LASER PRINTING OF MICROPOROUS PP FILMS PRODUCED VIA BETA NUCLEATION

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Phil Jacoby received a Ph.D. in Physical Chemistry from the University of Wisconsin in Madison, Wisconsin. Prior to joining Mayzo as Vice President of Technology in 2002, Dr. Jacoby was a Senior Research Associate with Amoco and BP-Amoco in the Polypropylene Product Development group. Dr. Jacoby holds 13 US patents and several international patents covering various polypropylene products, with particular emphasis on modifying the crystal structure of polypropylene. At Mayzo Dr. Jacoby created a new business based on the use of Beta Nucleation Technology in Polypropylene. The beta nucleant mastebatches that Mayzo offers are currently being used in the production of microporous oriented PP films, thermoformed PP parts, and various other extruded and injection molded applications. Dr. Jacoby is a past president of the Southern Section of the Society of Plastics Engineers (SPE), and a former board member of the Thermoforming Division of the SPE.

NEW DEVELOPMENTS IN BETA NUCLEATION OF POLYPROPYLENE AND LASER PRINTING OF MICROPOROUS FILMS

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Abstract:

Beta nucleation can be used to produce microporous polypropylene films for use in tapes and labels. In earlier work [1], we have shown that this technology allows one to make a white, low density PP film without the use of pigments or fillers. We have recently developed a new generation beta nucleant masterbatch that produces higher levels of beta crystallinity in extruded PP sheet, leading to higher microvoid content in the final oriented film. The extremely high activity of this new masterbatch allows it to be used at lower addition levels, and also allows it to work with PP resins that contain additives and pigments that would normally interfere with the production of beta crystals.

We have also developed a laser printing technology that takes advantage of the fact that the white microporous beta nucleated films contain no pigments or fillers. A CO_2 laser can be used to print clear transparent text or patterns on the white film background by locally melting the PP causing the voids to collapse. If a dark colored adhesive or dark film layer is applied to one side of the microporous film, the clear windows produced by the laser show through as dark print or patterns on the top side of the film. This print does not require any inks, solvents or corona treatment of the film, and is very cost-effective and durable. Examples of this technology will be illustrated in this paper.

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^{o}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^{o}C below that of the alpha form. If a PP sample contains both crystal forms, a double melting peak will often be seen when a DSC (differential scanning calorimetry) analysis is performed. An example of 2nd heat DSC melting thermograms for both non-nucleated and beta nucleated polypropylene are illustrated below in Figure 1.

