NatureWorks

Solubility Study of Ingeo Biopolymer Grades in Common Organic Solvents

Introduction

This study was conducted to provide meaningful solubility data for Ingeo™ poly(lactide), PLA, biopolymer grades in different common organic solvents to assist internal and external researchers working with these materials. The Ingeo grades selected for this study span crystalline/crystallizable grades (e.g., 4032D), to very slowly crystallizing, essentially amorphous grades (e.g., 4060D).

Experimental

Each Ingeo PLA sample was prepared as a 10% (wt/vol) mixture, whereby ~3 g of PLA was added into a 40 mL glass vial and the weight recorded to four decimal places. Several vials were prepared at the same time for a selected solvent. To each glass vial was then added 30 mL of an appropriate solvent. Vials were then capped and placed onto a shaker bath, set at 175 rpm, and left to shake for various amounts of time at room temperature.

For samples that were heated during dissolution, a stir bar was placed in the 40 mL scintillation vial. The vials were then placed into a heating block set to 65 °C and stirred for varying amounts of time.

Sampling of vials was accomplished by removing ~1 g of liquid from the vials, which was then added to a scintillation vial and accurately weighed. After the addition of 1,3-butanediol internal standard to scintillation vial, the contents were exhaustively hydrolyzed in 1M methanolic potassium hydroxide solution at 65 °C for 1 hr. After cooling, the hydrolysate solution was diluted with acetonitrile solvent and derivatized with BSTFA (BSTFA= bis(trimethylsilyl) trifluoroacetamide) silylation reagent to form the trimethylsilyl derivatives of internal standard and lactic acid, which are separated by gas chromatography (GC) and detected by flame ionization detector (FID). Method quantifies wt% total lactic acid equivalents in each dissolution solution. Since all lactic acid equivalents in these solutions originate from PLA, one can simply divide evaluated wt% total lactic acid equivalents by 1.25 to obtain wt% PLA (i.e., hydrolysis of 1.0 g PLA yields 1.25 g lactic acid).

Results

The different Ingeo grades studied along with the physical forms evaluated and measured properties of note to this study are specified in **Table 1**.

Table 1

INGEO GRADE	EVALUATED %D LACTIC ACID CONTENT BY GC/FID	PHYSICAL FORM	CRYSTALLINE?	EVALUATED CRYSTALLINITY (J/G) BY DSC
4060D	12.0	pellets	no	0
2003D	4.5	pellets	yes	33.3
2003D	4.5	injection molded bars	no	0
4032D	1.6	pellets	yes	44.3
4032D	1.6	Injection molded bars	yes	9.1

Found in **Table 2** are organic solvents used in this study.

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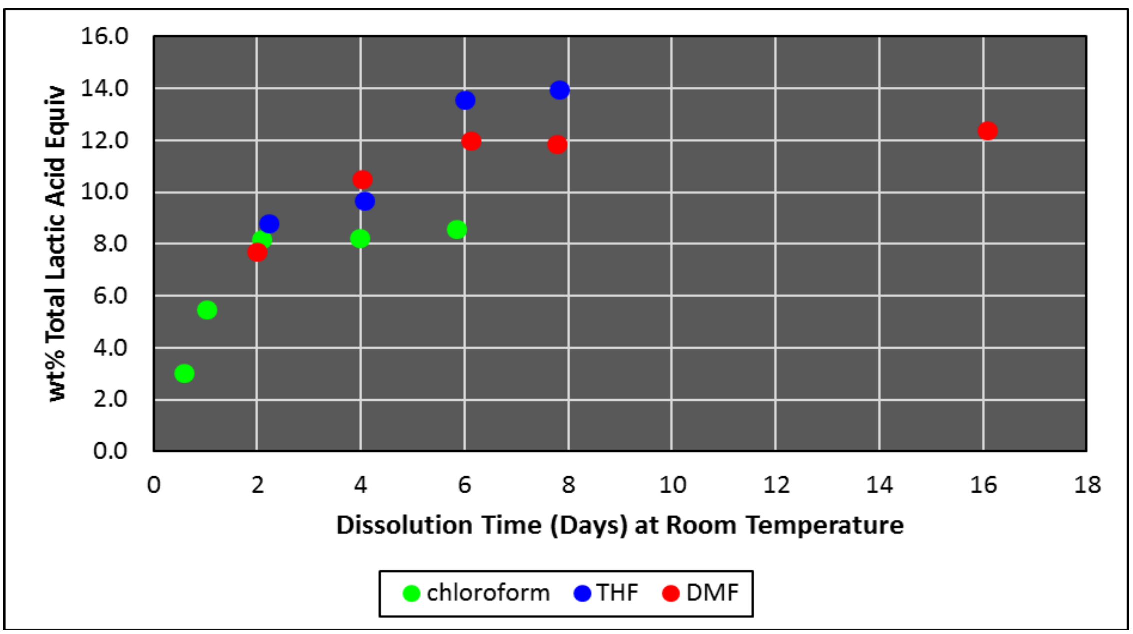
Table 2

SOLVENT NAME	BOILING POINT (°C)
acetone	56
chloroform	61
cyclohexane	81
dimethyl formamide (DMF)	153
ethyl acetate	77
tetrahydrofuran (THF)	66
toluene	111

The first series of experiments were focused on the evaluation of time to achieve 10% wt/vol solution of the different Ingeo grades in the organic solvents identified in **Table 2**. The first Ingeo grade studied was 4060D, which has the highest %D lactic acid content of all commercial Ingeo grades, 12, and is considered to be an amorphous material.

