NatureWorks

Ingeo™ Extrusion Blow Molding

1.0 Using Additives for Improving EBM Bottle / Container Performance

This document is designed to provide an overview of using Ingeo along with extrusion blow molding technology to produce Ingeo based bottles or containers. This information is intended to be used only as a guide and because production of extrusion blow molded bottles can be a complex process, an experimental approach may be required to achieve desired results.

2.0 Background

Ingeo 7001D and 7032D grades are for bottle applications where the process utilizes injection stretch blow molding (ISBM). This method of bottle manufacturing involves the injection molding of a preform, and then reheating, stretching, and blowing it into the desired container shape. The orientation achieved as the perform is warmed slightly above Tg in this process helps to achieve bottle strength, toughness, and good wall thickness and material distribution control.

Another method for making bottles is called extrusion blow molding (EBM). EBM is a process where resin is extruded through an annular die to create a molten parison. The parison is then clamped between two halves of a cold mold where it is blown into a bottle and trimmed for labeling, filling, and packaging. EBM is a relatively economical way to produce bottles that go into many different types of applications (i.e. - liquid food, cosmetics, pharmaceutical, toiletries, household chemicals, oil). The majority of EBM bottles are made using HDPE, but other polymers such as PP, PVC, PETG, and PC are also used. While stretching occurs in the EBM process, it happens well above the glass transition temperature (Tg) of the polymer and because of this, as the polymer cools there is very little orientation imparted into the bottle. In general, the inherent physical properties of the polymer (flex modulus, ductility, crystallinity level) give an EBM container its required processing and performance characteristics. Comparing PLA for EBM versus ISBM, the lack of strain-hardening in EBM means there is no enhancement of the properties for EBM bottles like that which happens during ISBM bottle manufacturing.

Past work with PLA in EBM has shown that the material lacks adequate melt strength and drop impact properties to make any useful bottle for practical applications development and commercialization. However, new developments in additive technologies for biopolymers have changed these characteristics. In particular, there have been additives which help to enhance processing and impact properties for Ingeo, such as melt strength enhancers, impact modifiers, and also polymer blends.

3.0 Additive Technology

There has been a lot of recent activity around providing additive technologies to change the physical and / or thermal property characteristics of biopolymers and in particular, for Ingeo grades. Additives can be introduced into an Ingeo based system in two ways. One method involves the use of additive master batches that are blended directly in the forming extruder, in this case, an EBM machine. An alternative approach takes the additives either in raw or masterbatch form and blends them into Ingeo using a compounding extruder; generally a twin screw compounder. In this application study, commercially available additives were used both via masterbatch during EBM processing and also as a fully compounded product. Table 1 is a list of additive options that were used for producing bottles in this analysis, and Table 2 gives the details for the bottle production on the EBM machine.

Table 1: List of Masterbatch / Compound Options for Ingeo Biopolymer++

Supplier	Additive	Loading (%wt)	Description
Teknor Apex (Terraloy 90003A)	Arkema Biostrength 150	50	Master batch; opaque impact modifier; not FDA compliant for food contact
Teknor Apex (Terraloy 90000A)	Arkema Biostrength 280	50	Master batch; clear impact modifier; FDA compliant up to 10%
Teknor Apex (Terraloy 90001A1)	Arkema Biostrength 700	30	Master batch; clear melt strength enhancer; FDA compliant
Plastic Color Corp.	Blue toner	< 1	Master batch for color correction
Eastman	Titanium Dioxide (TiO_2)	2.5	Master batch for whitening / opacity
NatureWorks compounded	Ingeo 7001D DuPont Biomax Thermal Arkema Biostrength 150 TiO2 opacifier	87.5 5 5 2.5	Blend compounded on 40-mm Leistritz twin screw extruder

++For guidance on any additive or masterbatch use and/or its limitations, contact the appropriate supplier for more information.

