Multi-Layer Ingeo™ Bottles

NatureWorks LLC

Ingeo biopolymer is a thermoplastic resin derived primarily from annually renewable resources and is available in grades specifically designed for packaging applications. Ingeo biopolymer 7000D is a clear, bottle grade polymer and processes easily on conventional injection stretch blow molding (ISBM) equipment for mono- and multi-layer bottles.

Applications

- Potential applications for multi-layer bottles include:
- Edible oil
- Juice
- Beverages (non CSD)
- Transparent food containers requiring increased barrier properties

Performance

Ingeo biopolymer exhibits higher transport rates for water vapor, carbon dioxide, and oxygen by a factor of 8-10 times than that of PET. Table 1 compares these values.

Table 1 – Permeation Rate Comparisons*

Property	WVTR	O_2	CO_2
Ingeo biopolymer	18-22	38-42	170-200
PET	1.0-2.08	3.0-6.1	15-25

*units: cc-mil/100 in^2 day atm) @ 20°C and 0% RH for O_2 and CO_2; g-mil/100 in^2 day for WVTR.

Multi-layer preform manufacturing is a proven technology, where approximately 70% of all barrier bottles made use a multi-layer structure. There is an established converter base and costs are competitive versus competing technologies. Multi-layer technology also demonstrates flexibility in that the barrier polymer can be selected to provide a wide range of performance improvements with minor composition in the final article. Multi-layer technology offers a viable cost effective option for meeting product performance requirements. Shelf life can be extended with minor use of barrier layer polymers (5-20%). Table 2 presents Barrier Improvement Factors (BIF) for resins that may be used in a multilayer structure to help prevent water loss and oxygen loss.

Ingeo biopolymer is easily processed on conventional injection molding and stretch blow molding equipment. Multi-layer bottles made from Ingeo biopolymer have been processed on standard Kortec co-injection systems. A range of barrier polymers have been evaluated in a 3-layer structure to provide increased moisture barrier (see Appendix A for reference).

Multi-Layer Preform & Design

Preform design is critical in getting a container with good clarity and physical properties. Designing a preform is, to an extent, specific to the blow mold equipment, bottle design, and mold tooling. As a starting point, designing a preform with an areal (axial x hoop) stretch ratio (SR) of 8-11, an axial SR of 2-3, and a hoop SR of 3-4, should allow for the blow molding of the desired container. A preform designed with less aggressive transitions and/or a thinner end cap might also be desired in order to prevent excess material accumulating in the base of the blown container.

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Table 2 – Barrier Improvement Factors of Various Barrier Resins to Improve WVTR and OTR

	Barrier Improvement Factor (BIF)*			
Polymer	**O_2**	**CO_2**	**WVTR (23°C/50%RH)**	**WVTR (40°C/80%RH)**
Ingeo PLA	1.0	1.0	1.0	1.0
EAA	0.7	0.7	3.7	1.9
PP	0.7	0.9	4.5	3.6
PE	0.8	0.8	6.5	3.6
Ticona COC	-	-	13.9	5.6
Honeywell Aegis, nylon nanocomposite	8.1	-	1.2	-
Honeywell Aegis, nylon nanocomposite with O_2 scavenger	46.2	-	1.3	-
Mitsubishi Gas, MXD6	13.0	-	1.8	-

*All multi-layer bottles contain ~8-9% by weight barrier polymer in a three-layer structure. Barrier improvement factors calculated using base PLA as reference.

Injection Molding of Preforms

A general-purpose screw designed to minimize residence time and shear is recommended. It is best to injection mold at conditions that keep the molded-in stresses in the preforms to a minimum. One should optimize injection speeds, especially when filling the end cap of the preform, and melt temperature in order to minimize prefrom stress. This will help keep shrinkage of the preform low during reheating during blow molding. Table 3 illustrates typical processing parameters for Ingeo biopolymer.

