The Use of Beta Nucleation to Produce Breathable PP Film

Breathable Films 2018

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Outline

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  - Properties and Characteristics of Beta crystalline PP
- Commercial Applications of Beta Nucleated PP Films
  - Mono-oriented film (MOPP)
    - For Tape, label and carpet backing applications
  - Breathable Microporous films (BOPP)
    - For Protective Clothing & Roofing Membranes
    - For Lithium Ion Battery Separator membranes
- Unique Film Products Made Using Beta Nucleation
  - Laser printed films using no inks, or other consumable additives
  - “See through” breathable wound dressings
  - Controlled drug release implants
  - Modified Atmosphere Food Packaging
- Conclusions
- Contact Information

Properties & Characteristics of β-crystalline PP

- Polypropylene is a semi-crystalline polymer that has three different crystal forms (α, β, and γ)
- There are very few effective beta nucleating agents, and almost no commercial PP resins that are β-nucleated
- Beta nucleation can produce very unique PP products
- Mayzo has developed β-nucleant masterbatches that can be added to any non-nucleated PP resin to achieve the benefits of beta nucleation.

Differences Between Alpha and Beta Crystal Phases in PP

Alpha Phase

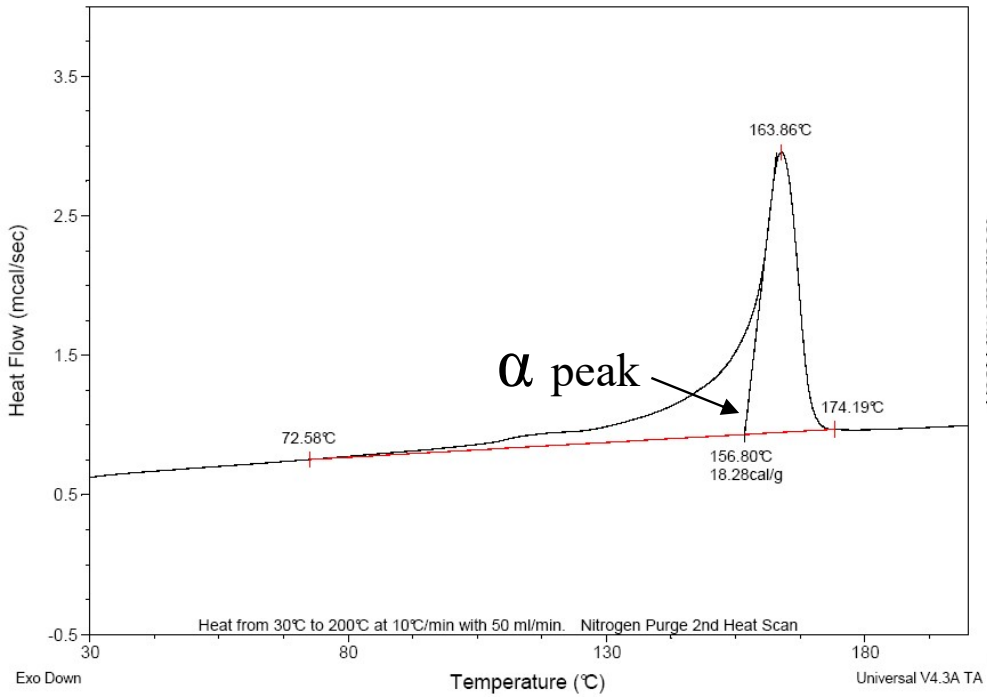
- Monoclinic crystal
- Melts at ~ 164 ^{o}C (HPP)
- Most common phase
- Many nucleants known

Beta Phase

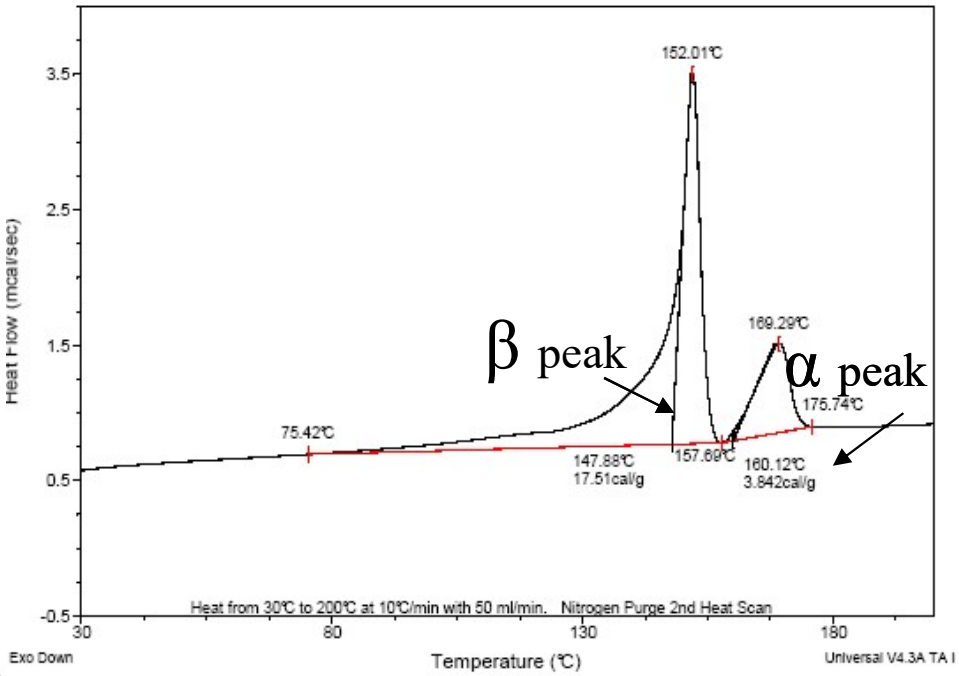
- Hexagonal crystal
- Melts at ~ 150 ^{o}C (HPP)
- Transforms to alpha phase on stretching
- Lower yield stress and different drawing behavior
- Microvoids if stretched in solid state
- Very few known nucleants

