

## Technology Focus Report: Blends of PLA with Other Thermoplastics\*

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### Introduction:

Poly(lactic acid) (PLA), as supplied by NatureWorks®, is a single, homogeneous polymer and is not blended with other polymers. 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 by blending with other polymers. 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, 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 organoleptic 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.<sup>1</sup>

### 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 polymer blends, except rubbery polymer which are covered in the Technology Focus Report on Impact Modified PLA.

A blend of two polymers can be characterized as miscible or immiscible, depending on whether the polymer chains of the two components form a homogeneous single phase or phase separate into individual domains of the two components. Further, the terminology "compatible" or "incompatible" is often used to describe how well the two components mix or as an assessment of their resultant properties. The term "compatible" has been used to describe blends that range from totally miscible (one phase) to interactions that are favorable and result in good physical properties. "Incompatible" usually refers to blends that have poor physical properties, delaminate upon impact, and often differ greatly in viscosity, polarity, or stability. Two phase blends are often called incompatible.

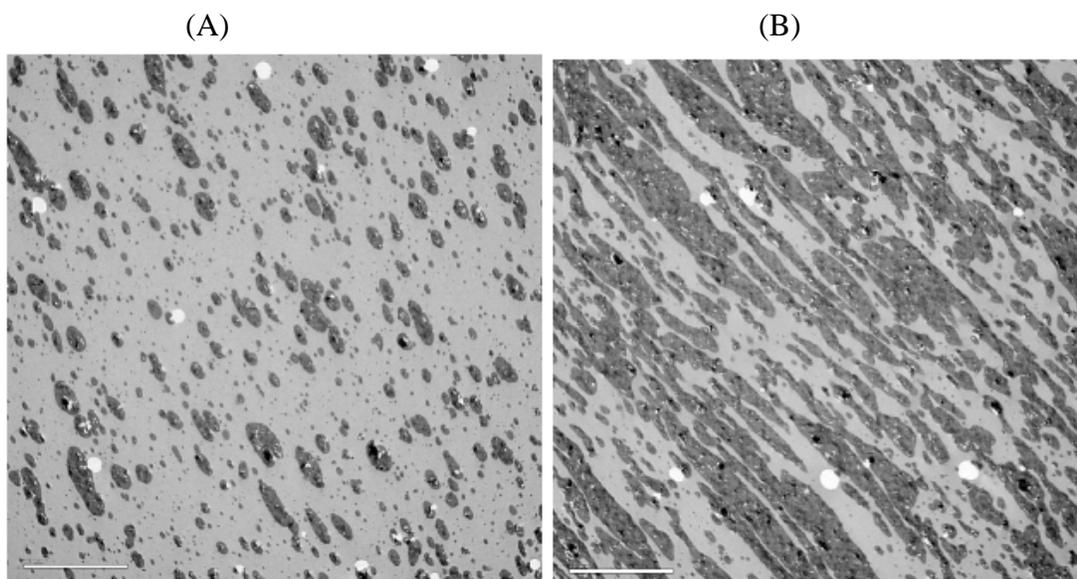
Most polymers are not miscible with other polymers because both entropy and enthalpy factors are generally unfavorable. There are a limited number of examples of miscible polymer systems. The commercial blend of polystyrene and polyphenylene oxide sold under the trade name NORYL™ by General Electric is one example of a miscible blend. Miscible polymer blends typically result in an average of the properties of the individual components and have fewer issues of appearance, directionality of properties, and rheology. Most commercial polymer blends, however, are immiscible, two phase systems, but still have very useful properties. Polycarbonate/ABS and Polycarbonate/Polyesters are examples of these types of blends. One advantage of two phase blends is the potential to obtain properties greater than the weighted average of the components if all the controlling factors are optimized.

When blending two different polymers, many factors must be considered in order to obtain a blend with useful properties. Generally twin screw extruders are used for preparing blends. Melt mixing must be done above the glass transition temperature of amorphous polymer components and above the melting point of semi-crystalline polymer components in order to manage the viscosity and to obtain optimum dispersion. For PLA blends, the lower limit will be about 180 °C. Additionally, polymers that require very high processing temperatures (> 270 °C) will result in thermal degradation of PLA and are not good candidates for PLA blends. Crystalline PET must be processed close to this temperature and PLA molecular weight loss has been observed in PET blends.<sup>2</sup> Co-polyesters with lower melting points are more suited for blending with PLA. The viscosity ratio (ratio of melt viscosity of PLA to that of the other polymer) at the processing

temperature should be between 0.1 and 10 to obtain good dispersion. Either the processing temperature or the molecular weight of the components should be changed to enhance mixing. The process equipment also plays a role in obtaining good mixing and screw design, RPM, feed rate and other process conditions should be optimized. Chemical reactions and degradation must also be considered. Polymers that have nucleophilic additives or contain high levels of water can cause molecular weight loss of the PLA during compounding and result in blends with poor physical properties. Thorough drying of all components is essential.