Multi-Layer Co-Injection

Producing multi-layer bottles involves the use of a co-injection melt delivery system where the separate skin and core materials can be melt processed and combined in a precise and controlled way to create the desired multi-layered structure. For example, Kortec's co-injection systems have been used to make multilayer bottles made out of Ingeo biopolymer. Skin and core layer ratios can be optimized to achieve the desired properties of the bottle. The temperature of the manifold delivery system must be optimized in order to accommodate the melting temperatures and behaviors of the different polymers that may be utilized when making a multi-layered preform. Appendix A and B reference general injection molding multi-layer processing information for various barrier resin options.

Re-heating of Preforms

The heating of the preform is critical in order to get a container with good clarity and material distribution. Normal preform temperatures for running on a two-stage process have been between 80-100˚C. This temperature may be lower or higher depending on the preform design, bottle design, and re-heating equipment that is being used. This temperature may also depend upon the barrier material being used for the inner layer, relative to the reheat temperature of Ingeo preforms.

Blow Molding the Container

Ingeo biopolymer has a lower extensional viscosity than PET, and so is easier to stretch. The use of pre-blow pressure and timing are important control parameters to help manage material distribution throughout the bottle. The base of any given bottle may have thicker material distribution than the sidewall. This thick area in the bottle base needs to be distributed well and cooled quickly. This helps keep the base from deforming because the material is still warm in this area. Depending on the application and bottle design, a base design that includes ribs and a high pushup for reinforcement may be desired.

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Processing Details

Startup and Shutdown

Ingeo polymer is not compatible with a wide variety of resins, and special purging sequences should be followed:

1. At normal operating temperatures for current polymer in injection molder, purge with polypropylene (PP), preferably starting with a low MI (high viscosity) PP, switching to a high MI (low viscosity) PP.
2. Bring injection molder to steady state at normal operating temperatures for Ingeo PLA while running PP.
3. Vacuum out dryer and/or hopper system and any other potential points where contamination could occur. Ensure resin is dried below 200 ppm moisture before processing. Refer to NatureWorks drying guides for more information.
4. Introduce Ingeo resin into the injection molder at the recommended operating temperatures.
5. It will be obvious when pure Ingeo PLA is being extruded, as it gives a clear, steady melt.
6. At shutdown or if the machine will be idle for some time, purge the machine with a high-viscosity resin, such as PP.

Table 3 – Nominal Processing Parameters for Ingeo biopolymer*

Typical Processing Parameters*		
Melt Temperature	390-430ºF	200-220ºC
Feed Throat	70ºF	21ºC
Feed Section	355ºF	180ºC
Compression Section	410ºF	210ºC
Metering Section	410-430ºF	210-220ºC
Nozzle	410-430ºF	210-220ºC
Mold	70-100ºF	21-38ºC
Back Pressure	100-200psi	
Mold Shrinkage	0.004 in/in.+/-.001	

*Note: These are starting points and may need to be optimized. It is very important to optimize back pressure, process temperature, mold temperature, and injection speed such that the cycle time and the internal stresses in the finished part are kept to a minimum. This will help keep the shrinkage of the preform upon re-heating to the lowest level possible while keeping preform production as high as possible. Using a hot runner system in the injection-molding step is also recommended to help keep shear stress and preform shrinkage to a minimum.

Drying

In-line drying capabilities are essential for processing Ingeo biopolymer, which is supplied with a moisture content of less than 0.04% (400 ppm). The recommended moisture content to prevent viscosity degradation and possible lactide reformation is less than 0.010% (100 ppm). Typical drying conditions are 4-6 hours at 149-185ºF (65-85ºC) using dehumidified air with a dew point of -40ºF (-40ºC), airflow rate greater than 0.5 cfm/lbs per hour of resin throughput. The resin should not be exposed to atmospheric conditions after drying. Transfer lines and hoppers should be sealed or padded with inert gas. Keep resin package sealed until ready to use and promptly reseal packages of unused material.

Multi-Layer Recycling

Typical barrier polymers can be used and easily separated from the Ingeo biopolymer by conventional material separation technologies - for example, using inherent material density differences or analytical separation equipment. The recycling impact will depend upon the barrier polymer used.