DSC Melting Curves for Alpha and Beta PP

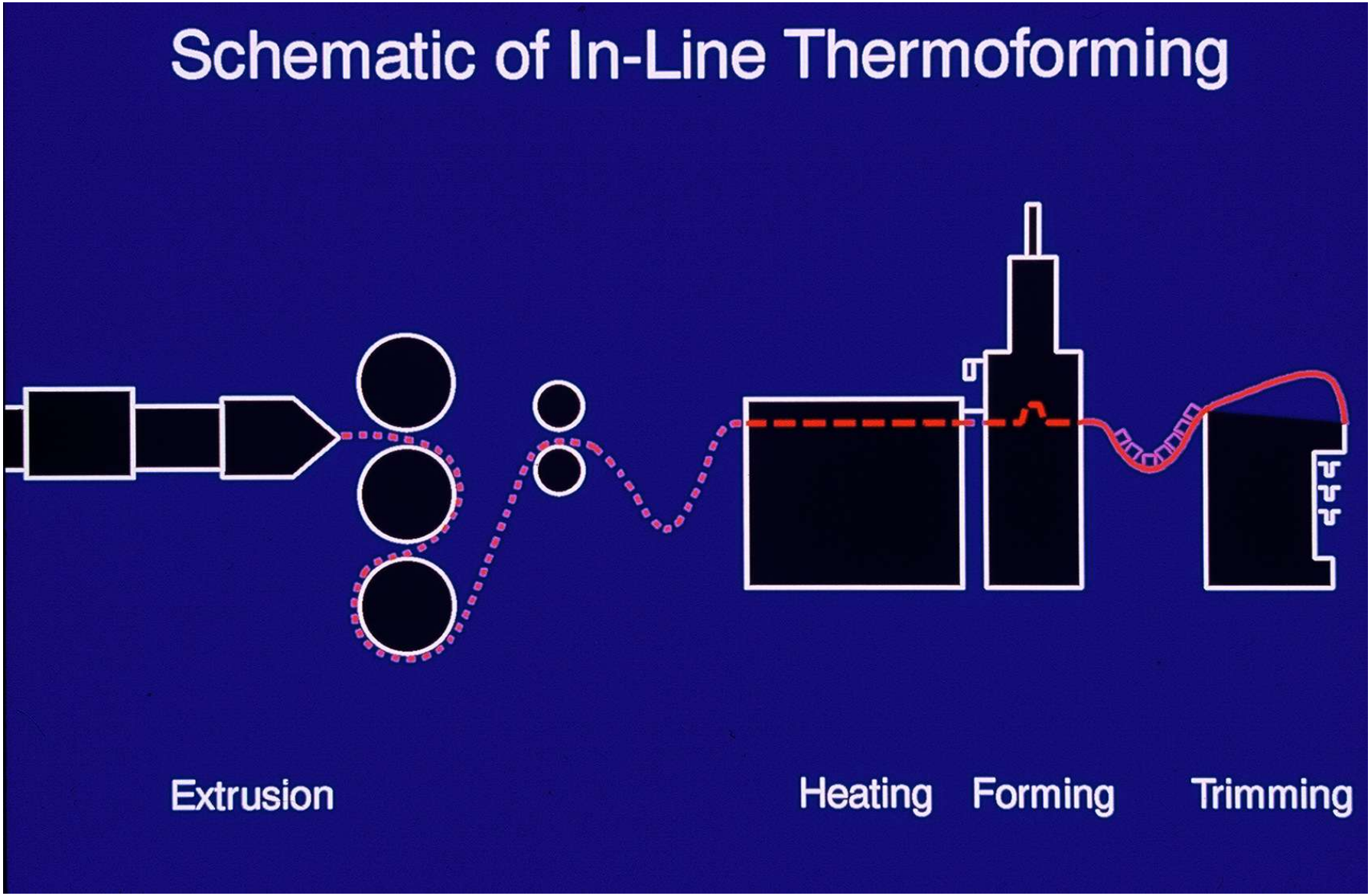
Alpha PP



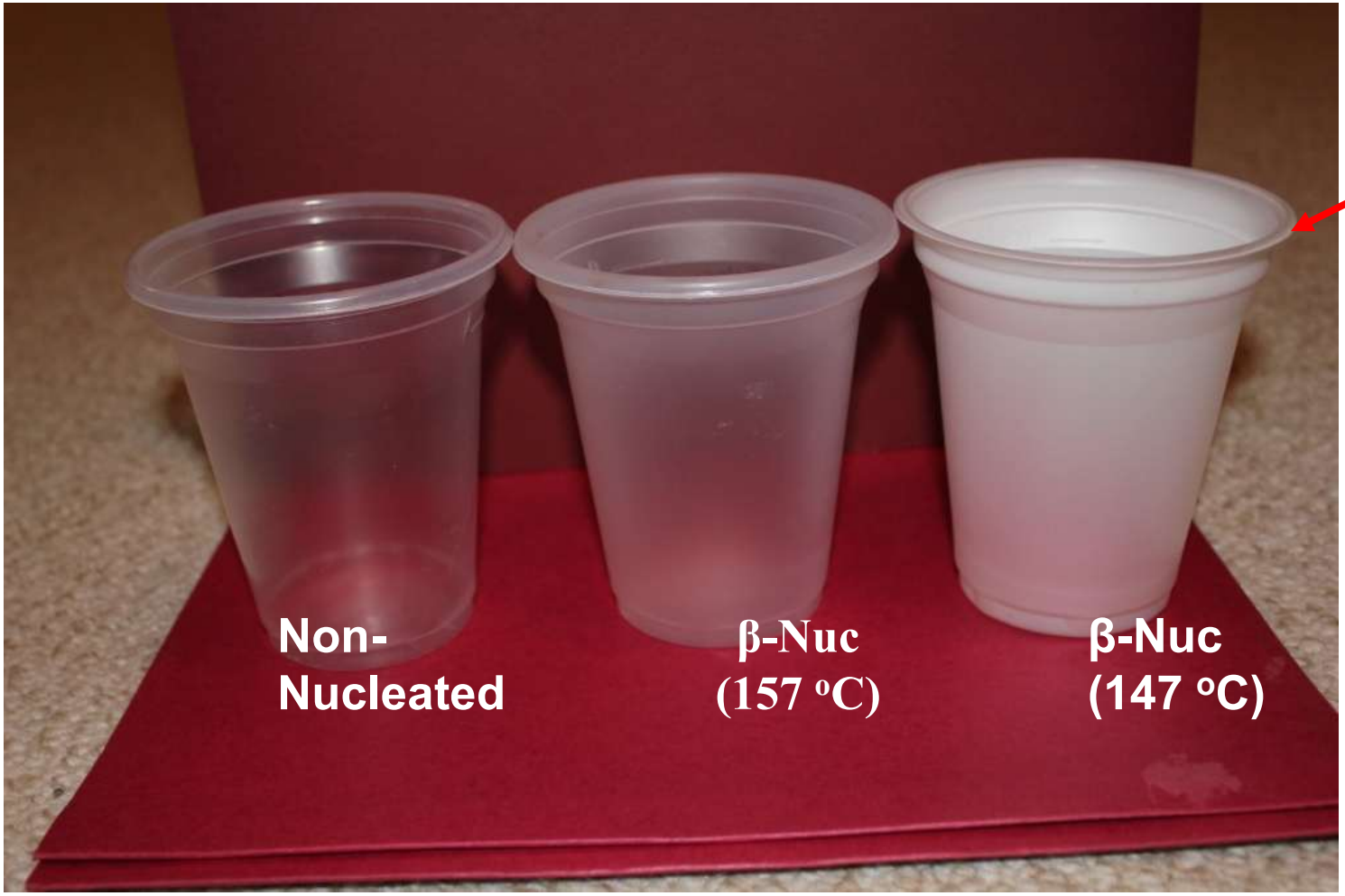
Beta PP



Microvoid Formation During the Thermoforming of β-Nucleated PP



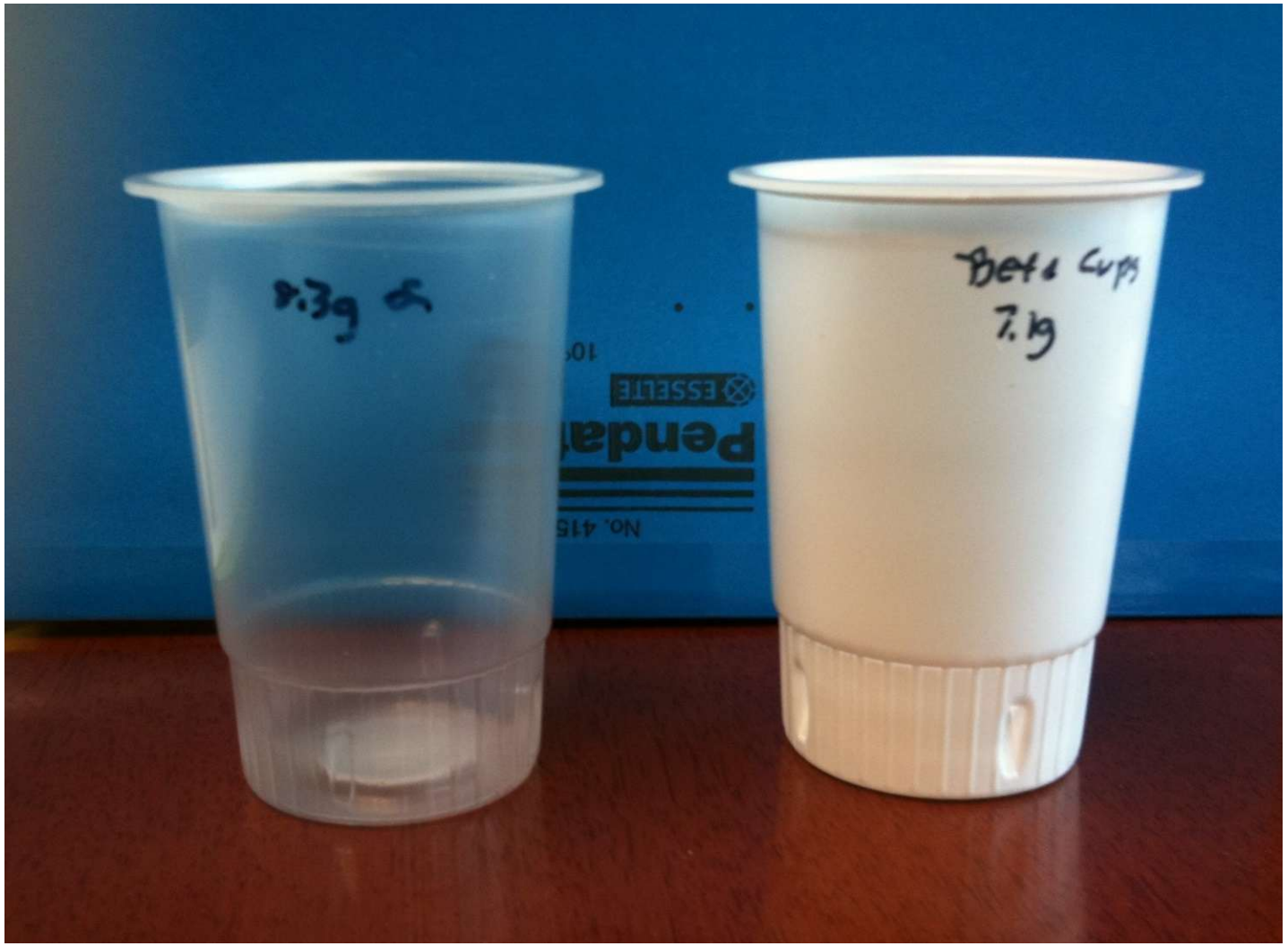
Cups Thermoformed at Different Temperatures



Note microvoiding at lowest forming temperature

Solid Phase Thermoformed Cups Made With and Without β-nucleation