In two phase (immiscible) blends, the morphology and thus the physical properties, are controlled by the weight (volume) ratio of the two components, the viscosity ratio, as well as the interfacial tension between the phases and these factors have been studied extensively in blends of polycarbonate and ABS.<sup>3</sup> At low levels of one polymer in the blend, the minor component will be dispersed as small, sub-micron domains. Between 30-70% of the component, a co-continuous morphology can exist. The properties of the blend are dependant on both the morphology of the blend and the physical properties of each component, as well as the adhesion between the micro-domains of the dissimilar polymers. These phase morphology characteristics can be seen in the TEM photomicrographs of PLA/ABS blends below. The physical and thermal properties of immiscible blends are dominated by the properties of the major phase when one component exists as a discontinuous phase in the other polymer.

Poor interfacial compatibility of the polymer components leads to de-bonding of the phases at low applied stress, followed by crack formation. The strength of the polymer-polymer interface is quantified by sophisticated techniques such as the “fiber retraction method” which measure the interfacial tension between two polymers.<sup>1</sup> Low interfacial tension is necessary to allow good dispersion of one polymer in another and to have good interfacial adhesion for physical properties. These methods are not routine and generally visual observation of the appearance of the blend and especially of broken test specimens are used to assess the compatibility of the polymer components. Microscopy (TEM & SEM) is also used to quantify domain size and to detect de-bonding at interfaces, both good indicators of the degree of polymer compatibility.



Transmission electron photomicrographs of blend of (A) 20% & (B) 50% MAGNUM™ ABS 555 with NatureWorks® PLA 2002D at 2000 X magnification (10 micrometer bar). The ABS phase has been stained dark using Ruthenium tetra oxide.

## Problems or Issues When Incorporating Other Polymers into PLA:

The desired beneficial affects from addition of other polymers does not always come without some negative consequences. There are fewer issues with miscible blends, but chemical interactions and degradation, due to additive or polymer reactions can occur, leading to color formation or loss of molecular weight. Two phase polymer blends will be opaque and generally not be as easily colored in dark blues and blacks. The most obvious issue with two phase blends is obtaining good interfacial adhesion which will directly affect the morphology and physical properties. If the added polymer is not very compatible with PLA, then a lot of development work will be necessary to identify compatibilization technology. Poor interfacial adhesion will result in embrittlement as well as two phase morphology that will constantly change depending on the processing conditions and the design of parts being produced. Additionally, some polymers are not bio-degradable and blending them with PLA will affect its compostability.

## PLA Blends with Commercially Available Polymers

### Polyglycols:

Polyethylene oxide (PEO) and polypropylene oxide (PPO) have been blended with PLA. Lower molecular weight glycols (300-1000 Mw) are miscible<sup>ii</sup> with PLA while PPO becomes immiscible at higher molecular weight. These polymers, especially PEO, can be used to increase the water transmission and bio-degradation rate of PLA. They can also be used as polymeric plasticizers to lower the modulus and increase flexibility. High molecular weight PEG (20,000) is miscible in PLA up to about 50%, but above that level the PEG crystallizes, reducing the ductility of the blend.<sup>6</sup>

### Polyvinyl acetate (PVA):

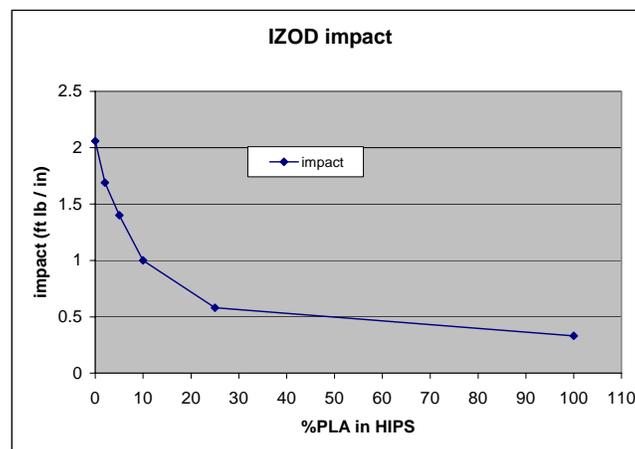
Another polymer reported to be miscible with PLA is PVA.<sup>iii</sup> Only one T<sub>g</sub> is observed at all blend ratios, with a constant decrease to about 37 °C at 100% PVA. Low levels of PVA (5-10%) increase the tensile strength and % elongation of PLA while significantly reducing the rate of weight loss during bio-degradation. When PVA was partially hydrolyzed to polyvinyl acetate-co-vinyl alcohol, the blend was immiscible at about 10% vinyl alcohol content.<sup>7</sup>

