Injection Stretch Blow Molding Ingeo™ Biopolymer

This information is intended to be used only as a guide for the manufacture of injection stretch blow molded (ISBM) bottles made from Ingeo biopolymer. Since there are many factors to consider with preform and bottle design, product development, performance criteria, and the manufacturing process, an experimental approach may be required in order to achieve desired results.

In general terms, blow molding is the process in which a hot parison or preform is inflated within a closed mold to impart the shape of the mold cavity. There are three types of blow molding processes: extrusion blow molding (EBM), injection blow molding (IBM), and injection stretch blow molding (ISBM). Ingeo biopolymer is best suited for the ISBM process, under which there are two specific types: the single-stage process and the two-stage process (also known as the reheat-stretch blow molding (RSB) process). The information presented here pertains to manufacturing Ingeo bottles ranging in volume from 300 to 2000 mL using the ISBM process. Depending upon the application, performance criteria, equipment type, and mold designs being used, this size range could vary so an experimental approach may be needed during bottle development.

Ingeo biopolymer 7001D is the NatureWorks LLC resin grade name specifically used for ISBM bottle applications. In general, preforms and bottles made from Ingeo biopolymer 7001D look and feel similar to ones made from PET. Both resins can be made on typical ISBM production equipment; however there are some processing differences between the two materials. These differences lie mostly in the thermal behavior of the polymers. Ingeo biopolymer gets dried and processed at lower temperatures than bottle grade PET and the preforms are typically blown at lower temperatures.

1.0 Safety & Handling Precautions

All safety precautions normally followed in the handling and processing of melted thermoplastics should be followed for Ingeo biopolymer resins.

As with most thermoplastics, melt processing and the variability of those conditions may result in minor decomposition. Lactide, a non-hazardous gaseous irritant, is a minor by-product of PLA melt processing. Appropriate air testing should be completed to ensure an acceptable Threshold Limit Value (TLV) of less than 5 mg/m³ is maintained. The use of process area point source remediation measures such as monomer fume hoods or exhausts near melt processing equipment are typically recommended.

Molten PLA is lower in viscosity and sticks more readily to cloth, metal, brass, and wood compared to other molten thermoplastics. Be prepared for this when cleaning die faces, purging equipment, collecting molten patties, and emptying purge containers. Unlike polyolefin, molten PLA will not release as cleanly from surfaces so use caution when cleaning or handling any stream or patty of PLA.

PLA is considered non-hazardous according to DOT (United States Department of Transportation) shipping regulations. When handling PLA resin at room temperature, avoid direct skin and eye contact along with conditions that promote dust formation. For further information, consult the appropriate MSDS for the PLA grade being processed.

As with any melted thermoplastic waste, melted PLA waste should be allowed to cool before being placed into any waste container to minimize fire risks.

2.0 Resin Storage Recommendations

PLA resins should be stored in an environment designed to minimize moisture uptake. Product should also be stored in a cool place at temperatures below 50°C (122°F).

Product that is delivered in cartons or super sacks should be kept sealed until ready for loading into the blending and/or drying system. Bulk resin that is stored in closed silos and hoppers for extended periods (more than 6 hrs) should be kept purged with dry air or nitrogen to minimize moisture gain. In the case of outside storage, if the product is supplied in boxes or other non-bulk containers, the unopened container should be brought into the extrusion production area and allowed to equilibrate for a minimum of 24 hours before opening to prevent excessive condensation.
3.0 Resin Properties

Ingeo biopolymer 7001D is the resin grade specifically for ISBM applications. Typical properties of 7001D are shown in the table below.

