

MICROPOROUS POLYPROPYLENE FILMS FOR TAPE AND LABEL APPLICATIONS

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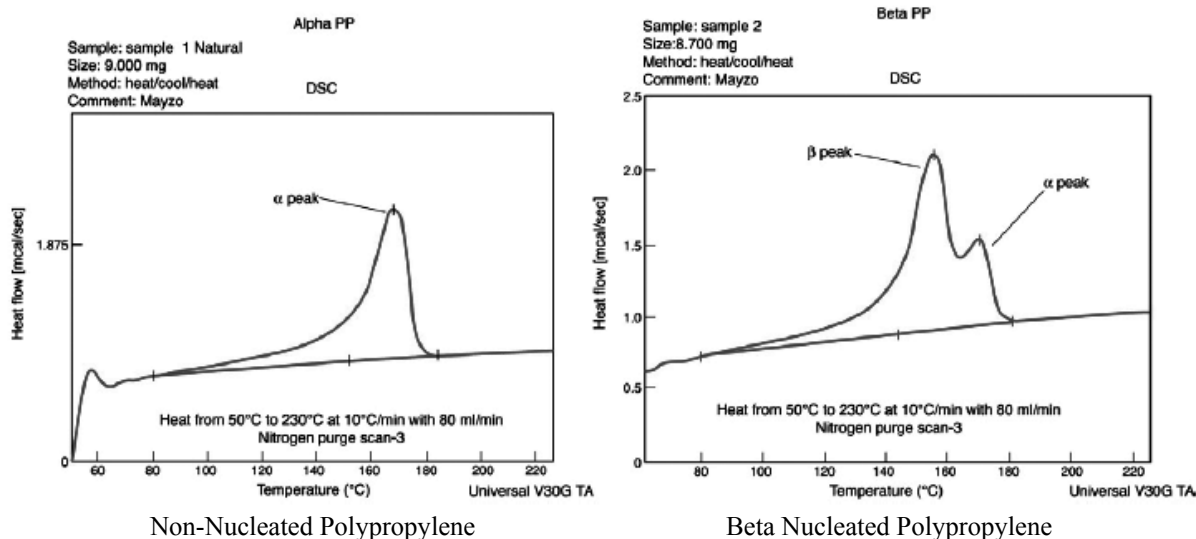
Abstract

We have developed a unique masterbatch that can be used to produce extruded polypropylene sheet containing high levels of beta phase crystallinity. When this sheet is stretched either uniaxially or biaxially to produce MOPP or BOPP film, the sheet undergoes extensive microvoiding resulting in a white/opaque appearance, a significantly reduced density, and improved printability. Under certain circumstances it is possible to produce a microvoided film that has very high moisture vapor transmission rates, so that the film is “breathable” while also being waterproof.

These microvoided films are less expensive to produce than conventional white films since the density reduction yields more square yards of film per pound of resin used, and the level of TiO₂ pigment that is required is drastically reduced. Application areas for these films include tape, labels, synthetic paper, and protective clothing.

Introduction

Polypropylene is a polymorphic semi-crystalline polymer which can crystallize in more than one crystal form. The most common crystal form of polypropylene is the alpha, or monoclinic form, which melts at about 160 °C for Zeigler-Natta polymerized homopolymer. In an injection molded or extruded part over 95% of the crystals are typically of the alpha type. A less common form, known as the beta or hexagonal crystal form, generally comprises less than 5% of the crystals. The beta crystals have a melting point that is typically 12-14 °C below that of the alpha form. If a PP sample contains both crystal forms, a double melting peak will often be seen if a DSC (differential scanning calorimetry) analysis is performed. An example of DSC melting thermograms for both non-nucleated and beta nucleated polypropylene are illustrated below in Figure 1.



Non-Nucleated Polypropylene

Beta Nucleated Polypropylene

Figure 1. Second Heat DSC Thermograms of Non-nucleated and Beta Nucleated PP

In addition to the melting point differences, the beta crystals produce other physical property changes, such as an improvement in impact strength and a lowering of the tensile strength. The improved impact strength is believed to partially come from the fact that when a large or rapid deformation event occurs, such as during impact, the beta crystals are transformed into alpha crystals while simultaneously developing microvoids. The lower tensile strength leads to higher breaking elongations, and the microvoid formation absorbs energy. If a film having a high level of beta crystals is stretched, it will generally turn an opaque white, since the microvoids scatter most of the light. This microvoiding can also result in a significant density reduction of the final film.

