Technology Focus Report: Polylactic Acid Containing Fillers and Fibers*

Introduction:

The grades of polylactic acid (PLA), as supplied by NatureWorks LLC, are not modified with fillers or fibers. The physical and rheological properties contained in the available specification sheets are those of the natural polymer and are representative of PLA in the amorphous or crystallized form, depending on the polymer grade. This document is designed to provide an overview, as well as a starting point, for end-users of PLA who would like to modify the polymer's physical or rheological properties with fillers or fibers. It is not intended to be a step-by-step procedure to obtain specific properties, nor be a processing guide for machine operation.

PLA has the ability to be stress crystallized, thermally crystallized, impact modified, filled, co-polymerized and processed in most polymer processing equipment. It can be formed into transparent films or injection molded into blow moldable preforms for bottles, similar to PET. PLA also has excellent organo-leptic characteristics and is excellent for food contact and related packaging applications. In addition, the starting material for the polymer, lactic acid, is made by a fermentation process from 100% annually renewable resources. The polymer will also bio-degrade in a compost environment and the byproducts are of very low toxicity, eventually being converted to carbon dioxide and water. The published literature on PLA is extensive and has been reviewed in detail in several recent publications.[1]

Background:

Although PLA has an excellent balance of physical and rheological properties, many additives have been combined with it to further extend the range of properties achievable and thus optimize the material for specific end use applications. This document focuses on fillers and fibers. The most common fibers that have been combined with PLA are glass fibers and a limited selection of natural fibers including wood fibers, and certain annually renewable plant fibers such as flax and kanaf. Fillers that have been have shown to afford beneficial properties with blended with PLA include talc, mica, kaolin, glass (milled/flaked), a variety of inorganic carbonates and sulfates, as well as starch. Nanocomposites of PLA with various Angstrom sized inorganic particles and platelets have been reported in the literature,[2] but this technology is in the early stages of development and will not be covered in this document.

In order to derive the maximum benefit from the fiber or filler additives, several factors must be considered. Regardless of the additive, good (uniform) dispersion must be achieved. This is normally obtained by controlled addition of the additive during melt mixing in a twin screw extruder or high intensity batch mixing device.[3] Visual inspection can detect poor mixing, but often microscopy techniques are required to assure that the additives are not associated in macro-clumps which can lead to rheological problems or a decrease in toughness. Optimizing the extruder screw configuration, through-put rate, RPM, temperature and other process parameters are necessary with every formulation. The particle size of the filler is important and generally particle sizes from 0.1-12 μm are used.[4] Smaller sizes have less detrimental effect on toughness and appearance, but generally cost more or can lead to dust handling problems.

Interfacial compatibility of the filler/fiber is also important in obtaining maximum benefits from the additive which will assist in dispersion and help minimize micro-defects in parts that can cause embrittlement. Coupling agents are often used with glass fibers[5] or coated fillers are used to enhance the interfacial adhesion of the additive to the matrix polymer. This is very common when polar additives are combined with non-polar polymers, but can be very useful in most systems. Silane and titinate coupling agents with various structures, depending on the polymer into which it will be blended, are often coated onto glass fibers and inorganic particulate fillers. These coupling agents can have beneficial effects on dispersion, toughness, rheology and often allow higher levels of incorporation.

Incentives and Benefits to Incorporate Fillers and Fibers:

Generally, fillers or fibers are combined with PLA to either reduce the cost in the final part or modify the physical, rheological, or optical properties of the resin. Very low cost fillers are available and if they do not detract from the end use properties of PLA, they can be a very effective route to cost reduction. Starch is an excellent example, which is available at less than $0.10/pound and which retains the renewable resource characteristics of PLA while still being bio-degradable.