### Polyolefins:

Because of the significant difference in polarity between PLA and polyolefins (polypropylene and polyethylene), blends of these components result in incompatible systems with poor physical properties. Third component compatibilizers, such as glycidyl methacrylate grafted polyethylene, have been used with some success. The epoxy group on the PE can react with the acid end group of PLA, forming a graft polymer which resides at the interface of the two components, lowering the interfacial energy and increasing the adhesion of the two phases.<sup>9</sup> Block polymer compatibilizers have also been synthesized separately and added to blends of PLA and polyolefins, increasing their ductility significantly.<sup>10</sup>

### Styrenic Resins:

Polystyrene and HIPS resins are also non-polar and blends with PLA are generally not very compatible. The interfacial tension between PLA and polystyrene was measured as 5.4 dyn/cm, using the imbedded fiber technique.<sup>11</sup> Poor interfacial adhesion such as this leads to a reduction in physical properties as shown in the graph.



### Polyacetals:

A number of polymer blends containing PLA and acetals, along with additional additives and fillers have been patented. Good heat resistance and other properties have been claimed.<sup>12</sup> Blends containing up to 30% acetal are reported to be transparent, suggesting that that PLA and acetals are miscible.<sup>13</sup> Acetals are very unstable in the presence of acid, generating formaldehyde and resulting in foaming or fuming. Trace levels of acids can be generated during processing of PLA and it is recommended that buffers or neutralizing agents be considered for these blends.

### Poly(meth)acrylates:

PLA appears to be miscible with polymethyl methacrylate and many other acrylates and copolymers of (meth)acrylates.<sup>14</sup> Only one Tg was observed in several PLA/PMMA blends, which followed the Gordon-Taylor theory for miscible systems. PMMA raises the Tg of the blend, but reduces the crystallization rate of PLA, which may be detrimental to high productivity in crystallized parts. Drawn films of PMMA/PLA blends are transparent and have high elongation.<sup>15</sup> High molecular weight acrylate resins, such as those from Rohm & Haas (Paraloid K-120N, K-125, and K-130B) at 1-5% in PLA, have been shown to significantly affect rheology and increase the melt extensibility of PLA.<sup>2</sup> TEM photomicrographs of PLA/PMMA stained with ruthenium tetra oxide do not show separate phase domains of the individual polymers, again supporting the concept of a miscible blend.<sup>2</sup>

### Polycarbonate:

Polycarbonate (PC) is combined with PLA to take advantage of its heat resistance and toughness. PC is also very easy to modify with non-halogen flame retardants and Fujitsu and Toray have developed a 50/50 blend of PC & PLA containing ignition resistance agents designed for notebook computers.<sup>16</sup> This composition has the processibility, heat resistance, and flame resistance required in larger IT devices. The incorporation of high levels of polycarbonate into PLA (greater than 50%) requires processing temperatures close to the thermal decomposition temperature of PLA, making it difficult to prepare these types of blends. Low levels of polycarbonate (e.g. 20%) result in opaque blends with properties similar to PLA.

### ABS:

High rubber (50-85% rubber) content ABS, also called ABS grafted rubber concentrates, have been used to toughen PLA with good success. Normal molding grade ABS, with rubber contents of 5-22% rubber, can also be blended with PLA. The melt processing temperatures of these two materials are very similar and they can be easily blended on standard melt mixing equipment. The polymers are not miscible and the blends are opaque with physical and thermal properties expected for two phase blends.

### Injection Molded Properties of Some PLA Blends with Commercial Polymers

	% Polymer in PLA Blend	Tensile Yield <sup>e</sup> (psi)	% Elong. <sup>e</sup>	Tensile Modulus <sup>e</sup> (psi)	DTUL <sup>f</sup> °C @ 66 psi	Izod Impact <sup>g</sup> (ft-lbs/inch)	Clarity
Polycarbonate <sup>a</sup>	20	9130	3.0	411,000	59	0.35	No
PMMA <sup>b</sup>	20	9730	4.0	453,400	58	0.33	Yes
	50	10,575	4.0	453,900	63	0.32	Yes
	80	10,625	5.1	446,500	73	0.29	Yes
ABS <sup>c</sup>	20	7950	2.9	414,000	58	0.48	No
	50	7130	2.5	377,700	61	0.29	No
	80	6660	4.9	343,000	89	0.59	No
PLA <sup>d</sup>	100	9150	3.5	429,500	59	0.35	Yes

a. Caliber™ 200-22 b. Magnum™ 555 c. Paraloid™ CA 86 d. NatureWorks® 2002D e. ASTM D638 @0.2 inch/min. f. ASTM D648-06 g. ASTM D256-92