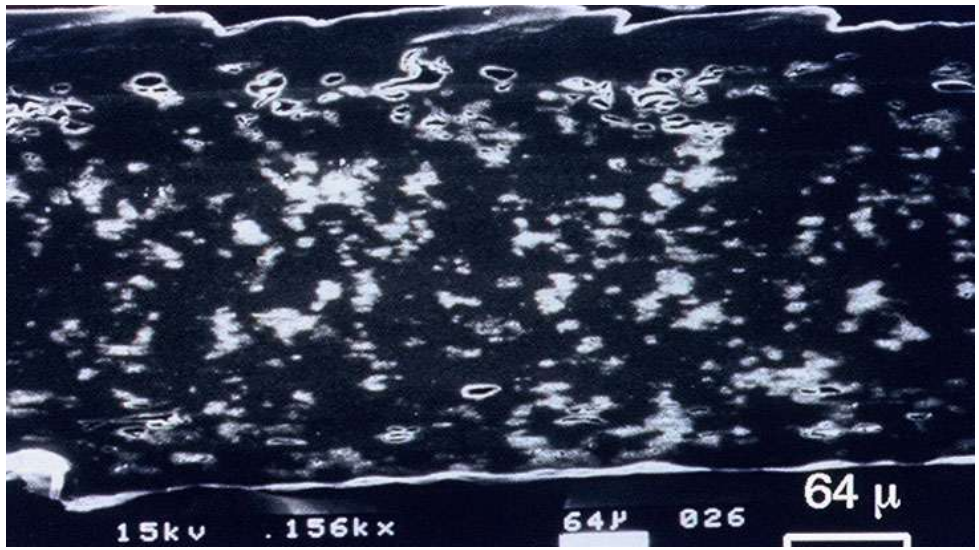
Note: No TiO_2 used in Beta nucleated HPP



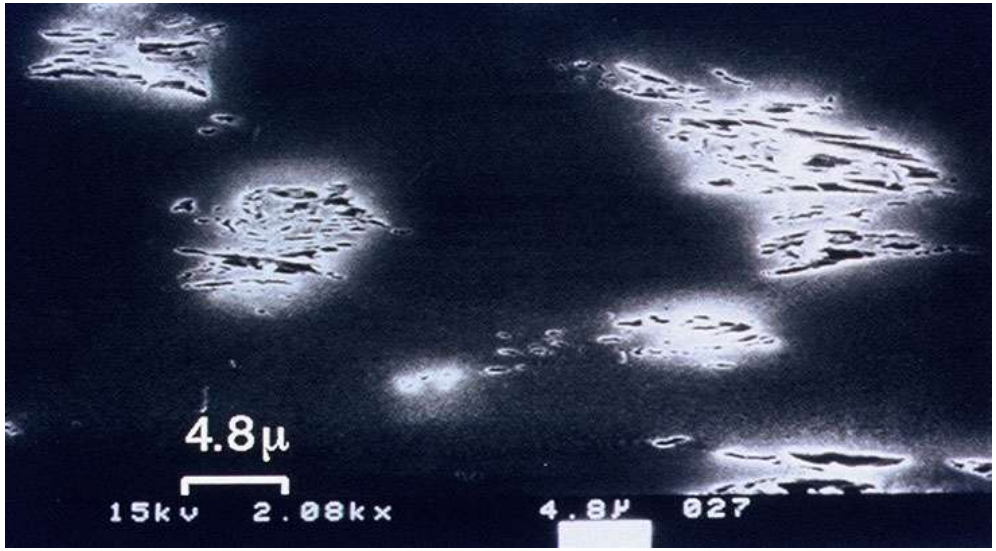
Non-nucleated Cup: 8.3g **β-nucleated Cup: 7.1g**

SEM Micrographs of Microvoided Container Cross-section

Note: Isolated clusters of sub-micron sized voids in the container sidewall produce whitening and density reduction without loss of barrier properties



