPP processing.

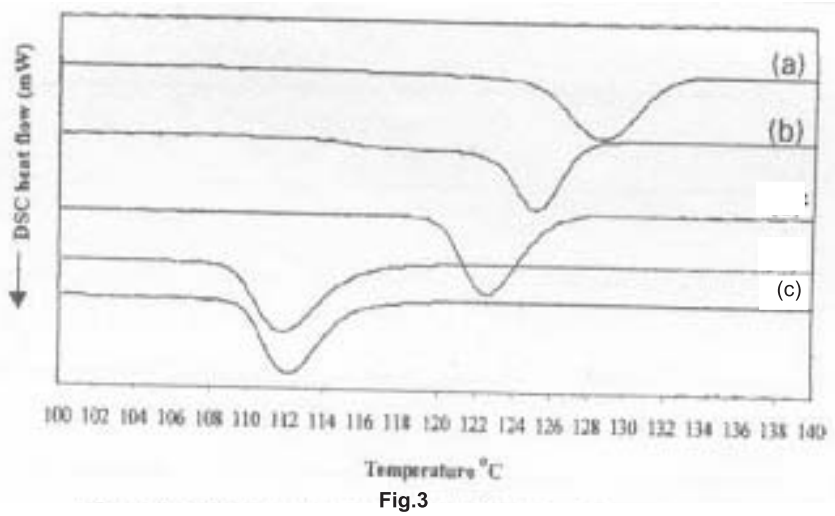


Fig.3

a 5wt-% nucleating agent; b FINA 4042S; e. FINA 4060S

DSC cooling thermograms for un-nucleated and pigmented PP cooled at 5 k min

DSC cooling thermograms

Cooling thermograms at 1K/min were done.

Sample a - 5000 ppm of Milad 3988 in Fina 4060S

Sample b - Fina 4042S - nucleated PP

Sample e - Fina 4060 S - unnucleated PP

Cooling thermographs indicate that nucleated PP crystallizes at high temperature hence,

1) Nucleated PP can be ejected at higher temperature from Injection moulding. Thus improving the productivity.
2) Nucleated PP similarly will improve productivity during thermoforming process as cycle time would reduce in both the processes.

For BOPP process cooling thermograms relate to MDO processing. The MDO temperature (roller stack) and speed of the film need change to eliminate shtretching marks & srinkage.

DSC measurements thus help the processor to understand the processing behaviour and morphology development with respect to the operating production line.

Additives added to neat polymers change crystallization behaviour. DSC experiments need to be carried out on neat as well as mixture of additives to understand their behaviour.

Compared to thermoforming, BOPP process is more complex due to

1) MDO & TDO stretching
2) Higher requirement of additives.

Therefore, very careful study needs to be done in understanding the combination materials and its impact on BOPP processing.

Measurement by DSC equipment and DSC equipment itself is a valuable tool in the hands of production & technical teams.

It is a valuable tool in the hands of R & D personnel for developing new products as well as investigating customer complaints.

References

Effect of nucleating agents and pigments on crystallization, morphology and mechanical properties of polypropylene by Y.Mubarak, P.J. Martin and E.Harkin Jones
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