Introduction:

Polylactic 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 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.

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. Co-polymers 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. 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 exits 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. 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 tetroxide.
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 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.

Polyvinyl acetate (PVA):
Another polymer reported to be miscible with PLA is PVA. Only one Tg 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.

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. Block polymer compatibilizers have also been synthesized separately and added to blends of PLA and polyolefins, increasing their ductility significantly.

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. 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. Blends containing up to 30% acetal are reported to be transparent, suggesting that PLA and acetals are miscible. 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. 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. 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. 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.

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. 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

<table>
<thead>
<tr>
<th>% Polymer in PLA Blend</th>
<th>Tensile Yield (psi)</th>
<th>% Elong.</th>
<th>Tensile Modulus (psi)</th>
<th>DTUL°C @ 66 psi</th>
<th>Izod Impact (ft-lbs/inch)</th>
<th>Clarity</th>
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<tr>
<td>Polycarbonate³</td>
<td>20</td>
<td>9130</td>
<td>3.0</td>
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<td>59</td>
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<td></td>
<td>50</td>
<td>10,575</td>
<td>4.0</td>
<td>453,900</td>
<td>63</td>
<td>0.29 No</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>10,625</td>
<td>5.1</td>
<td>446,500</td>
<td>73</td>
<td>0.29 Yes</td>
</tr>
<tr>
<td>PMMA³</td>
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<td>9730</td>
<td>4.0</td>
<td>453,400</td>
<td>58</td>
<td>0.33 Yes</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>10,575</td>
<td>4.0</td>
<td>453,900</td>
<td>63</td>
<td>0.32 Yes</td>
</tr>
<tr>
<td></td>
<td>80</td>
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<td>5.1</td>
<td>446,500</td>
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<td>0.29 Yes</td>
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<td>414,000</td>
<td>58</td>
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<td>9150</td>
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<td>429,500</td>
<td>59</td>
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</tr>
</tbody>
</table>


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NatureWorks™ internal information.


“Miscibility and Morphology in Blends of Poly (lactic acid) and Poly(vinyl acetate-co-vinyl alcohol)”, J. W. Park and S. S. Im, Polymer, 2003, 44(15), 4341-4354.


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