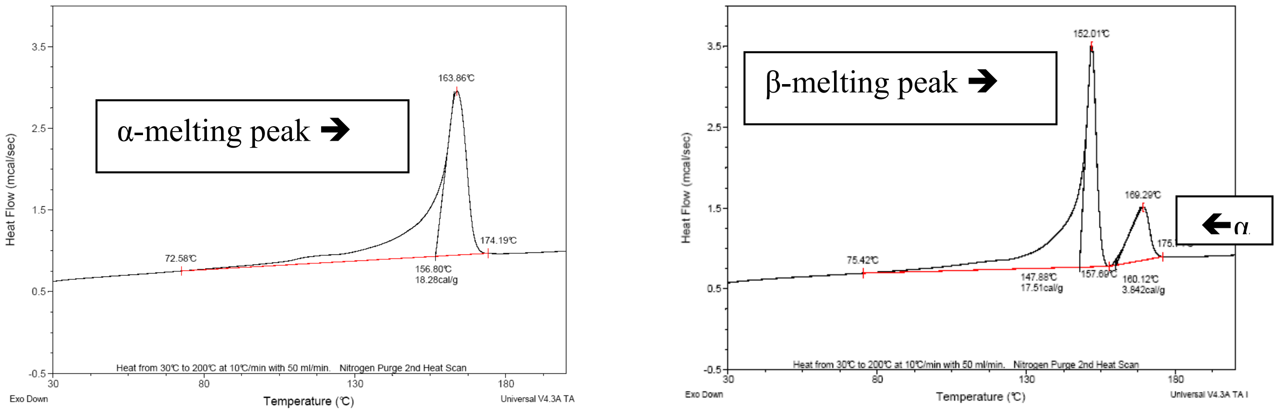


Figure 1. Second Heat DSC Scans of Non-nucleated and Beta Nucleated PP

One unique characteristic of an extruded sheet that contains beta crystals is the behavior of these crystals when the sheet is stretched below the melting point of the beta crystal phase [3]. As soon as the sheet is stretched past the yield point, the beta crystals transform into alpha crystals, and sub-micron sized voids (microvoids) simultaneously appear in the sheet. This crystal transformation occurs without melting, and the sheet immediately becomes white in appearance due to the light scattering caused by these microvoids. The microvoiding effect is believed to arise from the fact that the pure alpha and beta crystal phases have different densities (0.943 g/cm3 for the alpha crystals and 0.92 g/cm3 for the beta crystals). Since the crystal density goes up when beta crystals transform into alpha crystals, the volume occupied by these crystals must decrease, leading to the formation of the voids. The total void volume produced and the subsequent density reduction of the final oriented film depend on several factors, including the concentration of beta crystals in the sheet, the temperature at which the stretching takes place, and whether the stretching is monoaxial or biaxial. Monoaxial stretching that is used to produce MOPP film will typically lead to density reductions in the range of 10 – 20%. Biaxial stretching can produce density reductions as high as 70% where the resulting film is highly breathable.

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 [2]. 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 various samples discussed in this paper were produced on a variety of commercial and lab-scale extrusion, thermoforming and oriented film equipment. In all cases, the beta nucleant was added in the form of a masterbatch to a non-nucleated polypropylene resin at the hopper of the sheet extruder. The masterbatches used consisted of proprietary beta nucleating agents in a polypropylene carrier resin. The 3rd generation masterbatch, known as MPM 2000, contains the most active nucleant and it produces very high levels of beta crystallinity in the extruded sheet, as well as the highest crystallization temperatures (Tc). MPM 2000 can also be used at very low addition levels.

For thermoforming, the extruded sheets were cooled using a 3-roll stack containing polished rolls that were heated using circulating water. The temperature of the middle roll, where the sheet solidified, was in the range of 80 – 95 ^{o}C, since high crystallization temperatures are required in order to produce high levels of beta crystallinity in the sheet.

In the case or oriented film production, the extruded sheet was cooled using a heated chill roll whose temperature was in the range of 90 – 120^{o}C. The machine direction stretching (MDO) was done at temperatures in the range of 80 – 110^{o}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, Testing, and Laser Printing:
A portion of the extruded sheet was run in the DSC to assess the level of beta crystallinity in the extruded sheet, and the degree of nucleation. The 1st heat scan showed the melting of both the beta and alpha crystals in the sheet, and the relative area under these endothermic peaks (heats of fusion) can be used as a rough guide of the degree of beta and alpha crystallinity. During the cool-down scan, the peak crystallization temperature, Tc, is a measure of the nucleation activity, with higher Tc values reflecting more rapid crystallization. The 2nd heat scans show the melting of the two crystal phases produced during the cool-down scan, and the relative size of the beta melting peak is also an indication of the beta nucleation activity of the nucleant. All heating and cooling scans were done at a rate of 10^{o}C per minute.

The laser printing was done using a 10 watt CO_2 laser (model CO10) from Telesis Corporation. The film was exposed to the laser for times on the order of 0.5 seconds.

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

Thermoforming Examples
Before discussing the film work it is instructive to see the effect of microvoiding that is produced when an extruded polypropylene sheet is thermoformed. In the thermoforming process a flat sheet is extruded onto a 3-roll cooling stack and then conveyed into a reheat oven and a forming station. A schematic diagram of the thermoforming process is illustrated in Figure 2.