Typical Ingeo Biopolymer 7001D Properties

<table>
<thead>
<tr>
<th>Resin Property</th>
<th>Nominal Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Gravity</td>
<td>1.24</td>
</tr>
<tr>
<td>Relative Viscosity</td>
<td>3.9 – 4.1</td>
</tr>
<tr>
<td>Crystalline Melt Temperature, °F (°C)</td>
<td>295 – 310 (145-155)</td>
</tr>
<tr>
<td>Glass Transition Temperature, °F (°C)</td>
<td>125 – 136 (52 – 58)</td>
</tr>
<tr>
<td>Crystallization Temperature, °F (°C)</td>
<td>212 – 248 (100 – 120)</td>
</tr>
<tr>
<td>Thermal Conductivity, BTU/ ft-hr.-°F (cal / cm-sec-°C)</td>
<td>Amorphous 0.075 (3.1 x 10-4)</td>
</tr>
<tr>
<td></td>
<td>Crystalline 0.11 (4.5 x 10-4)</td>
</tr>
<tr>
<td>Specific Heat, BTU/ lb °F (cal / g °C)</td>
<td>Below Tg 0.29 (0.29)</td>
</tr>
<tr>
<td></td>
<td>Above Tg 0.51 (0.51)</td>
</tr>
<tr>
<td>Transmission Rates</td>
<td>Oxygen 550 cc-mil/m2/24 hr-atm</td>
</tr>
<tr>
<td></td>
<td>Carbon Dioxide 3000 cc-mil/m2/24 hr-atm</td>
</tr>
<tr>
<td></td>
<td>Water Vapor 325 g-mil/m2/24 hr-atm</td>
</tr>
<tr>
<td>Clarity</td>
<td>Transparent</td>
</tr>
</tbody>
</table>

4.0 Materials of Construction

Recommended materials of construction for vessels used for drying PLA resin should be corrosion resistant.

All metal parts in the extrusion process should be constructed of stainless steel to minimize corrosion. PLA should not be left in the extruder, shooting pot, polymer transfer lines, hot runner, or any other part of the extrusion system at PLA melt temperatures or higher for extended periods of time. Below is a guideline for the types of steel that should be used in the extrusion and tooling systems.

<table>
<thead>
<tr>
<th>Part</th>
<th>Steel Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melt pumps and bearings</td>
<td>SUS440B</td>
</tr>
<tr>
<td>Pump blocks</td>
<td>SUS631</td>
</tr>
<tr>
<td>Transfer lines</td>
<td>SUS440C</td>
</tr>
<tr>
<td>Mold tooling</td>
<td>Stainless steel that is hardened. Polished core and cavity surfaces.</td>
</tr>
</tbody>
</table>

5.0 Resin Drying

PLA is a hydroscopic thermoplastic. It readily absorbs moisture from the atmosphere. The presence of even small amounts of moisture will hydrolyze PLA in the melt phase, reducing the molecular weight. As a result, the mechanical properties of PLA decrease and the end-product quality is compromised. Therefore, PLA must be thoroughly dry just prior to melt processing. In many cases, recycled PLA may also have to be crystallized prior to drying.

Unlike other major packaging resins (e.g. polyolefin, polystyrene, and PVC), PLA is produced by a condensation reaction. This reaction, which also produces water, is reversible. Therefore, when undried PLA is melted the resin and water chemically react. Hydrolysis occurs and key mechanical properties of the PLA are reduced. This hydrolysis reaction also changes PLA’s melt viscosity and the crystallization rate, making it difficult to process into a quality end product.
Virgin PLA resin is crystallized and dried to less than 400 ppm moisture level prior to leaving the production plant. The resin is sold in boxes or super sacks with moisture resistant foil liners to prevent moisture uptake. If the PLA is received in undamaged boxes and liners, the drying requirements are minimal but still required. In addition, if the foil liner has been opened, drying will be required. 7001D resin is already crystallized to allow easier drying. Some other grades of Ingeo biopolymer are amorphous, however, and need special care during drying. Uncrystallized (amorphous) PLA becomes sticky and clumps when its temperature reaches approximately 131-140°F (55-60°C). This is PLA's glass transition temperature, the point at which the amorphous portion of the polymer begins to soften. Amorphous PLA resin or regrind should never be dried greater than 104°F (40°C) in order to prevent resin blocking in the dryer. Ingeo biopolymer 7001D resin, however, comes crystallized and therefore is not subject to changes that amorphous pellets or regrind flake go through at or around the glass transition temperature.