There are many nucleating agents that are used in polypropylene, and all of these provide sites where crystals can grow as the molten PP cools. These agents typically nucleate the alpha crystal phase, and their addition to PP causes the rate of crystallization to increase leading to faster cycle times, and higher levels of crystallinity in the final part. This higher crystallinity results in higher stiffness and strength characteristics. The presence of a nucleating agent also leads to a reduction in spherulite size, and this causes the clarity of the final part to improve.

There are only a handful of nucleating agents that preferentially nucleate the beta crystal phase [1]. Although there are many commercially available grades of alpha nucleated polypropylene, there are almost no commercially available beta nucleated PP grades. This situation has limited the number of commercial applications of beta nucleated polypropylene.

Experimental

Materials

The beta nucleant masterbatch, identified as MPM 1101, contains a proprietary mixture of a beta nucleating agent plus other additives, and was produced in a pellet form via melt compounding. The carrier resin in this masterbatch was a 12 MFR non-nucleated PP homopolymer resin. All of the beta nucleated films and molded parts described in this paper were prepared by blending this masterbatch with pellets of a non-nucleated PP resin using the masterbatch at a concentration of 2-3%. The PP resins used included homopolymer and impact copolymer, and all were made using Zeigler-Natta based catalyst systems.

Processing Conditions

The resins were extruded through a flat die to produce sheets ranging in thickness from 0.5 to 0.6 mm at melt temperatures of about 230 °C. The molten sheets were cooled by contacting a chrome polished roll that was part of a 3-roll stack, and the roll temperatures were in the range of 80 – 95 °C. The sheet was drawn in the machine direction by passing it over a series of heated rolls moving at different speeds. The draw ratio, as measured by the speed differential between the slow and fast rolls, was in the range of 5:1 to 6:1.

Characterization

The beta crystal content of the final part is dependent on both the concentration of the beta nucleant masterbatch used to produce the part, and the thermal and processing history used during fabrication. DSC testing is commonly used to assess beta nucleation, and a typical DSC melting curve for a beta nucleated and a non-nucleated PP resin are illustrated in Figure 1. Here the samples were first heated up

at 10 °C per minute to 230 °C to destroy any prior thermal history, and then cooled at a rate of 10 °C per minute. The curves illustrated in Figure 1 were obtained on the second heat scan. The beta nucleated material shows two melting peaks, as discussed earlier. The lower peak at 153 °C, which is due to the beta crystal phase, is the dominant peak, and the smaller peak at 166 °C is due to the melting of the alpha crystals. Although it is possible to measure the heats of fusion of the two melting peaks as a method of quantifying the amount of beta crystallinity, this tends to underestimate the beta content since after melting some of the polypropylene will recrystallize into the alpha form thereby contributing to the second melting peak for the alpha phase.

A more quantitative way of characterizing the beta content is to measure it directly on an extruded sheet or injection molded part using wide angle x-ray diffraction (WAXD). A typical WAXD scan of a sample containing both alpha and beta crystals is illustrated in Figure 2.

1D WAXD curve integrated from 2D pattern of PP-white

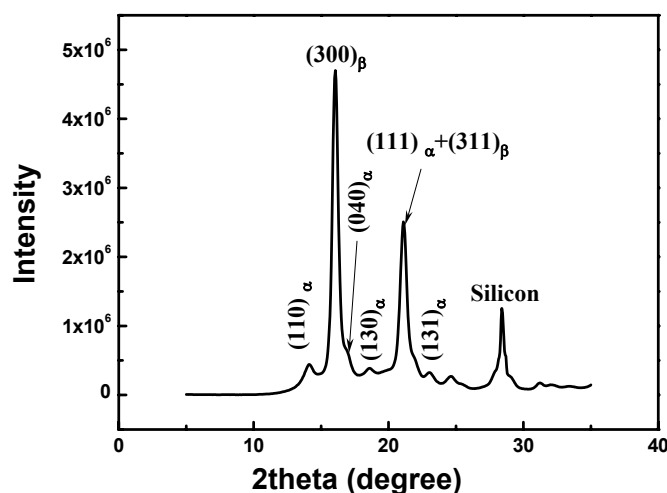


Figure 2. Wide Angle X-ray Diffraction Pattern for Extruded Beta Nucleated Sheet

The beta phase shows a particularly strong diffraction peak due to the (300) plane, while the alpha phase shows three strong peaks due to the (110), (130), and (040) planes. An empirical ratio of the intensity of these peaks known as the “K” value and defined [2] as follows is measured to define the beta content:

$$1. \quad K = I(300)_B / [I(300)_B + I(110)_\alpha + I(130)_\alpha + I(040)_\alpha]$$

Here K will vary from 0 for a sample with no beta crystals to 1.0 for a sample with only beta crystals. For most of the examples discussed in this paper, the K value for beta nucleated materials fell in the range of 0.8 – 0.9.