Other drivers to incorporate additives include the need to improve the modulus (stiffness) at room temperature or elevated temperature. The room temperature modulus of all PLA resins can be increased by fillers or fibers, but only crystallized forms of polymers,[6] including PLA, show a significant improvement in practical use temperature with them. With some of the additives (e.g. talc), increased nucleation rates are obtained which can lead to both faster cycle times and increased crystallinity in parts and thus improved heat resistance.[7]

Problems or Issues when incorporating fillers or fibers into PLA:

The desired beneficial effects from addition of fillers and fibers do not always come without some negative consequences. High levels of fillers/fibers can significantly increase viscosity, cause shear heating and degradation (MW loss and color formation), and affect the ability to fill thin walled parts. Appearance problems are also a potential with flow lines, poor colorability, and opacity being among the issues. Many fillers have high density and PLA filled with them will require more material to fill a part. Natural fibers contain high levels of moisture and drying them to prevent PLA molecular weight loss can be difficult. Also, adding high levels of natural fiber into the extruder requires side stuffers and close attention to the operation to maintain uniform operation. The batch-to-batch variation in natural fiber composition and quality can lead to consistency problems in the final blend. Finally, when considering applications that require compostability, the effect of the filler or fiber on the rate or extent of compostability should be evaluated.

Blends with Polysaccharides

Starch:

A significant amount of work has been done optimizing PLA-starch blends for disposable and short term applications. Besides reducing costs, starch has been reported to act as a nucleating agent for PLA[8]as well as enhancing the heat resistance and modulus of the material. Generally compatibilization of the starch with the PLA is necessary to obtain an overall improvement in properties. Maleic anhydride grafted systems[9] and addition of third component compatibilizing polymers such as polyvinyl alcohol,[10] and polycaprolactone [11]have shown beneficial effects on the interfacial adhesion of the starch and improvement in properties. The level of the compatibilizer and its molecular weight affect the balance of properties in the blends. The effect of the amylose content of the starch in PLA blends has also been studied and high-amylose content starches enhance water absorption and probably accelerate bio-degradation.[12]

Cellulose:

Walnut shell flour, pine wood flour, and other sources of cellulose fiber have been blended with PLA at levels up to ca. 60% while increasing stiffness and obtaining up to 10^{o}C improvement in heat resistance. Applications such as seedling planters for trees, which require bio-degradation in a short period of time are ideal applications for these filled products.[13] For both injection molding and extrusion/thermoforming, short fibers of less than 1 mm in length were found to perform best,[Error! Bookmark not defined.] however with kenaf fibers, lengths up to 20 mm have been reported to result in improved properties, using the bast portion of the fiber.[14] Commercial products have already been introduced combining PLA and natural fibers. Toyota introduced an automobile called the Raum, in May 2003, with parts made of a plastic dubbed “Eco-Plastic,” produced by combining kenaf fibers and polylactic acid. The material, developed jointly by Toray and Toyota, is used for the vehicle’s spare tire cover as well as floor mats.[15] To increase the compatibility of natural fibers with PLA, the fibers should be degreased and chemically modified on the surface by acylation or coated with silane coupling agents.[16] Flax-PLA composites are reported to have significantly better properties than flax-polypropylene composites and have the environmental advantage of being based on 100% renewable resources.[17] Other approaches to incorporate cellulose fiber include the use of up to 25% recycled paper, blended at a melt temperatures up to 230^{o}C resulting in a pressed sheet with good stiffness and appearance.[18]

Blends with Inorganic Fillers:

Generally when PLA is filled with inorganic materials such as talc, mica, glass, etc., the system is formulated with multiple other components to optimize a balance of physical properties, processing characteristics, and appearance for specific end use applications. For example, it has been proposed that compositions for disposable cards can consist of 5-85% PLA, 5-50 % of an aliphatic polyester, 10-45% polycaprolactone, and 5-300 parts of fillers such as talc.[19] It is common to utilize the “concentrate” approach for more efficient dispersion, where the filler or anti-blocking agent is first dispersed at a higher concentration, often in another polymer or with the use of dispersing agents such as decaglycerol oleate, and then let down to the required concentration in the PLA.[20] SiO_2 of very small particle size (< 0.05 m) has been dispersed at levels up to 40% without clumping by this approach while still maintaining a haze of less than 1% in 15 m, non-blocking films when let down to lower levels. Both talc and mica can be used to increase the modulus of PLA with 10-30% added. Mica is effective at lower levels, but talc also acts as a nucleator, which is advantageous in fast cycle injection molding applications such as cutlery.[21]