Most PLA drying is done in dehumidifying hoppers using hot air at a very low dew point. The dehumidified air passes through a bed of PLA to extract moisture from the resin. A desiccant material, such as silica, absorbs moisture from the circulating air. Dual desiccant bed systems are common, so that one bed is on-stream while the stand-by bed is being regenerated. Either a time cycle or a predetermined decrease in air dew point is used to shift airflow from one bed to the other.

5.1 Recommended Drying Practices

PLA resin can be successfully dried using most standard drying systems. Recommended conditions are provided for standard desiccant based column dryers. For other drying system designs, additional information can be provided upon request.

To prevent equipment corrosion, it is not recommended to dry or store hot PLA resin in carbon steel vessels (see Section 4.0).

In-line drying is essential for PLA resins. PLA must be dried to less than 250 ppm moisture and maintained at this moisture level to minimize hydrolysis during melt processing. This is not optional with PLA - it is absolutely essential. Dry resin will help control the viscosity loss and minimize thermal degradation. A reduction in melt viscosity due to thermally processing wet resin is an indication of significant loss in molecular weight, which may result in a loss of physical properties of the final product. Minimizing thermal degradation is critical to maintaining properties such as impact strength, melt viscosity, and other aspects needed to make a quality product.

Crystallized PLA should be dried at approximately 149-185°F (65-85°C) using dehumidified air with a dew point of – 40°F. Higher drying temperatures can lead to softening and blocking of polymer in the dryer. Lower drying temperatures will result in extended drying times.

Dew point is an absolute measure of air moisture and is independent of air temperature. Dew point should always be used to control dryer performance. Therefore, the dryer should be equipped with a dew point monitor and alarm, and also a temperature monitor on the dryer inlet line.

Airflow is another critical component to drying. Airflow to the dryer heats the resin and absorbs its moisture. Sufficient airflow maintains the resin at the proper temperature for its entire residence time. The data in the figures below were obtained using airflow of 0.25 cubic foot per minute (cfm). This was sufficient for the relatively small (200 pound capacity) dryer used in the experiments. Commercial production facilities typically require higher air volumes and generally use 0.5 – 1.0 cfm/pound of resin. NatureWorks LLC recommends consulting your dryer manufacturer and obtaining their recommendations for minimum airflow for their dryer design. A volumetric flow indicator is also recommended to monitor airflow.

In laboratory experiments, NatureWorks LLC measured the drying times for various grades of PLA at different drying air temperatures. Figure 1 below shows four different drying curves.
Drying Curve

![Drying Curve Graph]

**Figure 1:** Drying curve of PLA pellets at various drying temperatures. Airflow volume rate was 0.25 cfm/lb of pellets. The air dew point was -40°F.

From the curves above, one can extract drying half times \((t_{1/2})\), which is the time required for the PLA resin to reduce its moisture concentration to one half the initial value. The drying half times of amorphous and crystalline PLA resin are listed in **Table 1** below.

<table>
<thead>
<tr>
<th>PLA Product &amp; Temperature</th>
<th>Drying Half Time ((t_{1/2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Amorphous Resin</strong></td>
<td></td>
</tr>
<tr>
<td>40°C</td>
<td>4.0 hr</td>
</tr>
<tr>
<td><strong>Crystalline Resin</strong></td>
<td></td>
</tr>
<tr>
<td>40°C</td>
<td>4.3 hr</td>
</tr>
<tr>
<td>50°C</td>
<td>3.9 hr</td>
</tr>
<tr>
<td>60°C</td>
<td>3.3 hr</td>
</tr>
<tr>
<td>70°C</td>
<td>2.1 hr</td>
</tr>
<tr>
<td>80°C</td>
<td>1.3 hr</td>
</tr>
</tbody>
</table>