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Contacts

Multi-layer bottles made out of Ingeo biopolymer have been processed and demonstrated using standard Kortec co-injection systems. A range of barrier polymers have been successfully evaluated. NatureWorks LLC has collaborated with Kortec, Inc. for technical development purposes specifically related to multilayer preforms and bottles. Kortec's contact information is referenced below.

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Appendix A

General Ingeo Biopolymer Injection Molding Multilayer Process Information Using Barrier Resins to Impact Water Permeation Rate

Resin ID	**7000D with 7.5% Huntsman PE**	**7000D with 7.5% Atofina PP**	**7000D with 5% Ticona COC**	**7000D with 7.5% PET 8010**
Machine Type	#8 Arburg 420 C ML	#8 Arburg 420 C ML	#8 Arburg 420 C ML	#8 Arburg 420 C ML
Preform weight (g)	30.9	30.8	31.6	32.5
Mold Temperature (°F) [°C]	45 [7.2]	45 [7.2]	45 [7.2]	45 [7.2]
PLA Barrel Temperatures	**A-Layer Parameter**	**A-Layer Parameter**	**A-Layer Parameter**	**A-Layer Parameter**
Feed Zone (°F) [°C]	426 [219]	426 [219]	426 [219]	426 [219]
Zone 2 (°F) [°C]	435 [224]	437 [225]	437 [225]	437 [225]
Zone 3 (°F) [°C]	437 [225]	437 [225]	437 [225]	435 [224]
Zone 4 (°F) [°C]	437 [225]	435 [224]	437 [225]	437 [225]
Nozzle (°F) [°C]	437 [225]	435 [225]	435 [225]	437 [225]
Barrier Barrel Temperatures	**B-Layer Parameter**	**B-Layer Parameter**	**B-Layer Parameter**	**B-Layer Parameter**
Feed Zone (°F) [°C]	392 [200]	394 [201]	414 [212]	414 [212]
Zone 2 (°F) [°C]	408 [209]	410 [210]	446 [230]	466 [241]
Zone 3 (°F) [°C]	408 [209]	410 [210]	455 [235]	471 [244]
Zone 4 (°F) [°C]	417 [214]	421 [216]	455 [235]	471 [244]
Kortec Manifold Temperatures				
Blue Channel (°F) [°C]	437 [225]	437 [225]	437 [225]	464 [240]
Green Channel (°F) [°C]	437 [225]	437 [225]	437 [225]	464 [240]
Barrier Nozzle (°F) [°C]	437 [225]	437 [225]	437 [225]	455 [235]
Extended Nozzle (°F) [°C]	437 [225]	437 [225]	437 [225]	0

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Appendix B

General Ingeo Biopolymer Injection Molding Multilayer Process Information Using Barrier Resins to Impact Oxygen Permeation Rate

Resin ID	7032X with 8% Aegis CSDE	7032X with 8% Aegis OX	7032X with 8% MXD6
Machine Type	Husky Injection Molder	Husky Injection Molder	Husky Injection Molder
Preform weight (g)	23.5 g	23.5 g	23.5 g
Mold Temperature (°F) [°C]	45 [7.2]	45 [7.2]	45 [7.2]
PLA Barrel Temperatures			
Feed Zone (°F) [°C]	311 [155]	311 [155]	311 [155]
Zone 2 (°F) [°C]	356 [180]	356 [180]	356 [180]
Zone 3 (°F) [°C]	410 [210]	410 [210]	410 [210]
Zone 4 (°F) [°C]	415 [213]	415 [213]	415 [213]
Nozzle (°F) [°C]	415 [213]	415 [213]	415 [213]
Barrier Barrel Temperatures			
Feed Zone (°F) [°C]	455 [235]	455 [235]	455 [235]
Zone 2 (°F) [°C]	500 [260]	500 [260]	500 [260]
Zone 3 (°F) [°C]	554 [290]	554 [290]	554 [290]
Zone 4 (°F) [°C]	559 [293]	559 [293]	559 [293]
Nozzle (°F) [°C]	437 [225]	437 [225]	437 [225]
Kortec Manifold Temperatures			
Blue Channel (°F) [°C]	500 [260]	500 [260]	500 [260]
Green Channel (°F) [°C]	500 [260]	500 [260]	500 [260]
Barrier Nozzle (°F) [°C]	500 [260]	500 [260]	500 [260]
Extended Nozzle (°F) [°C]	500 [260]	500 [260]	500 [260]