It should be noted that in the case of the oriented film, the WAXD measurements must be made on the extruded sheet before it has been oriented, since the orientation process converts the beta crystal to alpha crystals. This was done by using the edge trim from the extruded sheet for the x-ray measurements.

Physical Property Testing

The tensile properties of the films were measured in both the machine (MD) and transverse (TD) directions using an Instron tester according to ASTM D886. Density measurements were performed using either hydrostatic displacement or by measuring the dimensions of a piece of film, and then dividing the mass of the film by its volume.

Results and Discussions

MOPP Films Made from ICP

A series of monoaxially oriented films (MOPP) were produced from impact copolymer PP (ICP). The precursor sheets were cast onto a heated cast roll that was set at 90 °C. The beta nucleated sheets contained 2.5% of the BETAPP masterbatch. The starting sheet thickness was about 0.58 mm, and the final film thickness was in the range of 0.12 – 0.135 mm. The x-ray “K” values of the precursor sheets and the properties of the MOPP films are given in Table 1 below.

Table 1. Data on Monoaxially Oriented PP (MOPP) Films

Film ID	"K" Value	Stretch Temp (C)	Thickness (microns)	Density (g/cc)	Basis Wt. (g/sq.m.)	Load @ 5% Elong. (N/cm)	Tensile (N/cm)	Break Elong. (%)
2	0.05	135	124	0.88	108.7	105	352	35.7
1	0.87	135	129	0.83	108.1	134	423	29.7
6	0.88	125	134	0.81	109.6	145	422	24.7

We see from this table that films #1 and #6, which contained high levels of beta crystallinity, had lower densities and improved tensile properties relative to that of film #2. The elongation at break values for these two high beta content films were somewhat lower than that of film #2. Films 1 & 6 were also more opaque than that of film #2 due to the presence of the microvoids in the film.

MOPP Films Made HPP and ICP

In a second series of runs non-nucleated and beta nucleated MOPP films were produced using both an ICP and a homopolymer PP (HPP) resin. The beta nucleated versions of these films also contained the MPM 1101 masterbatch at a few different levels, and the cast roll temperature was set at about 90 °C. The sheet thickness was about 0.50 mm, and the final film thickness was about 0.080 mm.

The films containing the beta nucleant were more opaque in appearance than the non-nucleated films, as illustrated by the following figure illustrating the two ICP film samples.



Figure 3. Appearance of Non-nucleated and Beta-nucleated ICP Films

In Figure 3 each of the films has been placed over two business cards, with the upper card being in direct contact with the film and the lower card positioned about 2 cm below the plane of the film, in order to illustrate the contact and see-through clarity of the two films. The relative opacity data for impact copolymer and homopolymer (HPP) films are illustrated in Figure 4.