Except for cyclohexane, where no measurable solubility was observed, all the solvents tested were found to fully dissolve 4060D and generate 10% wt/vol solutions. **Figure 1** compares the dissolution curves for 4060D in chloroform, DMF and THF solvents at room temperature.

Figure 1



The fastest dissolution was achieved using chloroform, while the slowest dissolution was observed using toluene. No testing was conducted to evaluate the solubility limit of 4060D, since it was thought that the high viscosity of such solutions would limit their value, for example, in accurately and reproducibly casting films.

4032D is an Ingeo grade of much lower %D lactic acid content than 4060D and is readily crystallized to achieve high levels of crystallinity. Dissolution studies were conducted on 4032D pellets, as produced in NatureWorks production facility in Blair, NE, and as injection molded bars of 4032D which were quickly cooled from the melt to limit the time for the development of crystallinity. The injection molded bars made and studied were of much lower crystallinity that the corresponding pellets, 9.1 J/g versus 44.3 J/g, respectively. Regardless of the crystalline content, both 4032D samples were readily transformed to 10% wt/vol solutions in chloroform in 2-4 hours at room temperature. None of the other solvents listed in Table 2 were found to dissolve significant quantities of the two 4032D samples when dissolution was conducted at room temperature, where all solutions regardless of hydrolysis times up to 10 days contained <1 wt% total acid equivalents. During the dissolution experiments with the low crystallinity injection molded bars, it was observed that the bars were transformed from clear to cloudy in appearance as dissolution time progressed. This is an indication that the material crystallized during the attempted dissolution as a consequence of solvent plasticization.

In a second part to this dissolution study of 4032D, samples were heated to 65°C during dissolution, above the ~60°C glass transition temperature (Tg) of PLA, to evaluate if higher concentrations could be achieved with solvents other than chloroform. Table 3 compares solubility results obtained using different solvents.

Table 3

SOLVENT	4032D PELLETS (Crystalline; 44.3 J/g)		4032D INJECTION MOLDED BAR (Lower Crystallinity, 9.1 J/g)	
	wt% Total Lactic Acid Equivalents	Time (Days)	wt% Total Lactic Acid Equivalents	Time (Days)
acetone	0.29	3	0.86	3
DMF	5.63	3	7.74	3
ethyl acetate	0.29	3	0.63	3
THF	9.31	1	6.58	1
toluene	0.08	3	0.06	3

The wt% total lactic acid equivalents reported is either the thermodynamic limited value (saturated solution value) or the kinetic limited value (based on crystallization of amorphous resin). Significant concentrations (4-7% wt/vol) of 4032D, whether of low or high crystallinity, can be obtained in DMF and THF heated to 65°CçSimilar to the study conducted at room temperature, it was again observed that the clear and low crystallinity injection molded bar of 4032D became cloudy during the course of the experiment, indicating that the material had crystallized during attempted dissolution. No measurements were conducted on the insoluble material remaining in the vials.

The final Ingeo grade studied is 2003D, a thermoforming grade with D lactic acid content between that of 4032D and 4060D, ~4.5%. 2003D crystallizes much slower than 4032D. Drastic differences in the solubility of the amorphous injection molded bar and crystalline pellets was observed in such solvents as THF at room temperature, where an 8.5% wt/vol solution was achieved for amorphous sample and only 0.8% wt/vol solution for the crystalline pellets.

Conclusions

Of the solvents studied, chloroform is the best solvent for quickly preparing 10% wt/vol solutions of all Ingeo grades and morphologies.

Only the Ingeo grade with the highest D lactic acid content, which is non-crystallizable, 4060D, is readily soluble at room temperature in all the organic solvents studied, other than cyclohexane, to prepare 10% wt/vol solutions.

Plasticization and crystallization of Ingeo 4032D during attempted dissolution prevents solubilization in many of the solvents studied, and crystallization from solution proceeds once solubility limit is achieved at a given temperature.

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.

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.

NOTICE REGARDING PROHIBITED USE RESTRICTIONS: Unless specifically agreed to in writing by NatureWorks, NatureWorks LLC will not knowingly sell or sample any product into any of the following commercial or developmental applications (i) components of or packaging for tobacco products, (ii) components of products intended for human or animal consumption, (iii) any application that is intended for any internal contact with human body fluids or body tissues, (iv) as a critical component in any medical device that supports or sustains human life, (v) in any product that is designed specifically for ingestion or internal use by pregnant women, (vi) in any application designed specifically to promote or interfere with human reproduction, (vii) in microbeads, including those used in personal care/cosmetic applications, or (vii) to manufacture bottles or bottle pre-forms in North America.

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