Low Magnification

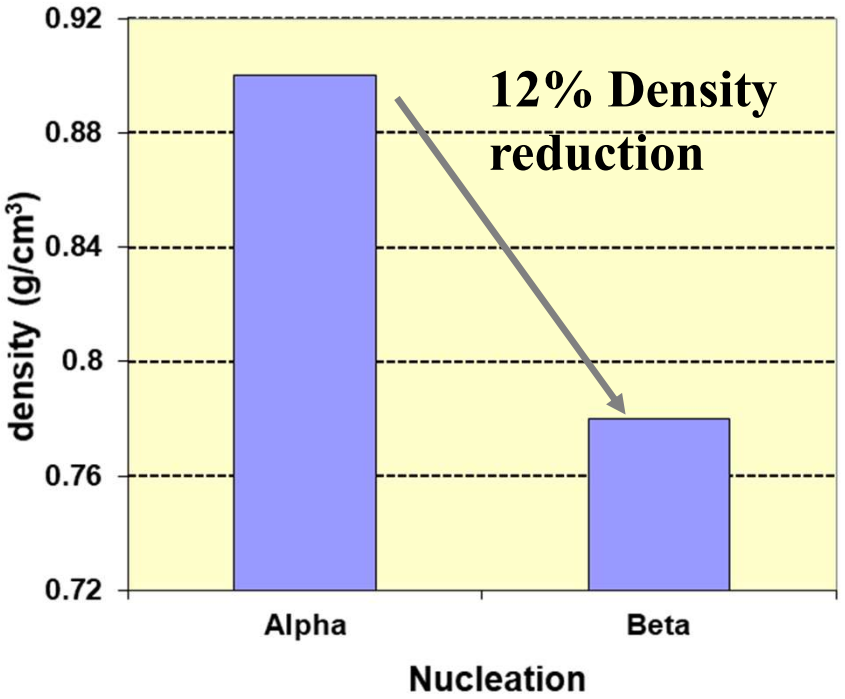


High Magnification

Beta Nucleation in Mono-oriented PP Film

α β

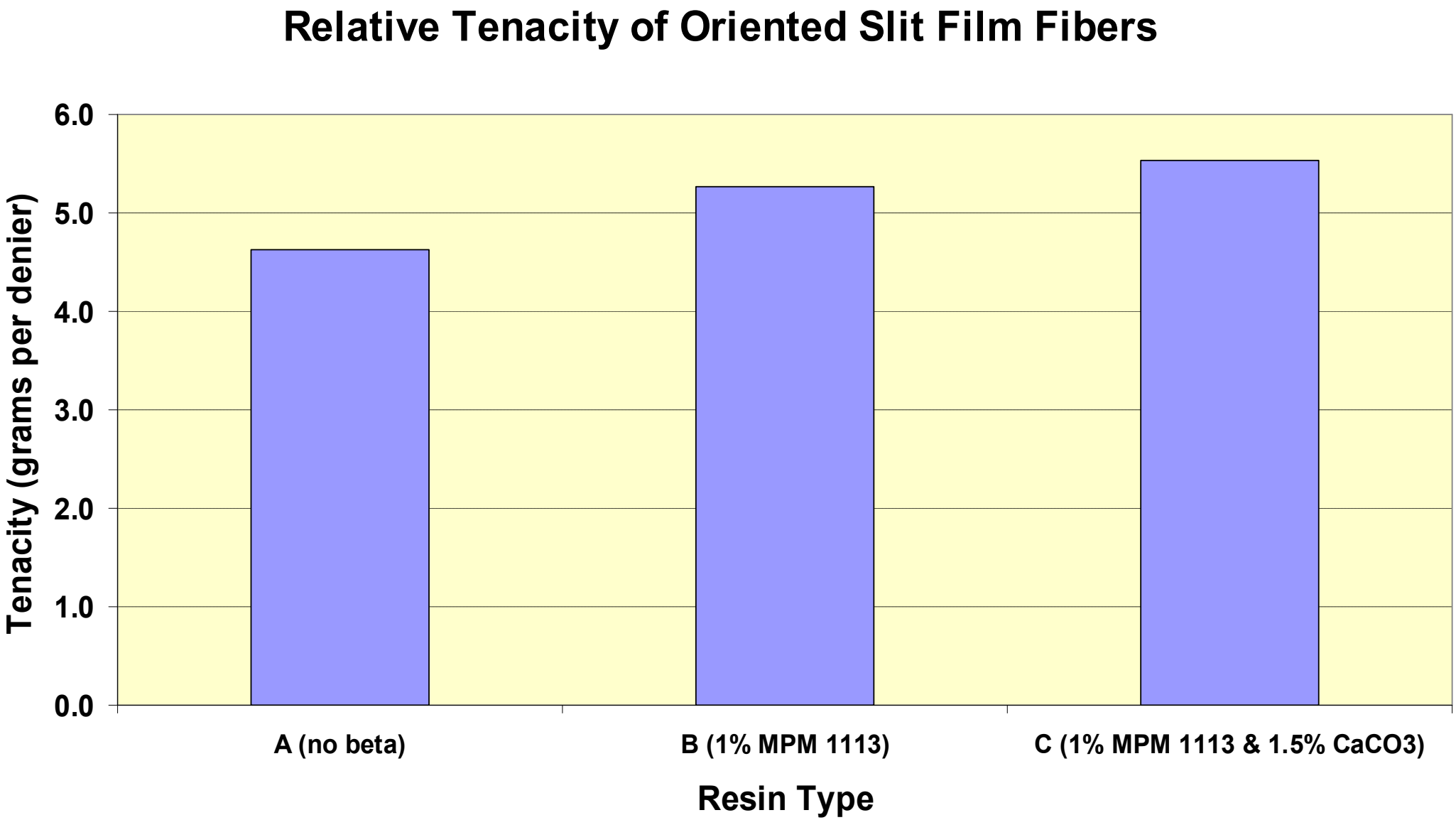
Monoaxially Oriented PP Film



Carpet Backing Tapes

- Higher Tenacity
- Higher yield (more m^2 per kg)
- Delustered without fillers

Improved Tenacity of Slit Film Fibers Using Beta Nucleation



Biaxially Oriented Microporous PP Films made using Beta Nucleation

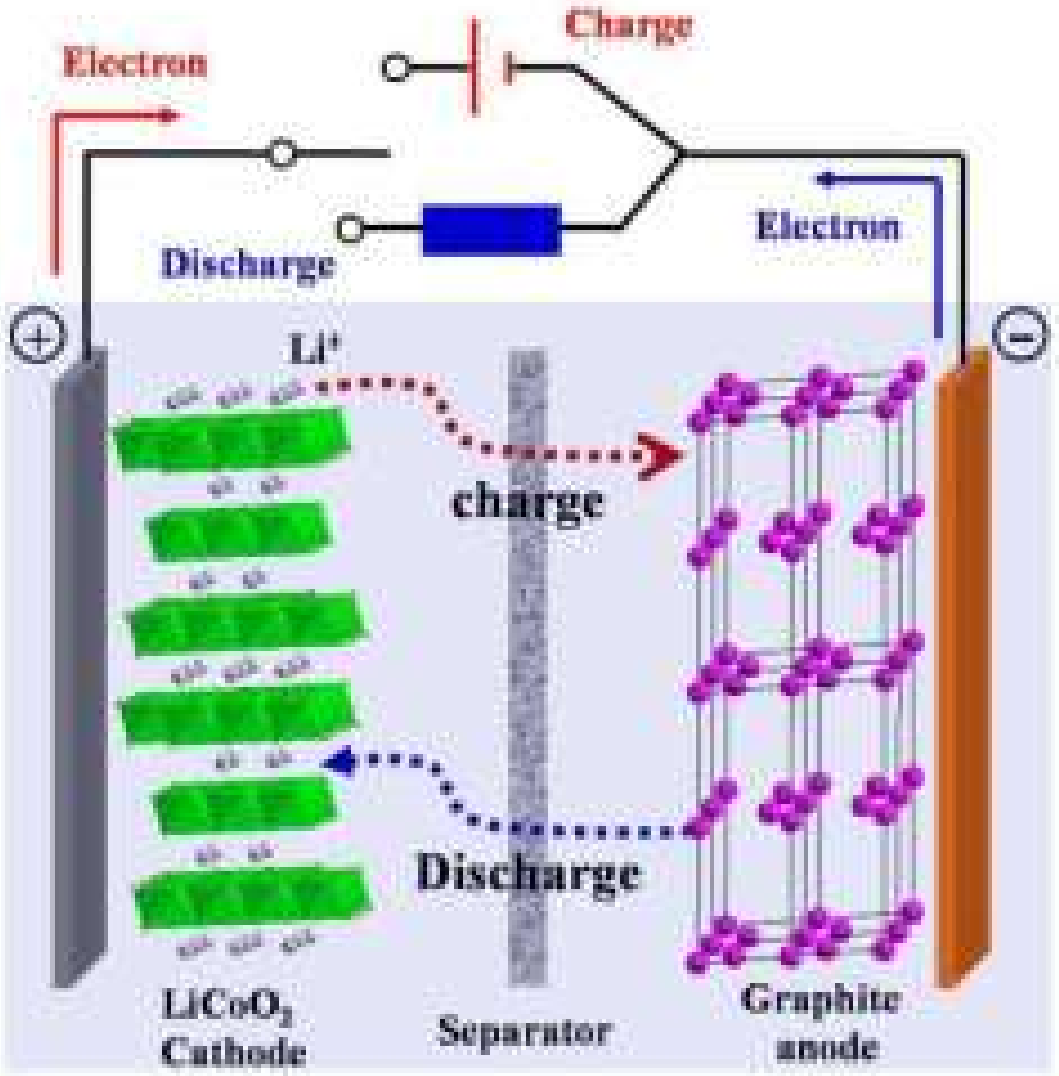
- Breathable PP films made using technology developed by P. Jacoby at Amoco (contains mineral fillers + polyolefin elastomers)
- Films made using PP homopolymer or impact copolymer (used for Lithium Ion Battery separator membranes)

Applications For Breathable-Waterproof Microporous Film

The Evolving Protective Apparel Market

- **Chemical/Medical Protective Suits (**films pass Viral Penetration and Blood Borne Pathogen Tests (ASTM F1671 and ASTM F1670)
- **Roofing Membranes**
- **Car Covers, and car protective films**
- **Lithium Ion battery separator membranes**