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- <sup>1</sup> 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.
- <sup>2</sup> NatureWorks™ internal information.
- <sup>3</sup> Bubeck, R. A.; Buckley, D. J., Jr.; Kramer, E. J.; Brown, H. R., *J. Mat. Sci.* (1991), 26(23), 6249-59.
- <sup>4</sup> A. Cohen, *Rheol. Acta*, 1989, 33, 681. C. Carriere, *J. Rheol.*, 1989, 33, 681.
- <sup>5</sup> "Dielectric study of dynamical heterogeneity in eco-friendly polymer blends: poly (lactic acid)/polyether" J. Ren, O. Urakawa, K. Adachi, Keiichiro, *Nihon Reoroji Gakkaishi* (2004), 32(4), 161-167.
- <sup>6</sup> "Biodegradable Polymer Blends of Poly (lactic acid) and Poly (ethylene glycol)", M. Sheth, R. A. Kumar, V. Dave', R. A. Gross, and S. P. McCarthy, *J. Appl. Poly. Sci.*, 1997, 66, 1495-1505.
- <sup>7</sup> "Miscibility and Biodegradation of Blends of Poly (lactic acid) and Poly (vinyl acetate)", A. M. Gajria, V. Dave, R. A. Gross, and S. P. McCarthy, *Polymer*, 1996, 37 (3), 437-444.
- <sup>8</sup> "Miscibility and Morphology in Blends of Poly (L-lactic acid) and Poly(vinyl acetate-co-vinyl alcohol)", J. W. Park and S. S. Im, *Polymer*, 2003, 44(15), 4341-4354.
- <sup>9</sup> "Compatibilization of immiscible poly(l-lactide) and low density polyethylene blends" Y.F. Kim, C. N. Choi, Y.D. Kim, K.Y. Lee, M.S. Lee, *Fibers and Polymers* (2004), 5(4), 270-274.
- <sup>10</sup> "The influence of block copolymer microstructure on the toughness of compatibilized polylactide/polyethylene blends", K. S. Anderson and M. A. Hillmyer, *Polymer* (2004), 45(26), 8809-8823.
- <sup>11</sup> "Interfacial tension of poly(lactic acid)/polystyrene blends" G. Biresaw, C. J. Carriere, *Journal of Polymer Science, Part B: Polymer Physics* (2002), 40(19), 2248-2258.
- <sup>12</sup> "Poly(lactic acid)/polyacetal resin compositions and heat-resistant high-strength moldings therefrom with good surface appearance and dimensional stability" H. Ome, S. Kumasawa, and J. Kumaki, Japanese patent 2003342460 A2, assigned to Toray Industries, Inc., 12/03/2003. "Polymer alloy fibers with good biodegradability and abrasion resistance consisting of blends comprising poly(lactic acid) and polyacetals" T.Ochi, Y. Maeda, and H. Ohme, Japanese patent JP 2003227037 A2 assigned to Toray Industries, Inc., Japan, 8/15/2003.
- <sup>13</sup> "Heat-resistant poly(lactic acid)-polyacetal blend with good processability, mechanical strength, and transparency for plastic moldings, films, and fibers" H. Ohme, S. Kumazawa, and J. Kumaki, WO 2003014224 A1, assigned to Toray Industries, Inc., Japan, 2/20/2003.
- <sup>14</sup> "Miscibility and phase structure of binary blends of polylactide and poly(methyl methacrylate)" G. Zhang, J. Zhang, S. Wang, and D. Shen, *Journal of Polymer Science, Part B: Polymer Physics* (2002), 41(1), 23-30. J.L. Eguiburu, J.J. Iruin, M.J. Fernandez-Berridi, J. Roman, "Blends of amorphous and crystalline polylactides with poly(methyl methacrylate) and poly(methyl acrylate): a miscibility study", *Polymer*, 1998, 39(26), 6891-6897.
- <sup>15</sup> "Poly(lactic acid)-type polymer drawn films with increased stiffness at high temperatures and good transparency, comprising poly(lactic acid) compositions containing (meth)acrylate polymers" T. Kamisawa and M. Kimura, Masahiro, Japanese Patent 2005036054 A2 assigned to Toray Industries, Inc., Japan, 2/10/2005.
- <sup>16</sup> Fujitsu, "Toray Develops PLA Notebook Housing", *Modern Plastics*, 2005, March, p. 11.

#### 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

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.

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