Flame retarded PLA compositions have been prepared by combining PLA with a variety of fillers, flame retardants, and additional components. For example, high levels (50-150 parts) of surface treated (silanes/titinates) metal hydroxides were combined with additional fillers (talc, kaolin, mica, glass, etc.) and toughening agents to produce a composition for domestic appliances.[22] Properties of injection molded PLA containing some inorganic fillers are presented in the following table. Most fillers increase the stiffness of PLA with little benefit to toughness. The acicular calcium carbonate, EMforce[TM] Bio at 30%, resulted in a surprisingly ductile failure with high energy adsorption.[23]

Properties of Filled PLA

	Flex Modulus[b] (psi)	Dart Impact @23°C (ft.lbs)	IZOD Impact[c] (ft. lbs/In.)	
			Notched	Un-notched
Specialty Minerals MTAG**D**609 Talc @ 1.5%	571,936	2.3	0.8	6.2
Specialty Minerals MTAG**D**609 Talc @ 10%	726,130	2.1	0.5	5.1
Specialty Minerals MTAG**D**609 Talc @ 30%	1,342,439	1.3	0.5	3.3
Vicron [a] 15-15 $CaCO_3$ @1.5%	552,943	2.0	0.6	5.1
Vicron 15-15 $CaCO_3$ @10%	622,236	2.4	0.5	5.4
Vicron 15-15 $CaCO_3$ @30%	813,718	2.4	0.6	3.5
Specialty Minerals Mica 5040 @1.5%	581,908	2.3	0.6	4.8
Specialty Minerals Mica 5040 @10%	778,865	2.6	0.5	3.7
Specialty Mica 5040 @30%	1,433,271	1.6	0.6	2.3
Synthetic silicate @1.5%	559,541	2.7	0.6	5.7
Synthetic silicate @10%	630,742	2.2	0.5	4.0
Synthetic silicate @30%	836,343	1.8	0.4	2.1
EMforce[TM] Bio [a] @1.5%	562,600	2.4	0.6	3.8
EMforce[TM] Bio @10%	647,000	2.5	0.6	3.2
EMforce[TM] Bio @30%	825,470	19.8	2.3	5.5
Unmodified NatureWorks[TM] PLA 4032D	530,039	3.0	0.7	4.4

a. Trademark of Specialty Minerals. b. ASTM D 790. c. ASTM D 256-92

1 Hartmann, M.H., Biopolymers from Renewable Resources, ed. D.L. Kaplan, Chapter 13, Springer-Verlag, Berlin Heidelberg New York, 1998. Dubois, P., Jerome, R., Lofgren, A., and Albertsson, A.C., J.M.S. Rev. Macromol. Chem. Phys., C35(3), 379, 1995. Tsuji, H., Polylactides in Biopolymers, Chapter 5, Wiley-VCH, 2002. Drumright, R., Gruber, P. and Henton , D. E., Advanced Materials, 12(23), 1841, 2000.
2 "The dispersion behavior of clay particles in poly(L-lactide)/organo-modified montmorillonite hybrid systems", Journal of Applied Polymer Science (2004), 93(6), 2711-2720. Unusual Crystallization Behavior of Organoclay Reinforced Poly (L-lactic acid) Nanocomposites, V. Krikorian and D. Pochan, J. Macromolecules (2004), 37(17), 6480-6491.