Schematic Charge/Discharge Process in a Lithium Ion Battery



Microporous Films Used as Battery Separators in Li-ion Batteries

Separator Function:

The separator is a micro-porous membrane, which prevents contact between the anode and cathode. The separator is made of either polyethylene or polypropylene. The separator allows lithium-ion flow, and has a safety function called a “shutdown.” If the cell heats up accidentally, the separator melts closing up the pores and preventing ionic flow.

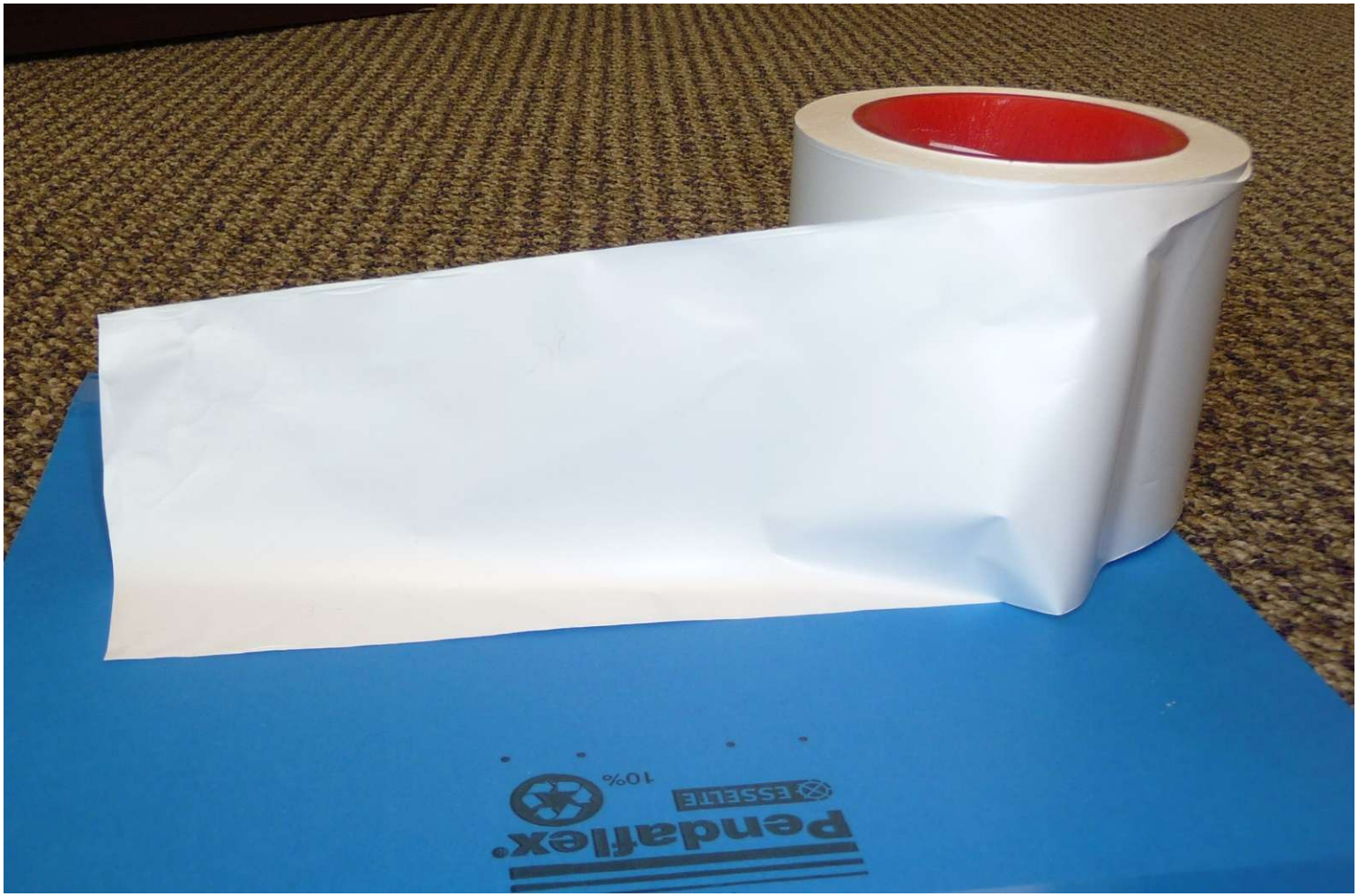
While most common separators in the consumer market have a thickness of 20-25 μm, separators with thickness of 9-16 μm will be preferred in the future to increase the energy density of the battery.

Types of Separators

- **Wet Process**: Polyolefin is mixed with a mineral oil in an extrusion system and cast into a film which is then oriented either in machine direction (MD) only or biaxially. After extraction of the oil in a volatile solvent such as DMC, the final stretched film has a distinct porous sponge-like structure.