**Table 1:** Drying half times for Ingeo biopolymer resin with dry air (-40°F dew point) at 0.25 cfm/lb

Drying times are determined by measuring the initial moisture content and using the drying half time values in **Table 1**. The half time is the time in hours it takes for the moisture level in PLA to drop to \(1/2\) of its initial value. For example, to dry PLA with an initial moisture content of 1600 ppm down to 200 ppm at 175°F (80°C) would take approximately 3.9 hours. For this example, it would take 1.3 hours to drop the moisture level from 1600 ppm to 800 ppm. It would then take an additional 1.3 hours to drop the moisture from a level of 800 ppm to 400 ppm. Finally, it would take an additional 1.3 hours to drop the level from 400 ppm to 200 ppm, for a total of 3.9 hours at 175°F (80°C). Other times and temperatures may be appropriate depending upon the initial moisture level and time available for drying. Amorphous PLA resin should never be dried above 40°C, in order to prevent resin blocking in the dryer.
Another best practice for minimizing moisture related degradation of PLA is to dry any additives, if possible, such as colorants, master batches, or regrind that could potentially contribute moisture to the base resin. If any portion of the formulation is hygroscopic, it must be dried according to the supplier's recommendation. Some non-hygroscopic components may not have to be dried if their equilibrium moisture content and percentage of the formulation are small. Any amorphous regrind should be either crystallized prior to drying, or should be dried at 40°C with low dew points to prevent resin blocking in the drier. Consult NatureWorks' “Drying and Crystallizing” guide for more information.

Notes

1. Typical desiccant dryer regeneration temperatures may exceed the melting point of PLA resins. To prevent issues with pellet bridging, sticking, or melting, the drying system operation should be verified to ensure temperature control is adequate during operation, as well as during regeneration cycles since valve leakage is common in many systems.

2. The above recommendations are based using resin taken from boxes at 400 ppm moisture or less. Actual drier performance may vary and resin moisture level after drying should be measured.

6.0 Melt Processing & Preform Manufacturing

Prior to introducing PLA into any melt processing system, the equipment should be properly cleaned and purged to prevent any polymer cross contamination. Insure that the feeding and blending equipment is thoroughly clean and free from dust and contamination, and all metal magnates have been wiped clean. Insure that all hang-up areas such as elbows, transitions, and slide gates have any and all dust and granules completely removed. The purging procedures below are recommended for optimal removal of other polymers. Injection molding machines with shooting pots can take some extra time to purge due to added areas where PET can hang up.

6.1 PLA Purging Procedure

Following PET, PA, or HDPE in your system

1. Purge with low MI (<1) PP at normal PET operating temperatures. Purge 10-30 minutes as necessary. Let system empty as much as possible. Clean out hopper as much as possible.
2. Introduce a high melt flow PP (5 - 8 MI) and change to normal PLA operating temperatures.
3. Purge 10-30 minutes as necessary. Let system empty as much as possible.
4. Alternatively, you can purge with a high flow PETG (similar to Eastman copolymer 6763). Then reduce temperatures to PLA conditions.
5. Stop injection molder and completely clean all hoppers, elbows, slide gates, dryers, hopper loaders bins, hopper loader filters and material conveying lines of residual PET, PA or HDPE and PP. Load PLA into material handling system.
6. Transition to purge PLA and purge until melt is clear of any contamination. Base PLA melt should be clear. If it is opaque, then contamination is still present.
7. At the completion of the run, purge all PLA from the extrusion system, using a moderate to low melt index PP, immediately after completion of the production run.

Notes

1. It is critical that all drying, conveying, and receiving systems be free of all PET or PP and is vacuumed to ensure that there is no remaining polymer dust, residual pellets, or other contamination, before adding PLA. PET will not melt at PLA operating temperatures and will block screens if it is present in the system.
2. The brand of PP used for purging is unimportant, as long as it does not thermally cross-link.
3. The use of a purging compound may also work in place of another thermal plastic to purge any PET in the system. To ensure the best results with this approach, please follow the recommendations of the purge compound and consult with the purge compound manufacturer.
6.2 Injection Mold Machine Recommendations

Ingeo 7001D biopolymer will injection mold on most conventional equipment designed for the injection molding of PET preforms. Typical molding conditions are listed below.