3 German Patent DE 100279 A1, K. Kjeschke, R. Timmermann, and M. Voight, assigned to Bayer AG, 12/13/2001.
4 European Patent 776927 A1, S. Ikado, N. Kobayashi, T. Kurokit, M. Saruwatarim, K. Suzuki, and H. Wanibe, assigned to Mitsui Toatsui Chem, Inc., 6/04/1997.
5 U.S. patent application 20040180990 A1, T. Mochizuki and F. Suzuki, assigned to Fuji Photo Co Ltd., 9/16/2004
6 "Towards an Understanding of the heat Distortion Temperature of Thermoplastics" M. T. Takamori, Polymer Engineering and Science (1979), 19(15), 1104-1109
7 R. Bopp and J. Whelan, World Patent, WO 200316015 A1, to NatureWorks LLC 2/27/2003
8"Mechanical properties and crystallization behavior of poly(lactic acid) blended with dendritic hyperbranched polymer", J.-F. Zhang and X. Sun, Polymer International (2004), 53(6), 716-722.
9 "Mechanical Properties of Poly(lactic acid)/Starch Composites Compatibilized by Maleic Anhydride", J.-F. Zhang and X. Sun, Biomacromolecules (2004), 5(4), 1446-1451.
10 "Biodegradation of starch/polylactic acid/poly(hydroxyester-ether) composite bars in soil",R. L. Shogren, W. M. Doane, D. Garlotta, D., J.W. Lawton,and J. L. Willett, Polymer Degradation and Stability (2003), 79(3), 405-411. "Starch, Poly(lactic acid), and Poly(vinyl alcohol) Blends", T. Ke and X. S. Sun, Journal of Polymers and the Environment (2003), 11(1), 7-14
11 "Biodegradable Polymer Blends of Poly (lactic acid) and Starch", J. W. Park, D. J. Lee, E. S. Yoo, S. S. Im, S. H. Kim, and Y. H. Kim, Korean Polymer Journal, 1999, 7(2), 93-101.
12 "Blending of poly(lactic acid) and starches containing varying amylose content", T. Ke, X. S. Sun, and P. Seib, Journal of Applied Polymer Science (2003), 89(13), 3639-3646
13 European Patent Application, 0 533 314 314 A2, J. Lunt, J. Kwok, J. M. Makuc, and M. Castrlotta, assigned to Novacor Chemicals, 3/24/1993.
14 World Patent WO 200463282 A1 assigned to NEC Corp, K. Inoue, M. Iji and S. Serizawa, 7/29/2004.
15 Japan Chemical Week , 19 Feb 2004, 45 (2258), 7.
16 Japanese Patent JP 2003313417 A, assigned to Toyota, 11/06/2003.
17 "Natural Fibers as Reinforcement in PLA Composites", K. Oksman, et. Al., Composite Science and Technology, 2003, 63(9), 1317-1324.
18 "heat Resistant lactic Acid Polymer Compositions with Good Discoloration Resistance of Fillers, Their Manufacture, and Moldings Using Them"' S. Kumasawa and H. Ome, Japanese patent application JP 2005035134 A2, assigned to Toray Industries, Inc., 2/10/2005.
19 U.S. Patent Application 2002/0094444 A1, 7/18/2002, K. Nakata, M. Ishikawa, K. Shimizu, T. Daito, K. Nishimura, and T. Murakami, "Biodegradable Polyester Resin Compositions, Biodisintegrable Resin Composition, and molded Objects of These".
20 "Aliphatic Polyester Composition for Masterbatch and Process for producing Aliphatic Polyester Film with the Composition", T. Kuroki and S. Ikado, Assigned to Mitsui Chemicals, Inc., U.S. Patent 6,462,105 B1, 10/8/2002
21 Internal NatureWorks LLC data.
22 World Patent WO 200422650 A1, J. Takagi and K. Tanaka, assigned to Mitsubishi Plastics, 3/18/2004.
23 Specialty Minerals and NatureWorks LLC internal information.

Safety and Handling Considerations
Material Safety Data (MSD) sheets for PLA polymers 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 PLA polymers; 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
PLA polymers 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 recommended 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 PLA polymers. Use gloves with insulation for thermal protection when exposure to the melt is localized.

Combustibility
PLA polymers 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
NatureWorks LLC encourages its customers and potential users of its products to review their applications for such products 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 LLC literature, including Material Safety Data sheets, should be consulted prior to the use of the company's products. These are available from your NatureWorks LLC representative.

NatureWorks®

For additional information in the U.S. and Canada,
call toll-free 1-877-423-7659
In Europe, call 31-(0) 35-699-1344
In Japan, call 81-33-285-0824

15305 Minnetonka Blvd., Minnetonka, MN 55345