- **Dry Process**:
  - Celgard Process: Pores are formed through multiple orientation and annealing steps in which a stacked lamellar structure is produced that forms slit-like pores during subsequent orientation in the Machine Direction (MD).
  - Beta Nucleation: Produced by self-cavitation when the β-PP crystals transform to α-PP crystals during the first orientation step. Microvoids propagate during the subsequent orientation in the Transverse Direction (TD).

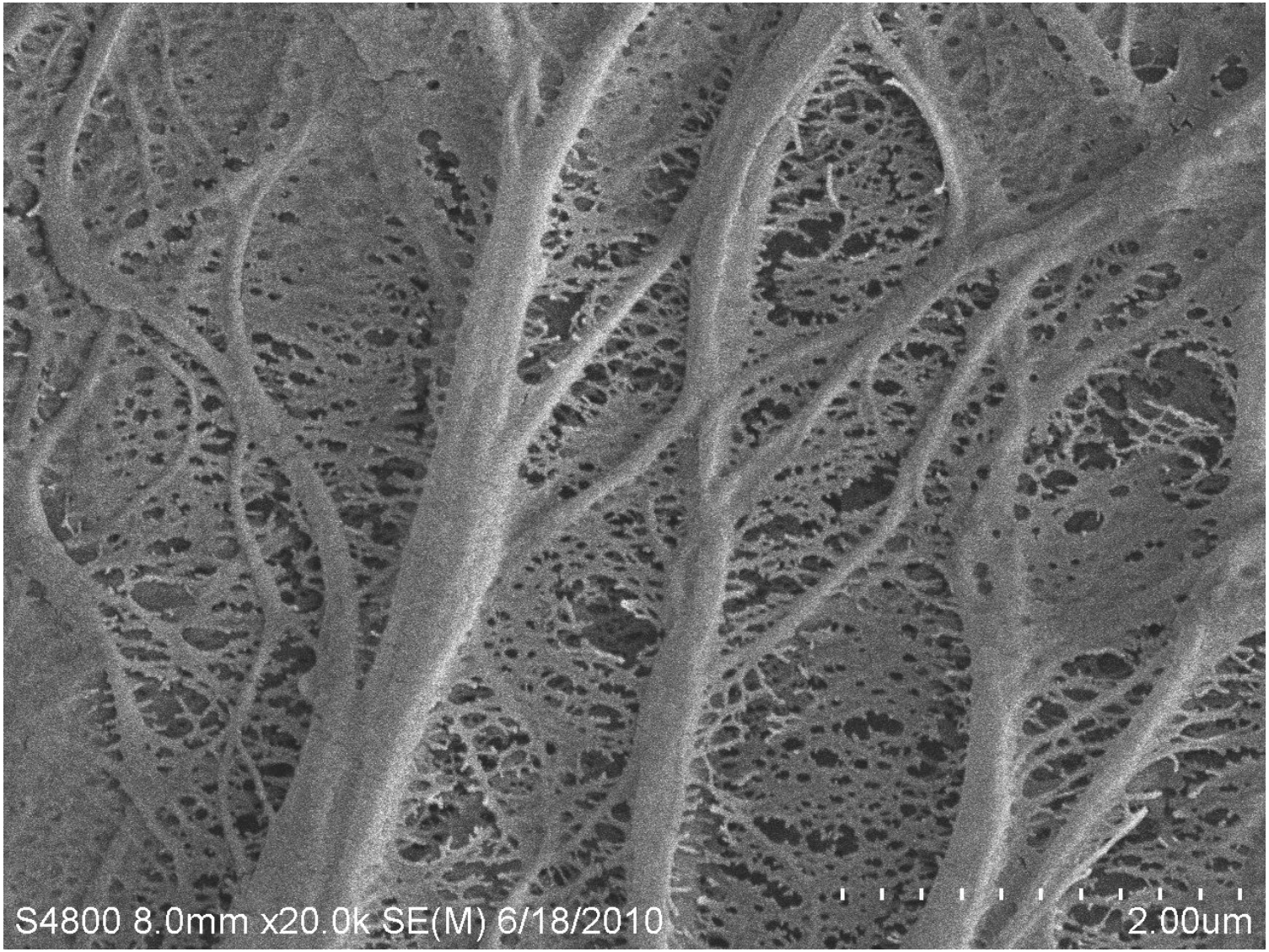
Beta Nucleated BOPP Film for Li-Ion Batteries and Supercapacitors



Film Thickness: 22 microns Film Density: 0.28 g/cm^3

(Over 70% porosity)

SEM Micrograph of Beta Nucleated Battery Separator Film



Battery Separators made using the Celgard "Dry" Process and "Wet" Process Films

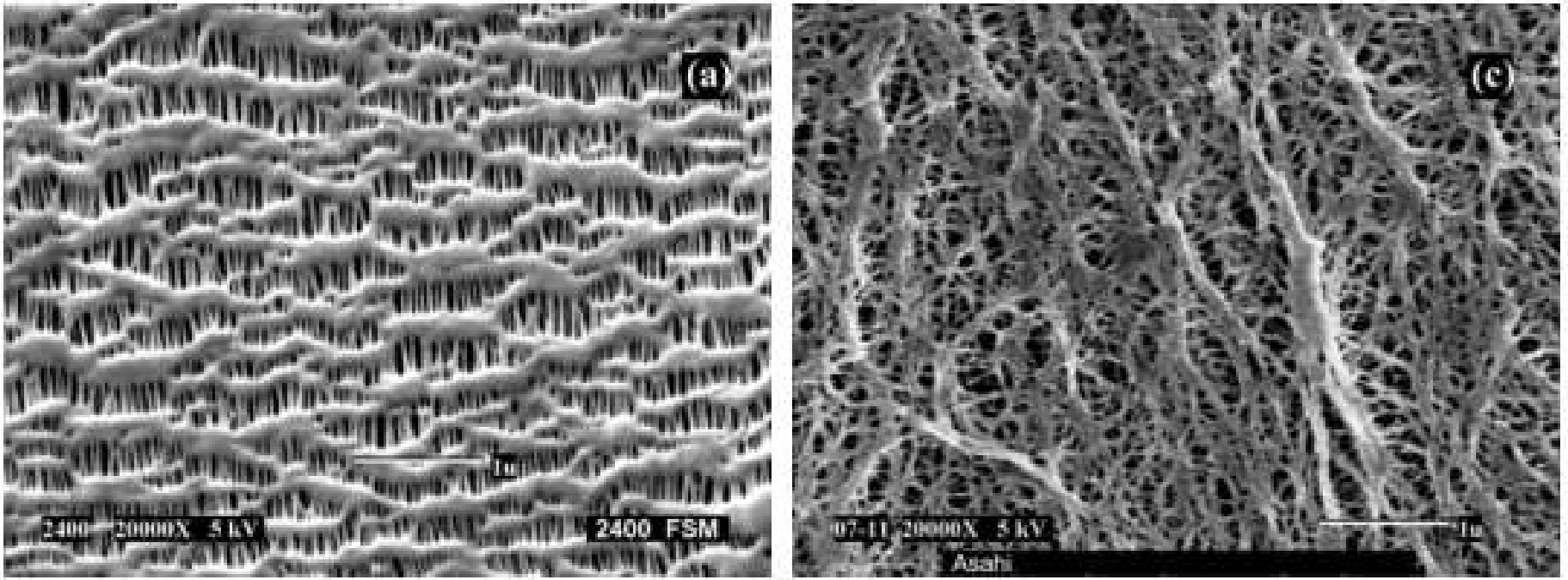


Figure 2.4: SEM images of commercial battery separators produced in the dry process (left, Celgard 2400, PP) and the wet process (right, Asahi, HiPore, PE)[31].