<table>
<thead>
<tr>
<th>Typical PLA Molding Conditions &amp; Parameters*</th>
<th>Barrel Temperature Setting, °F (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed throat</td>
<td>70 (20)</td>
</tr>
<tr>
<td>Feed Section</td>
<td>355 (180)</td>
</tr>
<tr>
<td>Compression Section</td>
<td>410 (210)</td>
</tr>
<tr>
<td>Metering Section</td>
<td>415 (213)</td>
</tr>
<tr>
<td>Hot Runner</td>
<td>415 (213)</td>
</tr>
<tr>
<td>Nozzle Tips</td>
<td>420 (216)</td>
</tr>
<tr>
<td>Mold</td>
<td>77 (25)</td>
</tr>
<tr>
<td>Screw Speed</td>
<td>50-100 rpm</td>
</tr>
<tr>
<td>Back Pressure</td>
<td>150-200 psi</td>
</tr>
<tr>
<td>Mold Shrinkage</td>
<td>0.004 in/in +/- 0.001</td>
</tr>
</tbody>
</table>

*Please note that these temperatures are only starting points and may need to be optimized.

Since PLA has a lower glass transition temperature than PET (~ 136°F or ~58°C for PLA vs. ~167°F or ~75°C for PET), one may experience longer cooling times for the parts to set up in the mold. Finding an optimum mold temperature is recommended in order to get the best quality preforms at the shortest cooling times. Plate-out of lactide can occur over time if injection speeds are not optimized, and/or mold temperature is too cold. Robot-take offs or indexing machines can also help with part cooling and cycle times.

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 the frozen-in stresses. This will help keep shrinkage in the preform low during reheat. A polarized light box can be used to understand the stresses in the preform.

Hot runners are also acceptable for injection molding PLA preforms. However, this will depend on the type of injection molding machine and hot-runner system being used. This is because hot runners are typically designed for a specific temperature differential (delta T) between the heated manifold and the water cooled mold plates. Since PLA processes at a lower temperature than PET, modifications may be needed to the hot-runner to account for proper metal thermal expansion to prevent resin leaking between the hot runner nozzle and manifold. Consult your equipment manufacturer to ensure your hot runner is designed for properly processing PLA resin. PLA cannot be processed at PET temperatures, since at this temperature significant thermal degradation can occur.

For more information on PLA behavior data for injection molding, please refer to the report by Mold Flow Labs located on the NatureWorks LLC website (www.natureworksllc.com).

6.3 Mold/Tooling Recommendations

For the injection mold it is recommended that both the core and cavity be polished. Stainless steel that is hardened is best, especially for molds running full production and for long periods of time. Other tooling parts should be corrosion resistant.

6.4 Preform Design

Preform design is critical in getting a container with good material distribution, clarity and physical properties. Designing a preform for use as a PLA container is, to an extent, specific to the blow mold equipment, bottle design, and mold tooling. Most likely, a preform design used for PET will have to be changed in order to run PLA. It is typical to use a PET preform design on
the first PLA trial to better understand where changes in the design will need to be made. As a starting point, however, 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 blow molding of the desired container. A preform designed with a thinner end-cap might also be desired in order to prevent excess material accumulating in the base of the blown container; however this will depend on machine, bottle, and design considerations.

If the container has issues, for instance, with stress whitening and material distribution that cannot be alleviated through processing, then a change in the preform might be necessary. An understanding of the problem and issues in the container is a must if an accurate re-design of the preform is to be successful. If there is no one available at the production facility with experience in preform design, then contacting a professional consultant or someone with experience in designing preforms for ISBM containers will be essential.

6.5 Additives

Colorants and slip agents can be added as a masterbatch (typical concentrations of 10-30%wt in PLA) by dry blending with the neat resin in the required amount and adding the blend to the injection molder. The addition of colorants and reheat additives has been successfully done using liquid injection additives/technology and also wax prill type additives. The addition of a reheat additive can be helpful for the two-stage process to help establish sufficient heating of the inner wall surface of the preform during the reheat step before blow molding. This is especially the case for smaller blow molding machines with short oven lengths. A reheat additive may or may not be needed for single-stage operations. Since PLA is not compatible with most incumbent resin materials, it is important that all additive master batches use PLA as the carrier system. Some potential additives are inappropriate for extrusion with PLA because they are hygroscopic or hydrated salts (e.g. calcium carbonate) that would lead to severe PLA molecular weight degradation and property loss. In some cases, slip or process aids may be used to help improve PLA’s frictional properties for such things as improve preform loading and preform/bottle transferring in machines or filling lines.