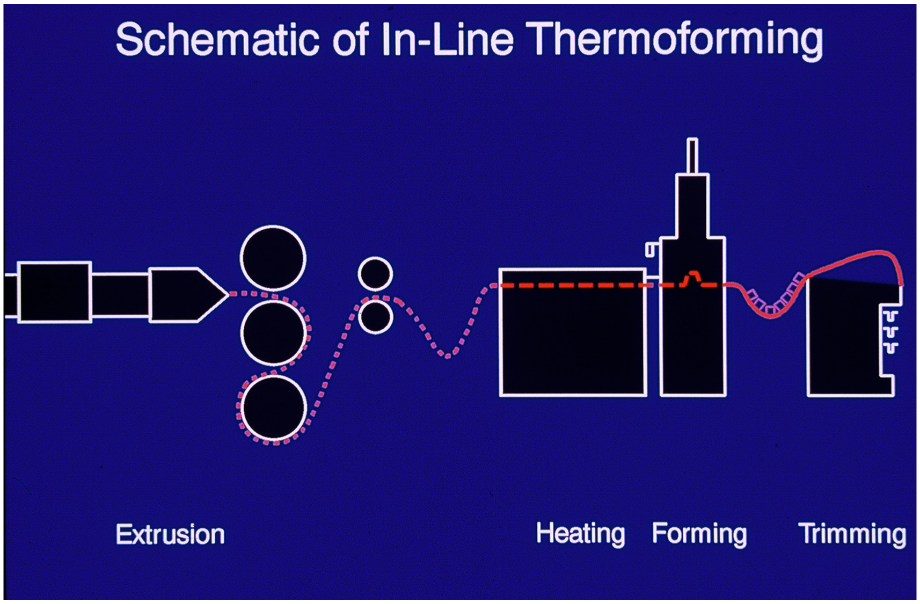


Figure 2. Schematic of the Thermoforming Process

Normally the extruded sheet coming off of the cooling rolls is re-heated to a temperature that is very close to the melting point of the PP, which would typically be in the vicinity of 160^{o}C. At this point the sheet is soft enough for forming to take place under the influence of air pressure, plug assist and vacuum. If the sheet temperature is so high that all of the crystals melt, then unacceptable sagging of the sheet can occur since the polypropylene has poor melt strength. If the sheet is too cold then it may be too stiff to properly reproduce the mold detail required in the final part. Generally this thermoforming window is quite narrow, and may be only a few degrees.

When beta nucleation is used, the forming window is much broader due to the presence of the two different crystal phases, and this processing window can often range from about 146^{o}C to 160^{o}C. It is actually quite easy to thermoform beta nucleated PP in the solid state, since the beta crystals are more ductile than the alpha crystals, and less force is required during the forming step. By the appropriate choice of roll temperatures it is possible to produce an extruded sheet containing high levels of beta crystals. The 1st and 2nd DSC heat scans for an extruded PP sheet containing 0.8% of our 3rd generation beta masterbatch (MPM 2000) is illustrated in Figure 3.