Typical Properties of Beta Nucleated Battery Separator Film

Property	Value	
Thickness	15 - 25 microns	
Density	0.3 - 0.4 g/cm3	
Porosity	> 50%	
Gurley permeability	130 sec./m^2/100 cm^3	
Pore size	0.2 - 0.5 microns	
	MD	TD
Tensile Strength (MPa)	200	47
Break Elong. (%)	40%	20%
Young's Modulus (Mpa)	1000	350
Shrinkage @ 100 ^oC	<1.5%	<1.5%
Shrinkage @ 120 ^oC	<3%	<5%

Other Possible Applications from Microporous Film made Using Beta Nucleation

- Laser printing without the addition of special heat sensitive additives
- Reversible clarity for use in bio-medical applications
- Modified atmosphere food packaging

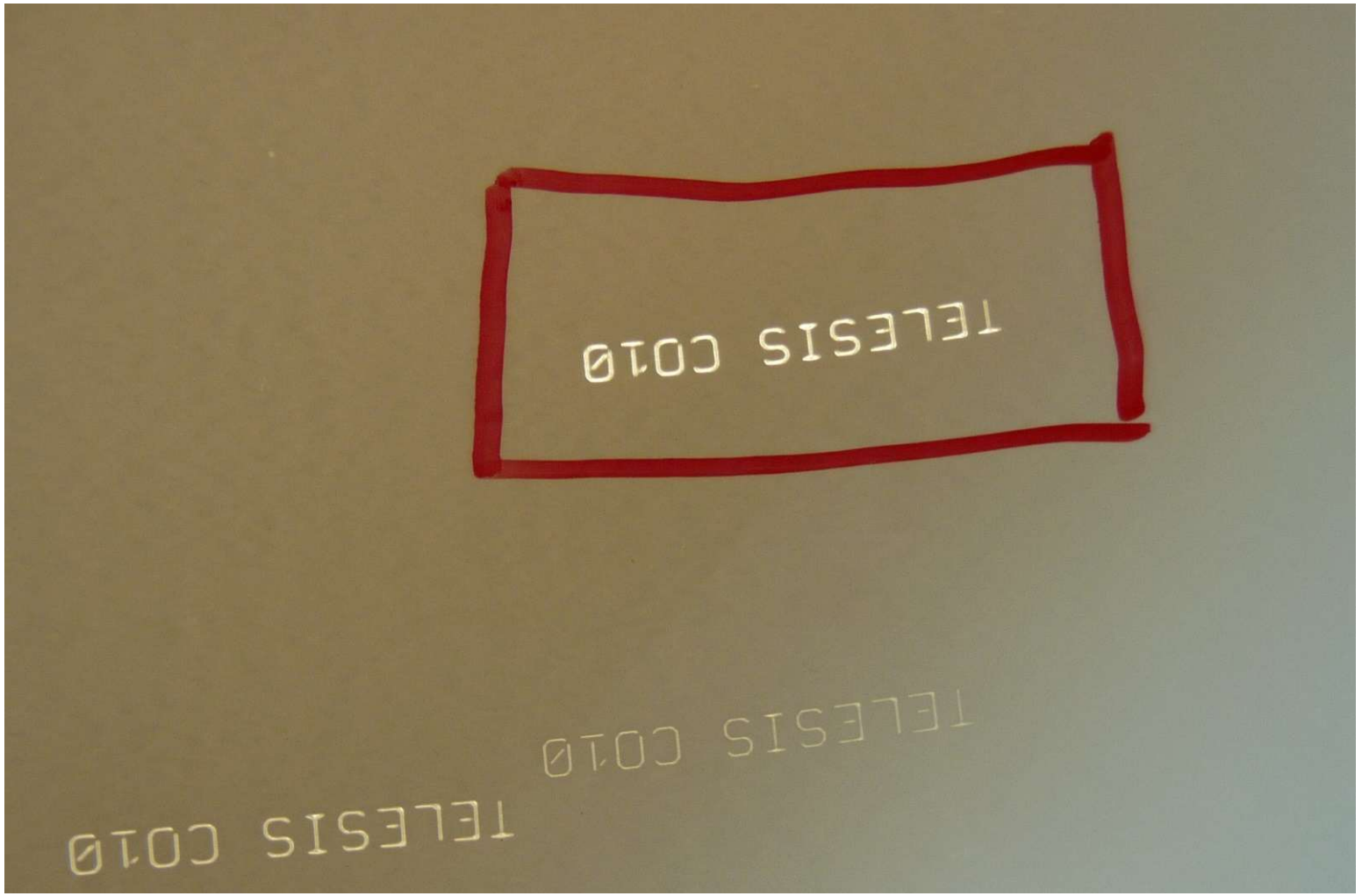
Traditional Laser Marking of Plastic Substrates

- High energy lasers (e.g. Diode, Nd:YAG, CO_2) irradiate the polymer and generate heat
- Marking is typically achieved using additives to induce dark (charring) or light (foaming) marks from the laser-induced heating
- Difficult to achieve “good” marking with certain color combinations/contrast
- Marks are permanent
- No inks, solvents, or chemical handling is needed
- Cost savings (speed, no consumables, reliability)

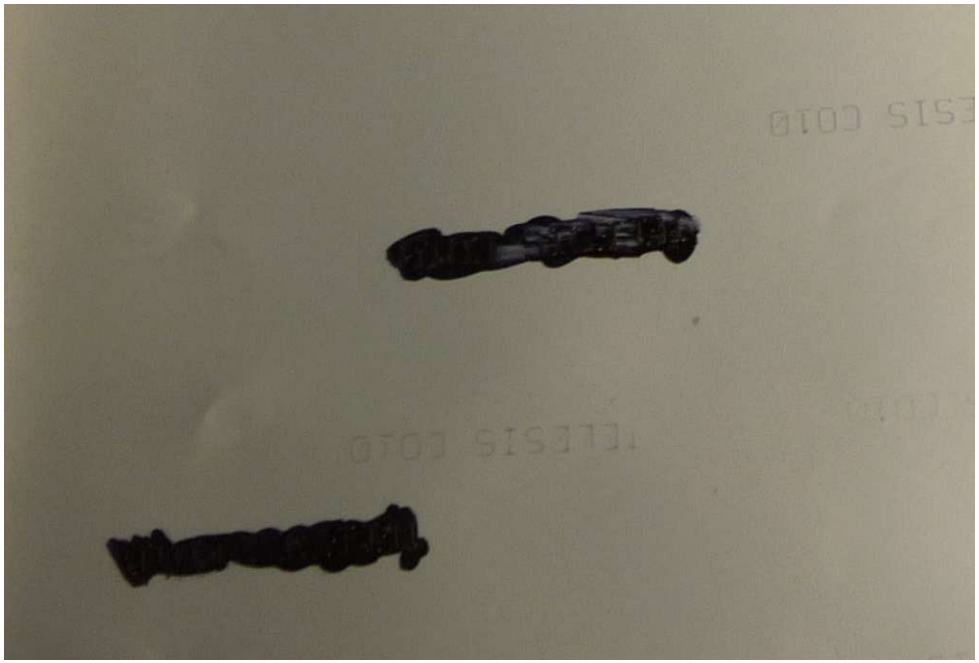
Laser Marking of Microporous Films

- The microvoids produced during the stretching of beta nucleated PP film result in a white film due to light scattering
- If the white microvoided film is heated near the melting point of the PP (> 165 ^{o}C) using a laser, the voids will collapse, and the melted region will turn clear and remain clear when the film solidifies
- If a dark backing layer is placed on one side of the microporous film (co-extruded, laminated, or pigment-containing adhesive), the dark color will show through the laser heated portions of the film and appear as a dark pattern on the film surface.

