

Technology Focus Report: Toughened PLA

Introduction:

Poly(lactic acid) (PLA), as supplied by NatureWorks LLC, is a single, homogeneous polymer and does not contain impact modifiers. The physical and rheological properties contained in the available specification sheets are those of the natural polymer. 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 impact or ductility characteristics by blending with rubbery polymers. It is not intended to be a step-by-step procedure to obtain specific properties, nor be a processing guide for machine operation. The published literature on PLA is extensive and has been reviewed in detail in several recent publications.¹

The definition and quantification of toughness varies depending on the end use application and the expectations for its use. Toughness in a drinking cup may be resistance to cracking when squeezed, while toughness in an automobile dashboard might be plastic deformation without brittle failure in a high speed crash. Other measures of toughness are high elongation without cracking in "snap-fit" applications, resistance to crack formation and fatigue failure in living hinge parts, and low temperature ductility for outdoor applications or freezer packaging. PLA is considered to be a brittle polymer, but operations as simple as orientation during melt processing or drawing below the glass transition temperature² results in improved flexibility and ductility.

The many laboratory tests that have been developed to measure toughness have sought to reproduce conditions experienced in commercial applications. Many of the laboratory tests measure the energy to initiate a crack under certain conditions and the total energy to failure. Instrumented, hydraulically driven dart impact tests are typical of this type of equipment and have the advantage of varying the rate of testing as well. Varying the test rate is equivalent to varying the temperature of a test with high rates giving results one would experience at low temperature. In this test, a molded plaque is punctured with a dart and a load cell maps the stress strain curve from initial impact to final failure. Other tests utilized to quantify "toughness" include tensile tests, notched and un-notched pendulum impact tests such as the Notched Izod test, and simple falling dart tests, which generally give a single energy value or a pass/fail result. Each of these tests will provide information about the "toughness" of a material, but they will not all agree on which material is the "toughest". Tests that simulate the design, stress state, and end use conditions of the application are those one should select.

Background:

In order for a rubbery polymer to impart toughness to PLA or any other polymer, several criteria must be met. The rubber must be distributed as small domains (usually 0.1-1.0 μm) in the matrix polymer, the rubber must have good interfacial adhesion to PLA, the glass transition temperature of the rubber must be at least 20 $^{\circ}\text{C}$ lower than the test/use temperature, the molecular weight of the rubber must not be too low, the rubber should not be miscible with the matrix polymer, and the rubber must be thermally stable to PLA processing temperatures. If met, these factors will allow the rubber to induce energy dissipation mechanisms in PLA, which retard crack initiation and propagation and ultimately result in a material with improved toughness. PLA is similar to many polymers that can undergo plastic flow mechanisms, initiated by dispersed rubber domains.³ The increase in toughness comes from the transfer of the impact energy to plastic flow, either in the form of crazing or shear yielding mechanisms through a large volume fraction of polymer.

Generally, more toughness is obtained with increasing amounts of added rubber, but usually a threshold level must be reached before the toughness improves. In PLA, excellent toughness can be obtained with 15-25% impact modifier, but until 3-5% is added, little improvement is seen. Compounding is generally the most practical way for end-users to incorporate impact modifiers and success depends on both proper material selection and optimization of the mechanical operation.

Problems or Issues When Incorporating Toughening Agents into PLA:

The desired beneficial effects from addition of impact modifiers or elastomers does not always come without some negative consequences. Incorporating rubber into a rigid polymer always reduces the modulus proportional to the amount added. For

example, rubber modified polystyrene (HIPS) has a lower modulus than polystyrene (3000 psi vs. 6000 psi). The potential also exists for chemical interactions and degradation, due to additive or polymer interactions, leading to color formation or loss of molecular weight. Since most toughened materials are two phase blends, they will be opaque and generally not as easily colored in dark colors such as blues and blacks. However, the use of very small rubber particles and matching refractive index of the rubber to that of PLA can help maintain transparency. The addition of impact modifiers usually increases the viscosity of the system which may affect processing and require higher pressure or processing temperatures.

The main issue in producing toughened plastics is obtaining adequate dispersion (very uniformly dispersed, small domains) of an elastomer that will initiate the plastic deformation (energy absorbing) mechanisms of crazing or shear yielding. If the added rubber is not very compatible with PLA, then blending will not adequately disperse it into the PLA matrix into the required small domain sizes. In addition, even if partially dispersed during compounding, the domains of rubber are very likely to cluster during subsequent process operations, resulting in large domains which do not impact modify effectively and which can cause high die swell, surface imperfections, and property variability issues. Poor interfacial adhesion can also result in de-bonding of the rubber phase, void formation, and premature failure in a brittle mode. Additionally, some rubbers and impact modifiers are not bio-degradable and blending them with PLA will affect the compostability.

Examples of Toughened PLA Systems with Commercially Available Modifiers Natural Rubber:

Natural rubber would be a desirable impact modifier for PLA because it is a renewable resource. However, it is very incompatible with PLA and does not result in the desired improvement in toughness and has many property and appearance issues previously discussed for incompatible systems. Epoxidized natural rubber (ENR) with 25-50% of the unsaturation in the rubber functionalized with epoxy groups, is more compatible and has been shown to raise the impact strength from 0.2 to 1.0 ft-lbs/inch of notch by incorporation of 20% of the rubber.⁴ Higher levels of epoxy functionality (50%) are more effective at increasing toughness than the lower levels (25%).