Table 2: EBM Processing Approach

Machine / Extruder • Bekum H121 shuttle • 2 cavity • 75 HP Screw • 3.5” x 24:1 L/D • Xaloy Fusion screw Bottle • 610 cc, oblong • 58 mm finish • 45 – 47 g	Ingeo 7001D resin Additives • Melt strength • Impact • Colorant Evaluation • Parison strength • Processing • Drop impact

Samples were made at R&B Plastics Machinery in Saline, MI utilizing their EBM lab equipment. Only one mold was used during this processing run. The Ingeo 7001D base resin used was dried prior to extrusion along with all of the master batches. The master batches also used Ingeo resin as the carrier material. All drying, conveying lines and storage equipment was thoroughly cleaned before any Ingeo resin was introduced into the system. Also, the extrusion machine was properly purged to expel polymer out of the system to prevent polymer cross-contamination. Refer to the Ingeo resin drying and machine purging guides for further information on how to properly handle and dry the resin.

The extrusion conditions in **Table 3** were used to process the Ingeo material. Depending upon the EBM system, these conditions may need to be optimized for different runs based on the resin or blend material, equipment, & tooling being used.

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Table 3: Ingeo EBM Process Conditions

Process Parameter	Condition
Feed Throat	106°F (41°C)
Extruder Zone 1	350°F (177°C)
Extruder Zone 2	360°F (182°C)
Extruder Zone 3	370°F (188°C)
Extruder Zone 4	380°F (193°C)
Adapter	370°F (188°C)
Die Head Zone 1	350°F (177°C)
Die Head Zone 2	350°F (177°C)
Die Tip Zone 3	355°F (179°C)
Melt T	400°F (204°C)
Mold T	50°F (10°C)

4.0 Summary / Results

A summary of the data is shown in **Table 4**. The results show that 100% PLA containers made during this run had poor drop impact properties, since no bottles passed at a filled drop height of 3 or 4 feet, respectively. The melt strength enhancers did improve die swell and helped create a more robust parison for better blow molding and process control, however this effect was not quantified in the table.

The drop impact did improve when using Arkema's Biostrength 280 at 5%wt active loading and greater. However, Arkema's Biostrength 150 opaque modifier at 5%wt active loading did not change the filled impact performance. Only when the Biostrength 150 was used at the 10%wt and greater loading did it significantly improve impact performance.

The blend of the Biomax Thermal at 5%wt active level and the Biostrength 150 at 5%wt active level had good drop impact properties, where all 10 samples passed at a 4 foot filled drop height. These bottles were opaque in appearance, as well as the bottles that were made using Arkema's Biostrength 150 opaque impact modifier. The bottles made using Arkema's Biostrength 280 clear impact modifier were clear and transparent in appearance.

Table 4: EBM Sample Runs at R&B Plastics Machinery

Run No.	Resin	Additive(s)	Levels (% active)	3 ft Filled Drop (n=10)	4 ft Filled Drop (n=10)	Water Loss, g/day (23°C/50%RH)	Water Loss, g/day (40°C/10%RH)
HDPE	Chevron Marlex C579 (HDPE 0.35 MI)	-	-	-	10/10 Pass	0.03	0.01
1	7001D	-	-	0/10 Pass	0/10 Pass	0.08	0.31
2A	7001D	Clear MS* Clear IM**	2.5 5	7/10 Pass	5/10 Pass	0.08	0.28
2B	7001D	Clear MS Clear IM	5 10	-	10/10 Pass	0.09	0.32
2C	7001D	Clear MS Clear IM	2.5 12.5	-	10/10 Pass	0.10	0.34
3A	7001D	Clear MS	2.5	1/10 Pass	1/10 Pass	0.08	0.28

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		Opaque IM+	5				
3B	7001D	Clear MS Opaque IM	5 10	-	10/10 Pass	0.08	0.28
3C	7001D	Clear MS Opaque IM	2.5 12.5	-	10/10 Pass	0.08	0.30
4	7001D	Biomax Thermal Biostrength 150	5 5	-	10/10 Pass	0.08	0.27

*denotes Arkema Biostrength 700 melt strength additive (MS)

**denotes Arkema Biostrength 280 impact modifier (IM)

+denotes Arkema Biostrength 150 impact modifier (IM)

EBM Samples Using Ingeo Biopolymer

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 175ºC), 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 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.

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NatureWorks
15305 Minnetonka Blvd., Minnetonka, MN 55345