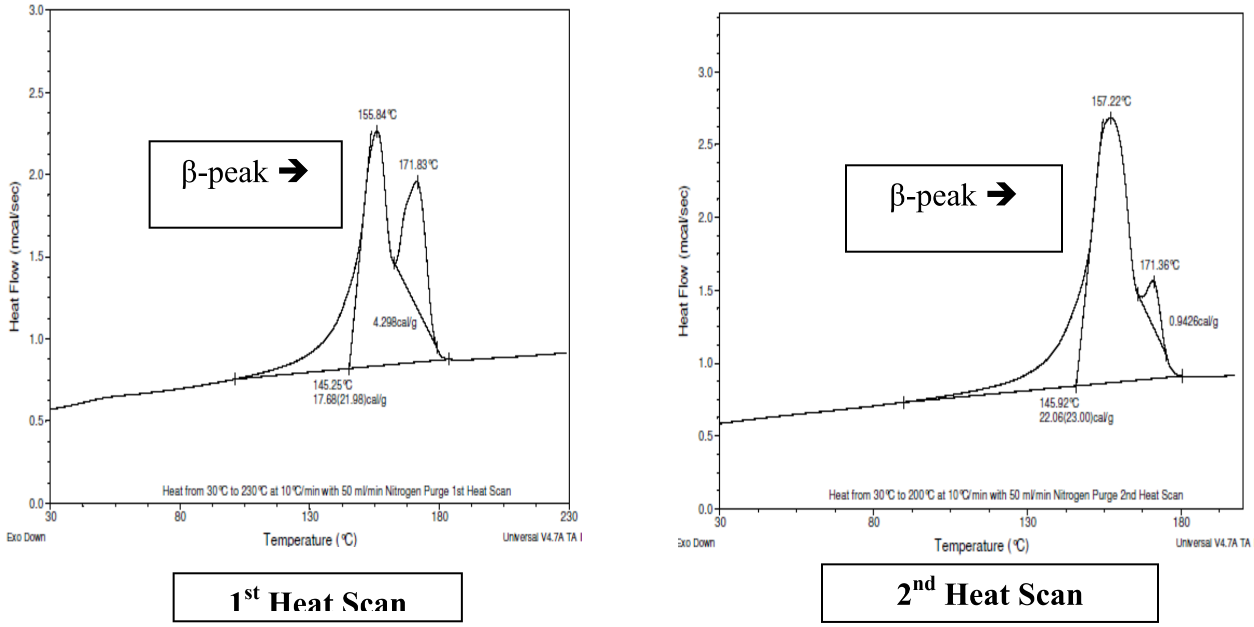


Figure 3. 1st and 2nd DSC Heating Scan for Beta Nucleated PP Sheet

The relative size of the beta and alpha melting peaks seen in the 1st heat scan reflect the actual morphology of the extruded sheet, and are sensitive to the roll temperatures used (hotter rolls give higher beta content). The 2nd heat scan reflects the morphology of the sample that cooled down in the DSC pan at a cooling rate of 10^{o}C/minute. This very slow cooling rate is very conducive to the formation of beta crystals, and this is the reason why such as large beta peak is seen in the 2nd heat scan.

The microvoiding that is produced during the forming step depends very strongly on the temperature of the sheet during the forming step. This is illustrated in Figure 4 which shows the appearance of non-nucleated and beta nucleated cups formed at different temperatures. Here our 1st generation beta masterbatch (MPM 1101) was used at a 2% addition level to beta nucleate the sheet.

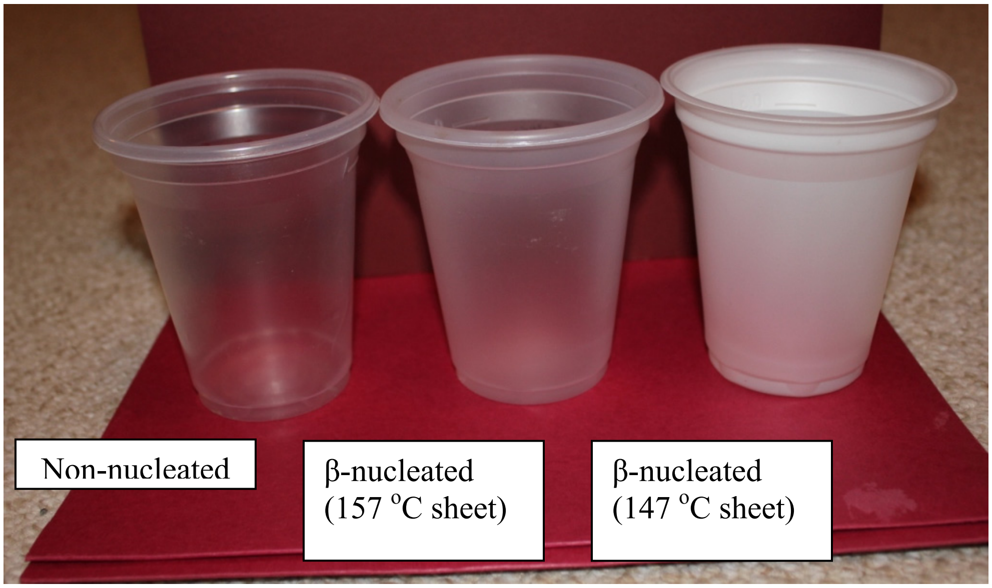


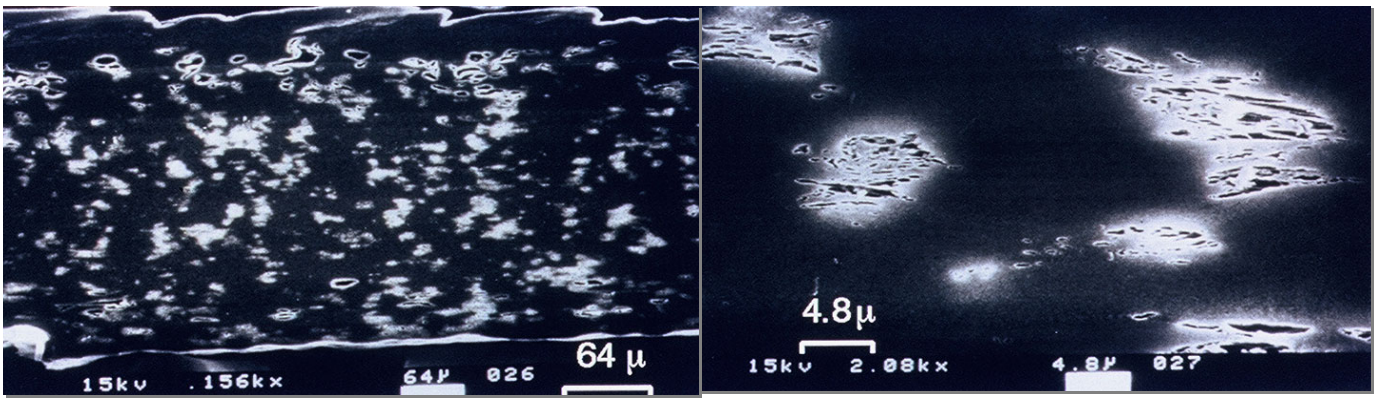
Figure 4. Non-Nucleated and Beta Nucleated PP Sheet Formed at Different Temperatures