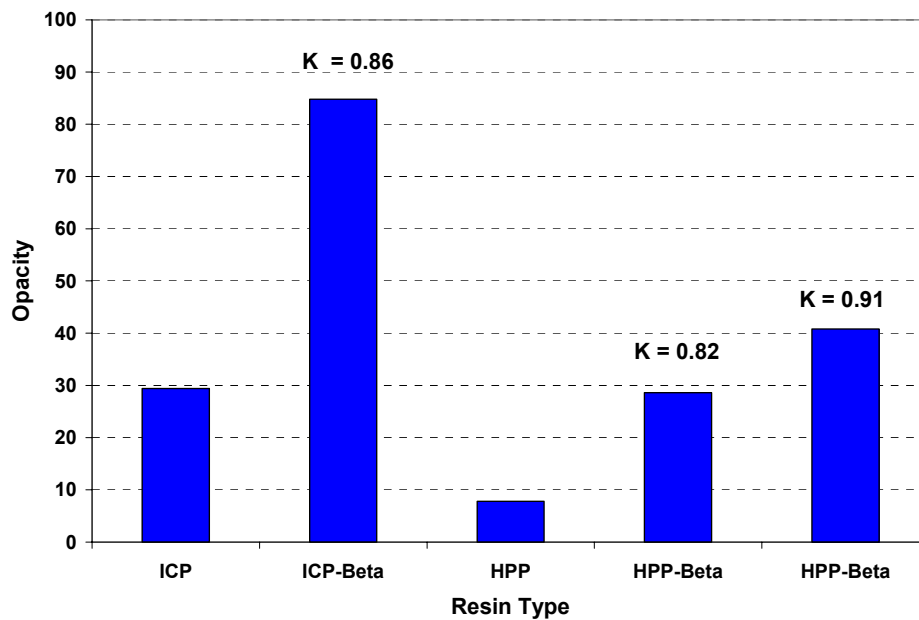


Figure 4. Relative Opacity of MOPP Films

From these figures we see that the opacity of the beta nucleated ICP film was much greater than that of the non-nucleated ICP film, and the opacity of both the ICP and HPP films increased with increasing beta crystal content as measured by the x-ray K value. The ICP film also exhibited a greater increase in opacity following beta nucleation compared to that of the HPP film. The densities of the different film samples are illustrated in Figure 5, and we can see that the trend in film density correlates quite well with the trend seen in the opacity values.

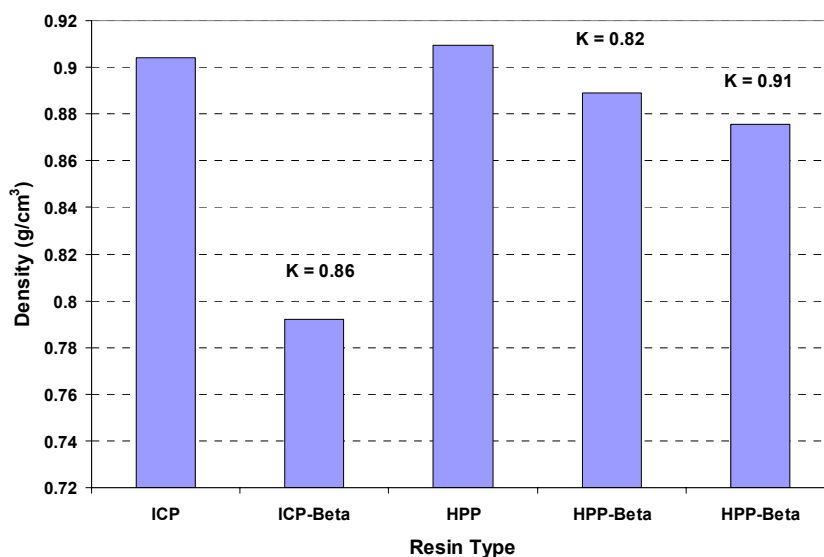


Figure 5. The Densities of Beta Nucleated MOPP Films

The ultimate tensile strength values of these films in the machine direction (MD) are illustrated in Figure 6. None of these samples showed any evidence of a yield point, and the maximum tensile strength occurred at break. Here we see a decrease in tensile strength with increased beta crystallinity for each resin type. The break elongations in the MD exhibit a similar trend with beta crystal content, as illustrated in Figure 7.