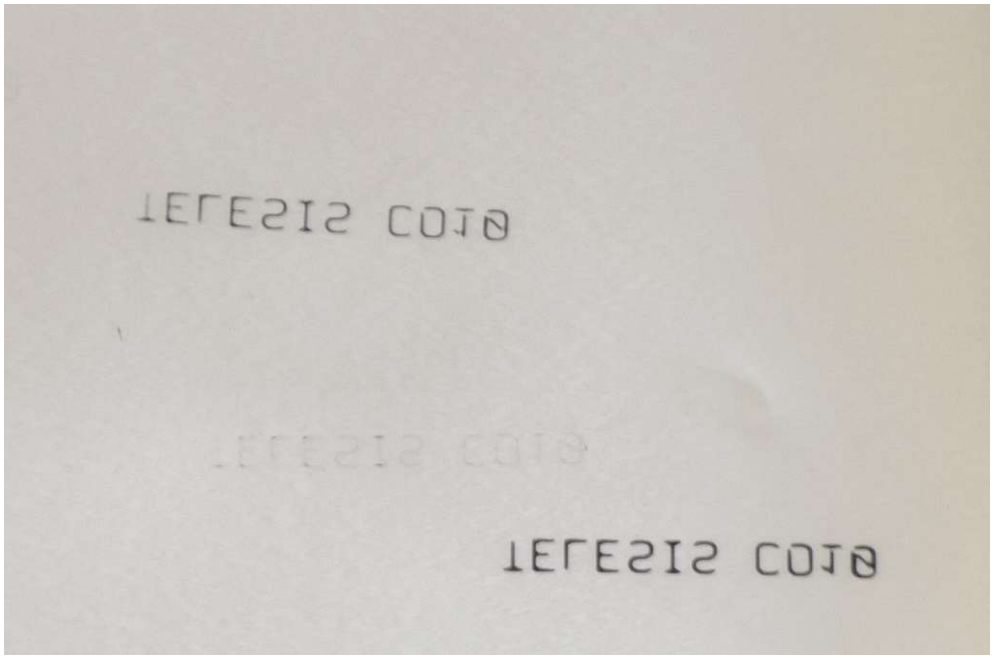
Back-lit MOPP Microporous Film Exposed to CO_2 Laser



Black Marker Used on One Side of Film



Top Side of Film



Reverse Side of Film

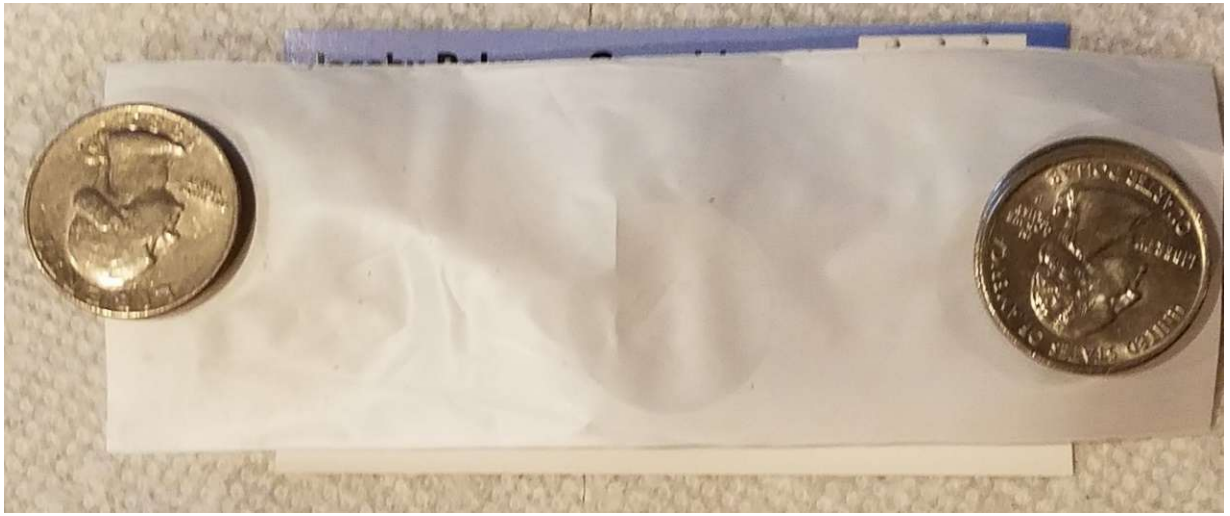
Benefits of Laser Printing on Microporous Films

- No inks, solvents or other consumable additives are used
- No pre-treatment, such as corona treatment, is required
- Can be done at very high production rates
- Can produce very detailed patterns due to the sub-micron size of the voids
- Ideal for barcode printing of white labels
- Can be used for back-lit displays
- Pigments can be incorporated in adhesives or co-extruded film layers
- Printed patterns are permanent and cannot be removed

Microporous Films with Reversible Clarity

Breathable Film after Contacting Vegetable Oil

Film Before Contact with Vegetable Oil



Film After Contact with Vegetable Oil

Reversible Clarity using Isopropanol

Applications of Breathability and Reversible Clarity in Microporous Films

- As a wound dressing, the breathability of the film can help to promote healing, while the small pore size prevents bacteria and viruses from entering the wound
- Applying a volatile liquid to the film, such as isopropanol, allows the physician to monitor the healing without having the remove the wound dressing
- The film can be used for transdermal drug delivery

Modified Atmosphere Packaging (MAP) to Extend the Shelf Life of Fresh Produce

- The shelf life of many types of fresh produce can be dramatically extended by allowing respiration of the produce through the exchange of CO_2 and Oxygen through the walls of the packaging
- An opaque “Window” of microporous film can be incorporated into the package design to provide the needed vapor transmission rates

MAP

Micro-perforated and breathable solutions to control in-pack gas atmosphere, enhancing freshness and prolonging lifecycle.

- Shelf-life extension
- Logistical benefits to packer & retailer
- Counters anaerobic respiration
- Enhanced texture, color & freshness
- Microbial spoilage reduction
- Added value through reduced waste

Suitable for most fresh-cut produce, and some whole produce products suffering color or texture loss under ambient atmosphere, such as cut salads, and prepared fruit and vegetables.

Conclusions

- Beta nucleation can be used to produce microporous biaxially oriented PP films with high breathability for use in Protective Clothing, Roofing Membranes, and Lithium Ion Battery Separators
- Mono-oriented Beta Nucleated Films can be used for Tape, Label, and Carpet Backing Applications
- Beta nucleated films can be used in novel film applications for the packaging and healthcare markets
- The Mayzo Beta Nucleant Masterbatches can be used directly by the film processor to produce these unique products

Mayzo Core Products

Stabilizers

Protection against the damaging effects of heat and light

Optical brighteners

Whitening and brightening effects, fluorescent tracers

Release coatings

Easy release
for tapes and labels

Beta-nucleating agents

Enhancing and extending the properties of polypropylene

Custom solutions

Improved productivity, hygiene, and convenience

Advanced solutions

Extending performance beyond the state of the art

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