It is quite clear from these figures that the colder sheet forms a white container due to the microvoiding effect. When the sheet temperature is above the melting point of the beta crystal phase (157°C) no microvoids are produced, and the cup is translucent rather than white. The extreme nature of this whitening is even more evident in Figure 5, which illustrates the appearance of a cup produced from a beta nucleated sheet containing only 0.65% of the MPM 2000, which is a much more powerful beta nucleating masterbatch as compared to the MPM 1101.

Figure 5. Thermoformed PP Cups Made With and Without Beta Nucleation (0.65% MPM 2000)

The degree of whitening produced here is very close to what one would get by adding 2% TiO_2 pigment. No pigment was used to make the white cup shown in Figure 5.

An illustration of the appearance of the actual microvoids seen in the cross section of a microvoided PP cup is shown in Figure 6.



Low Magnification **High Magnification**

Figure 6. SEM Micrographs of Cross Section of Thermoformed PP Cup with Microvoids

The clusters of microvoids are 5-10 microns in size, but the actual microvoids are <1 micron in size. Since the clusters of microvoids are isolated from one another, the thermoformed cup is not breathable. This is also true of MOPP microvoided films made using beta nucleation.

Oriented Film Samples:
In order to produce microporous oriented films a beta nucleated sheet is extruded onto a heated roll. In the film process a cast roll is generally used rather than a 3-roll stack, but similar roll temperatures must be used in order to produce high levels of beta crystallinity in the extruded sheet.

An example of microvoided MOPP films is shown in Figure 7, where non-nucleated and beta nucleated films are compared.

Figure 7. Appearance of Non-nucleated and Beta-nucleated ICP Films

Here the density of the white film was about 12% lower than that of the control film on the left.

Laser Printing of Films:

If the white microvoided product is heated to temperature close to or above the melting point of the PP (> 165^{o}C) then the voids will collapse, and the melted region will turn clear and remain clear when the molten PP solidifies. This effect allows one to create clear patterns on a white background by using a laser to melt portions of the microporous film or thermoformed cup. On a traditional white pigmented film or thermoformed cup the pigment will always be present, so producing clear windows in this manner is not possible. The appearance of a back-lit microporous PP film is illustrated in Figure 8.