7.0 Blow Molding

7.1 Reheating of Preforms

The heating of the preforms is critical in getting a container with good clarity and material distribution. Normal preform temperatures when running on a two-stage process have been in the range of 176-203°F (80-95°C). The correct preform temperature may be lower or higher, depending on the preform design, bottle design, and re-heating equipment being used. Reheat additives or dark toners/colorants may also change the preform temperature needed.

Because the heating of the preform is done using infrared heaters, the outside wall of the preform is heated first and, in general, to a higher degree than the inner wall. The inside of the preform, however, stretches to a greater extent and must be heated to the proper temperature before blowing. In order for the inner wall to get to the proper temperature, the preform should have adequate equilibration time in order for the preform wall temperature gradient to be more uniform. The needed equilibration time will depend on the preform wall thickness and blow molding machine being used. It is recommended that total oven length be adequate enough to provide enough equilibration time for even heating to occur throughout the preform. Also the addition of a reheat package might be useful. In order to prevent or minimize heat uptake in the finish or thread area of the preform, it is recommended that adequate shielding be used to protect against thermal deformation.

PLA is more sensitive to changes in blow molding process temperature versus PET. Figure 2 above shows that small changes in preform temperature (+/- 2-5°C) can significantly change where the material will go in the finished bottle. As the preform temperature increases, so does the base weight of the container. This means that establishing the correct oven profile is important for optimizing bottle material distribution and properties. For PLA, small changes in lamp output will affect the material distribution upon stretching and blowing. Consistent oven temperature control is important for PLA blow molding to help establish a consistent and robust blow molding process.

Preforms made out of PLA are less ductile and slightly more brittle than PET. Care should be taken during preform manufacturing, shipping, and storage. For example, during injection molding the preform drop height should be minimized to prevent damage. A soft-drop system is a practical method for handling preforms. Care should also be taken during preform unloading. Also, PLA preforms should not be mixed with PET preforms for obvious processing and quality reasons, since they process at different temperatures and conditions.
7.2 Blow Molding Containers

In most instances, PLA does blow slightly different than PET. As mentioned earlier, the overall temperature profile of the preform will be lower for PLA. Secondly, the extensional viscosity of PLA is lower, as well. This means that PLA will stretch easier than PET, so blow timing, blow pressures, and stretch rod speed will need to be optimized in order to get a bottle with good material distribution and properties.

What most customers notice when they first run PLA on their ISBM equipment is the difference in where material ends up in the final bottle. Most of the time the first few bottles that are made by a new user of PLA will end up being heavy in the base area and thin in the panel. One can help alleviate this problem by lowering the overall heating output of the machine. If this still does not work, then adjusting the preblow timing so that it comes on earlier will tend to help keep material in the sidewall and out of the base region. The downside of bringing the preblow on earlier is that the gates can tend to wander off-center. If this is the case, then if possible, increases in the stretch rod speed may help the gate come back on center. Stretch rod speeds are typically 1.2-2.0 m/sec for PLA. A machine with separate pre-blow and high blow pressures helps to better control material distribution during processing and final bottle.

Because PLA has a lower extensional viscosity than PET, it flows into mold detail very well which makes it conducive for molding of bottles with a significant amount of detailed artwork in the bottle design. This high detail feature might warrant changing the mold design such that vent holes and parting lines would not be as apparent on the container. This is especially the case if the blow mold has seen wear. If possible, lowering the blow pressures may help minimize excessive mold detailing. Also, the blow molder should avoid bottles designs which have sharp/aggressive corners or edges which may act as weak spots.

The glass transition temperature of PLA is ~131-137°F (~55-58°C). This presents some possible challenges in cooling of the bottle in the mold. This is especially true for the base of a bottle. Usually, the base of any given bottle has a thicker material distribution than the sidewall. This thick area in the bottle needs to be distributed well and cooled quickly. This helps keep the base from deforming because the material is still warm in this area. A base design that includes ribs and a pushup for reinforcement can help to improve drop impact. Other than the base of the mold, which should be kept as cool as possible, the rest of the mold can be set for a temperature range ~70-100°F (21-38°C). Sharp or aggressive corners and edges should be avoided for the base design.