Grafted Rubber Resin Blends:

Commercially, many materials are sold that contain rubber (polybutadiene and acrylic) that are chemically grafted with rigid phase polymers to compatibilize the rubber into other matrix polymers. Some materials contain low levels of rubber (5-20%), such as HIPS and ABS molding grade resins, and these materials are not very effective at significantly increasing the toughness of PLA. In some cases good alloys can be produced with other desirable characteristics. More effective at toughening are the high rubber content (35-80%) modifiers sold commercially for impact modifying other resins such as PVC, polycarbonate, and aromatic polyesters. Within this group of modifiers, styrene/acrylonitrile or methyl methacrylate grafted polybutadiene and acrylate rubber products have been shown to work very well at improving the toughness of PLA.⁵ High Notched Izod (5-15 ft-lbs/inch of notch), high elongation (> 100%), and high energy to fail in dart impact tests have been obtained with these types of products. Examples of some of these toughened blends are shown in the table below⁶.

Polyurethane Elastomer blends:

Thermoplastic urethane elastomers with both polyether and polyester soft segments have been shown to impact modify PLA at blend levels as low as 5-10%. These elastomers appear very compatible with PLA and give a good balance of properties⁶.

Aliphatic polyesters:

A variety of aliphatic, low T_g, polyesters have been combined with PLA and have shown significant improvement in ductility and impact properties. Polyhydroxyalkonates⁵, such as NodaxTM, are being developed by several companies (Metabolix and Procter & Gamble) and are one of the few renewable resource based elastomers that both toughen PLA and help retain the bio-degradability characteristics. These elastomers have been blended into PLA at levels up to 60%, with 10-20% being the preferred range. They form two phase blends with dispersed rubber domains on the order of 0.2-1.0 μm. BionelleTM is another aliphatic polyester that also toughens PLA and bio-degrades,⁶ although it is not based on 100% renewable resources. Polycaprolactone has also been blended with PLA, but does not appear to be very compatible and does not significantly increase the toughness of PLA at levels up to 20%.⁷

Aromatic/aliphatic polyesters:

Aliphatic/aromatic polyesters such as Ecoflex™ and Hytrel™ also are very compatible with PLA and increase the toughness in blends at levels of 5-30%. Even at low levels of rubber, very high elongation to fail and good impact properties are obtained ⁶.

Functionalized polyolefin elastomers:

Although standard olefin elastomers such as polybutadiene, ethylene-propylene, and EPDM elastomers are not compatible with PLA, functionalized elastomers of these structures can be blended into PLA to improve the toughness. Functionalized elastomers, such as Kraton™ FG1901X, at levels of 10-30% have shown improvements in toughness, with lower levels often providing a better balance of physical, rheological and optical properties than higher levels. ⁶

Table 1: Injection Molded Properties of PLA Containing Various Impact Modifiers.

Additive	% Additive	Notched Izod (ft-lbs/in)	Tensile Yield ^a (psi)	Elongation ^a (%)
PLA	0	0.5	9000	10
Blendex™ 415	15	0.9	6340	230
Blendex™ 360	20	2.0	6800	280
Blendex™ 338	20	9.7	6300	281
Paraloid™ KM 334	15	1.1	5300	165
Paraloid™ BTA 753	20	2.1	5170	300
Paraloid™ EXL 3691A	20	1.2	6200	280
Paraloid™ EXL 2314	20	1.0	5560	250
Ecoflex™	30	2.4	6180	100
Bionolle™ 3001	15	0.9	8500	230
Pellethane™ 2102-75A	30	14.4	6125	410
Kraton™ FG 1901X	20	N.M.	4850	100
Hytrel™ 3078	30	3.7	5000	430

a.) ASTM D-638 @ 2.0 inch/minute

Besides compounding, rubbery polymers can also be incorporated into PLA by *in situ* polymerization routes. Typical rubbers that can be incorporated during the polymerization include polyether, polyester, and similar uncrosslinked polymers, usually containing reactive groups which can be incorporated into the PLA polymer by forming graft or block co-polymers. ⁸

This technology is beyond the scope of end users of PLA and are not covered in this report. Plasticizers⁹ are also effective at increasing the ductility of PLA, but they result in a totally different balance of properties and are considered as flexibilizing agents and not impact modifiers.

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1 Hartman, 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., Poly lactides in Biopolymers, Chapter 5, Wiley-VCH, 2002. Drumright, R., Gruber, P., and Henton, D.E., Advanced Materials, 12(23), 1841, 2000.

2 "Improvements of the Mechanical Properties of poly(D,L-Lactide) by Orientation", D. W. Grijpma, H. Altpeter, M. J. Bevis, and J. Feijen, Polymer International, 2002, 51(10), 845-851.

3 "Chain Structure, Phase Morphology, and Toughness. Relationships in Polymers and Blends", S. Wu, Polymer Engineering and Science, 1990, 30(13), 753-761.

4 NatureWorks™ internal data.

5 "Polymer Alloys of Nodax Copolymers and Poly(lactic acid)", I. Noda, M. M. Satkowski, A. E. Dowrey, and C. Marcott, Macromol. Biosci., 2004, 4, 269-275.

6 "Polylactic Acid Based Blends", S. P. McCarthy, R. A. Gross, and W. Ma, U. S. Patent 5,883,199, 3/16/1999.

7 "Modification of Poly(L-Lactides) by Blending: Mechanical and Hydrolytic Behavior", M. Hiljanen-Vainio, P. Varpomaa, J. Seppala, and P. Tormala, Macromol. Chem. Phys., 1996, 191, 1503-1523.

8 "Method for Synthesis of Environmentally Degradable Block Copolymers", D. W. Verser, K. H. Schilling, and X. Chen, U.S. Patent 5,633,342, assigned to Chronopol, Inc., 5/27/1997.

9 "Citrate Esters as Plasticizers for Poly (lactic acid), L. V. Labrecque, R. A. Dave, R. A. Gross, and S. P. McCarthy, Journal of Applied Polymer Science, 1997, 66(8), 1507-1513.

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 170°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

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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.

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