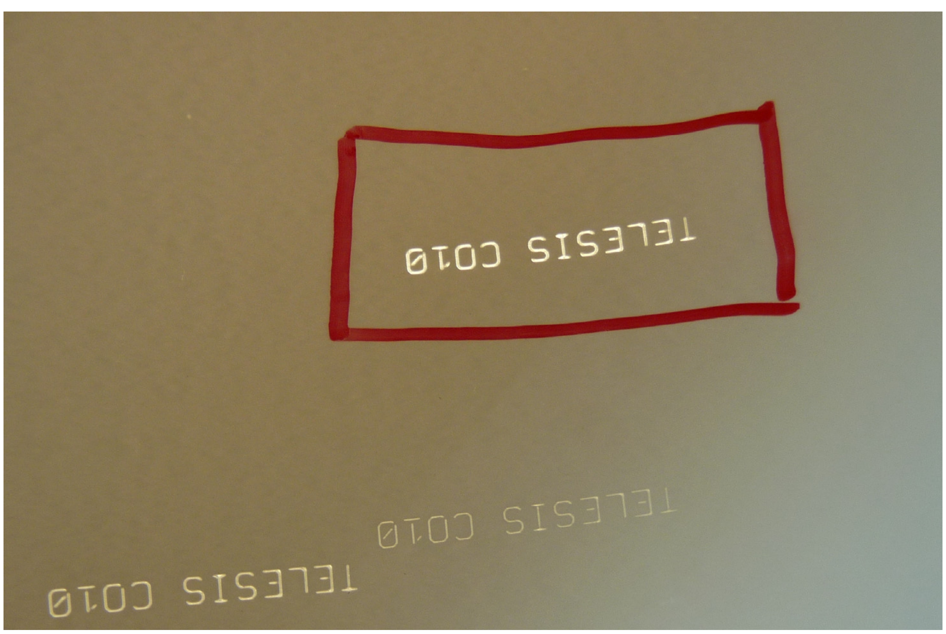
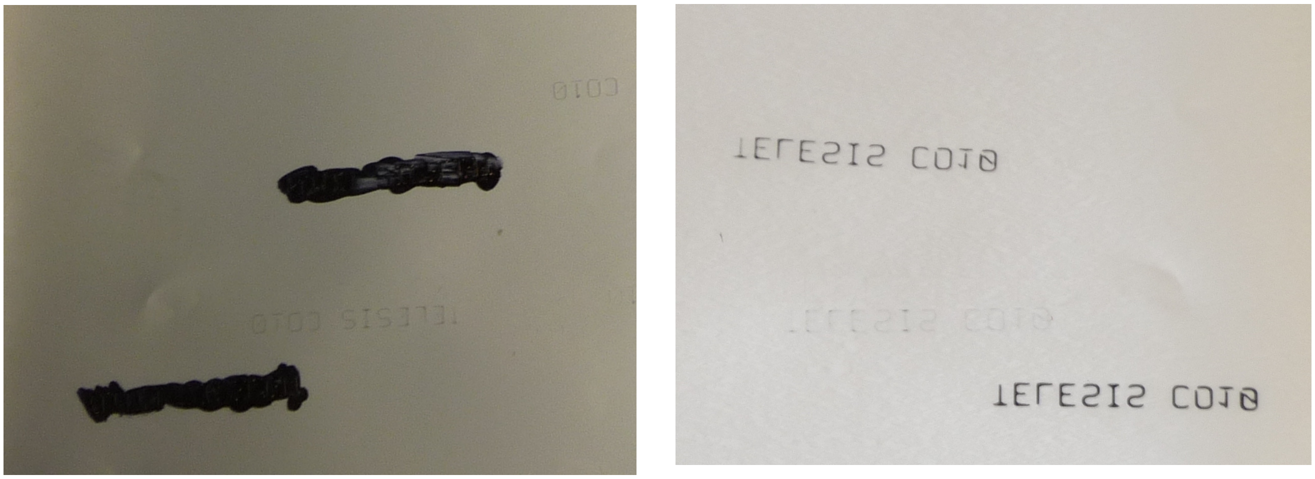


Figure 8. Back-lit Microporous MOPP Film Subjected to CO2 Laser for Various Times

If a dark colored adhesive or dark co-extruded film is applied to one side of this laser treated film, the color of this substrate will show through this clear window as illustrated in Figure 9.



Black Marker Applied to

Reverse Side of Laser etched and Marked Film

Figure 9. Laser-Etched Film with Black Marker Applied to One sSde of Film

The top side (un-marked) of the film shows very distinct black print on a white background. What is unique about this “laser printing” process is that no inks or solvents are needed. If this were a label film, an adhesive containing a dark pigment could be incorporated into the adhesive in order to produce this print-like effect.

This effect can also be used to print on thermoformed cups as illustrated in Figure 10 where one of the microvoided cups has been laser etched and then illuminated with back light. One could also use the color of the food product inside the container, such as tomato juice to produce the illusion of red print on a white background.

Figure 10. Laser-etching of a Microvoided Thermoformed PP Cup.

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. A very high degree of whiteness can be produced if our high activity, 3rd generation beta masterbatch is used to produce high levels of beta crystals in the precursor extruded sheet. Since the whiteness is only due to light scattering from the microvoids in the oriented film, a CO_2 laser can be used to etch clear patterns in a white background by heating the film to a temperature that causes the microvoids to collapse. By applying a dark colored adhesive or dark co-extruded film to one side of the microporous film, very sharp print-like detail can be produced on the opposite side of the film without the use of inks or solvents.

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