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Safety and Handling Considerations

Material Safety Data (MSD) sheets for Ingeo biopolymers are available from NatureWorks LLC. MSD sheets are provided to help customers satisfy their own handling, safety, and disposal needs, and those that may be required by locally applicable health and safety regulations, such as OSHA (U.S.A.), MAK (Germany), or WHMIS (Canada). MSD sheets are updated regularly; therefore, please request and review the most current MSD sheets before handling or using any product.

The following comments apply only to Ingeo biopolymers; additives and processing aids used in fabrication and other materials used in finishing steps have their own safe-use profile and must be investigated separately.

Hazards and Handling Precautions

Ingeo biopolymers have a very low degree of toxicity and, under normal conditions of use, should pose no unusual problems from incidental ingestion, or eye and skin contact. However, caution is advised when handling, storing, using, or disposing of these resins, and good housekeeping and controlling of dusts are necessary for safe handling of product. Workers should be protected from the possibility of contact with molten resin during fabrication. Handling and fabrication of resins can result in the generation of vapors and dusts that may cause irritation to eyes and the upper respiratory tract. In dusty atmospheres, use an approved dust respirator. Pellets or beads may present a slipping hazard. Good general ventilation of the polymer processing area is recommended. At temperatures exceeding the polymer melt temperature (typically 170ºC), polymer can release fumes, which may contain fragments of the polymer, creating a potential to irritate eyes and mucous membranes. Good general ventilation should be sufficient for most conditions. Local exhaust ventilation is recom-mended for melt operations. Use safety glasses if there is a potential for exposure to particles which could cause mechanical injury to the eye. If vapor exposure causes eye discomfort, use a full-face respirator. No other precautions other than clean, body-covering clothing should be needed for handling Ingeo biopolymers. Use gloves with insulation for thermal protection when exposure to the melt is localized.

Combustibility

Ingeo biopolymers will burn. Clear to white smoke is produced when product burns. Toxic fumes are released under conditions of incomplete combustion. Do not permit dust to accumulate. Dust layers can be ignited by spontaneous combustion or other ignition sources. When suspended in air, dust can pose an explosion hazard. Firefighters should wear positive-pressure, self-contained breathing apparatuses and full protective equipment. Water or water fog is the preferred extinguishing medium. Foam, alcohol-resistant foam, carbon dioxide or dry chemicals may also be used. Soak thoroughly with water to cool and prevent re-ignition.

Disposal

DO NOT DUMP INTO ANY SEWERS, ON THE GROUND, OR INTO ANY BODY OF WATER. For unused or uncontaminated material, the preferred options include recycling into the process or sending to an industrial composting facility, if available; otherwise, send to an incinerator or other thermal destruction device. For used or contaminated material, the disposal options remain the same, although additional evaluation is required. (For example, in the U.S.A., see 40 CFR, Part 261, "Identification and Listing of Hazardous Waste.") All disposal methods must be in compliance with Federal, State/Provincial, and local laws and regulations.

Environmental Concerns

Generally speaking, lost pellets are not a problem in the environment except under unusual circumstances when they enter the marine environment. They are benign in terms of their physical environmental impact, but if ingested by waterfowl or aquatic life, they may mechanically cause adverse effects. Spills should be minimized, and they should be cleaned up when they happen. Plastics should not be discarded into the ocean or any other body of water.

Product Stewardship

NatureWorks LLC has a fundamental duty to all those that make and use our products, and for the environment in which we live. This duty is the basis for our Product Stewardship philosophy, by which we assess the health and environmental information on our products and their intended use, then take appropriate steps to protect the environment and the health of our employees and the public.

Customer Notice

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