The glass transition temperature also represents the maximum temperature at which the plastic bottles should be stored and/or shipped. Shipping and storage temperatures >104°F (>40°C) should be avoided, along with excessive humidity levels. This is also true for preform shipment and storage.

8.0 Barrier Properties

At a similar thickness, PLA bottles exhibit higher transmission rates for water vapor, carbon dioxide, and oxygen by a factor of 8-10 times that of PET. However, PLA has lower oxygen transmission rates versus olefins. Table 2 below shows these differences. These water and gas transmission rate differences may present challenges to the packaged product depending on the product and its shelf-life requirements. Because of this, proper testing for any products packaged in PLA bottles and containers should be done in order to ensure fit-for-use and required shelf-life requirements are met.

<table>
<thead>
<tr>
<th>Resin</th>
<th>OTR*</th>
<th>WVTR*</th>
<th>CO2*</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA</td>
<td>38-42</td>
<td>18-22</td>
<td>201</td>
</tr>
<tr>
<td>PP</td>
<td>150-800</td>
<td>0.5-0.7</td>
<td>150-650</td>
</tr>
<tr>
<td>PET (OPET)</td>
<td>3-6.1</td>
<td>1-2.8</td>
<td>15-25</td>
</tr>
<tr>
<td>HDPE</td>
<td>130-185</td>
<td>0.3-0.4</td>
<td>400-700</td>
</tr>
</tbody>
</table>

Note: Units are cc-mil/100 sq. in-day for O2 and CO2; water vapor transmission rate in grams-mil/100 sq. in-da

Table 2: PLA permeability vs. common polymers
Safety and Handling Considerations

Safety Data Sheets (SDS) for Ingeo biopolymers are available from NatureWorks. SDS’s 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. SDS’s are updated regularly; therefore, please request and review the most current SDS’s 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. Pellets or beads may present a slipping hazard.

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. 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.

Good general ventilation of the polymer processing area is recommended. At temperatures exceeding the polymer melt temperature (typically 175°C), 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 recommended for melt operations. Use safety glasses (or goggles) to prevent exposure to particles, which could cause mechanical injury to the eye. If vapor exposure causes eye discomfort, improve localized fume exhausting methods or use a full-face respirator.

The primary thermal decomposition product of PLA is acetaldehyde, a material also produced during the thermal degradation of PET. Thermal decomposition products also include carbon monoxide and hexanal, all of which exist as gases at normal room conditions. These species are highly flammable, easily ignited by spark or flame, and can also auto ignite. For polyesters such as PLA, thermal decomposition producing flammable vapors containing acetaldehyde and carbon monoxide can occur in almost any process equipment maintaining PLA at high temperature over longer residence times than typically experienced in extruders, fiber spinning lines, injection molding machines, accumulators, pipe lines and adapters. As a rough guideline based upon some practical experience, significant decomposition of PLA will occur if polymer residues are held at temperatures above the melting point for prolonged periods, e.g., in excess of 24 hours at 175°C, although this will vary significantly with temperature.

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 option is to recycle into the process 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. Disposal must be in compliance with Federal, State/Provincial, and local laws and regulations.

Environmental Concerns

Generally speaking, lost pellets, while undesirable, are benign in terms of their physical environmental impact, but if ingested by wildlife, 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 environment.

Product Stewardship

NatureWorks has a fundamental duty to all those that 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
Injection Stretch Blow Molding Ingeo Biopolymer

environmental information on our products and their intended use, and then take appropriate steps to protect the environment and the health of our employees and the public.

Customer Notice

NatureWorks encourages its customers and potential users of its products to review their applications from the standpoint of human health and environmental quality. To help ensure our products are not used in ways for which they were not intended or tested, our personnel will assist customers in dealing with ecological and product safety considerations. Your sales representative can arrange the proper contacts. NatureWorks literature should be consulted prior to the use of the company’s products.

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