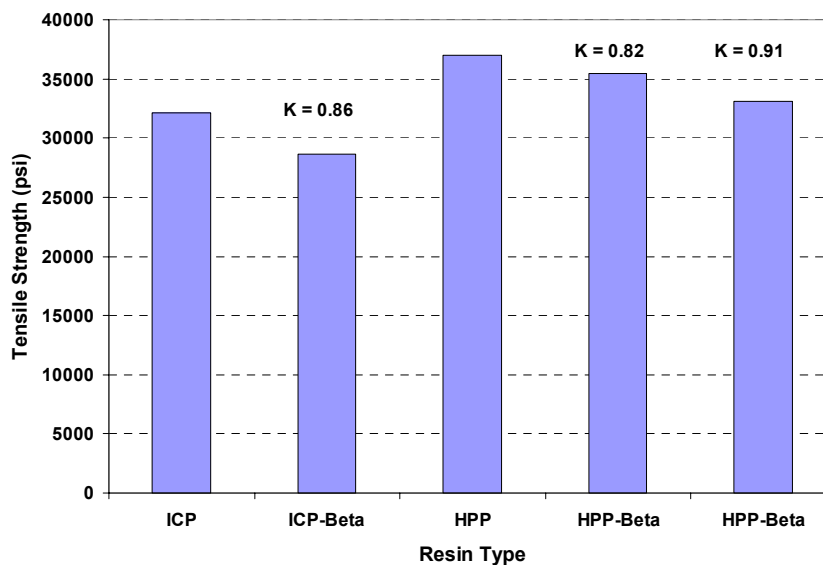


Figure 6. Tensile Strength of MOPP Films in the Machine Direction

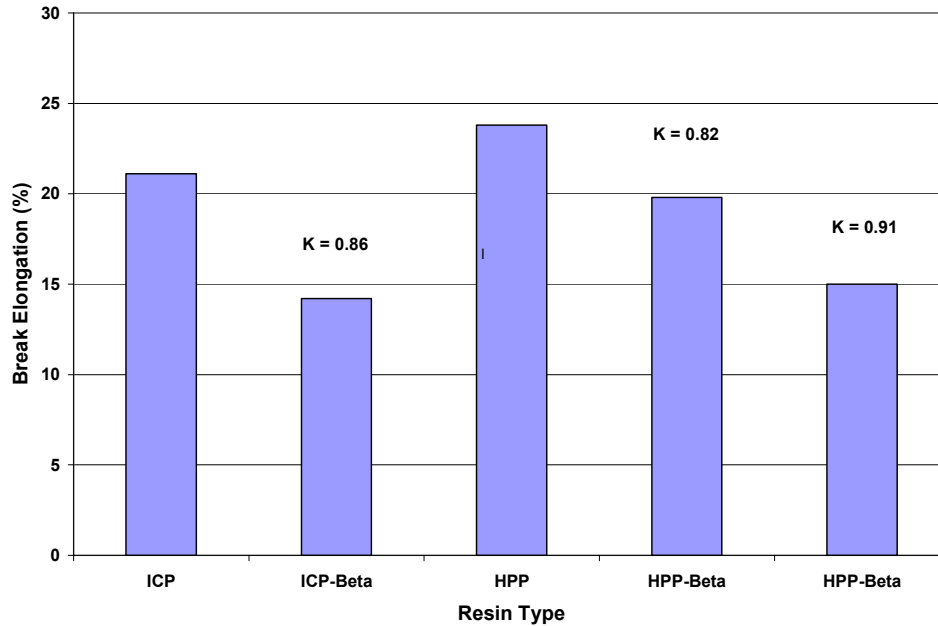


Figure 7. Break Elongations of MOPP Films in the Machine Direction

Breathable Films

About 14 years ago this author invented [3] a beta nucleated PP film product that developed a very high level of microvoiding when it was biaxially stretched on a BOPP line (biaxially oriented PP film). By incorporating certain other components in the formulation, we were able to produce an open-celled structure, where the microvoids interconnected with one another. This film had the unique property of having very high levels of vapor transmission (i.e. it was “breathable”), while still repelling liquid water. The breathable/waterproof nature of the film allows it to be used in protective clothing, where the wearer’s comfort is increased due to evaporation of perspiration, while liquids are kept out. In addition to blocking liquids, this microporous film also blocks microorganisms (it passes ASTM F1670 – Blood Borne Pathogen & ASTM F1671 – Viral Penetration), which allows it to be used in medical protective gowns and drapes. This breathable film is also used in house wrap, roofing membranes, and other protective clothing products.

Summary and Conclusions

We have shown that opaque/microvoided films can be produced by adding a unique masterbatch containing a beta nucleating agent to a non-nucleated polypropylene resin, and then stretching an extruded sheet of that resin below the melting point of the beta crystalline phase. When the extruded sheet is made from an impact copolymer resin, the degree of opacity and density reduction is much greater than when the base resin is a polypropylene homopolymer. The degree of opacity and density reduction also increases at higher levels of beta crystal content. The reduction in film density and the ability to produce a white film without the use of white pigment permits a reduction in both raw materials and cost. Breathable, waterproof films can also be produced using beta nucleation technology. The new Mayzo beta nucleant masterbatch permits the film producer to beta nucleate a conventional non-nucleated PP resin at the extruder hopper in order to achieve these benefits and the associated cost savings.

References

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