

# **Poly lactides: A New Paradigm in Polymer Science**

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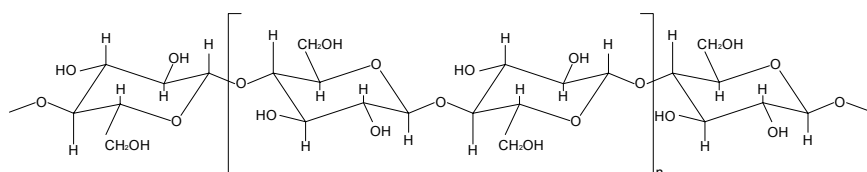
## **Introduction**

In past several decades, extensive research has been performed regarding the possibilities of using renewable resources for the production of chemicals and fuels instead of fossil resources, which will eventually become rare and therefore expensive. Increasing the use of materials based on renewable resources for packaging and other applications not only holds significant advantages in economics and security, but also promises improvements regarding long-term sustainability. The growing problems of disposal, especially in countries with dense populations such as Europe and Japan, as well as low acceptance of incineration require alternative routes to reduce the amount of plastic material in society's waste stream. In addition, the production of polymeric materials based on fossil fuels produces CO<sub>2</sub> and contributes to global warming. Biodegradable macromolecules based on renewable resources are a possible answer to these issues.

Poly(lactic acid) (PLA) is a biopolyester derived from lactic acid which is generally produced by the fermentation of corn sugars. It has been known for decades as a suitable material for medical applications. A wide range of its properties have been extensively studied, such as the synthesis of the homopolymer as well as a wide variety of co-polymers, mechanical properties and thermal behavior. So not only is PLA a well known material, but E. Vink et. al. [1] also demonstrated using life cycle assessment that it has the lowest non-renewable fossil resource content compared to a variety of other common polymers. PLA possesses a suite of favorable material properties that are enabling its penetration into diverse markets. It can be used in fiber form in traditional textile applications in combination with other natural materials like cotton and wool. In addition, its clarity and physical properties enable its use in food and product packaging applications. It also can be engineered to degrade in composting environments. PLA is currently being commercially produced at a large scale for packaging material.

In order to spread the possible applications for this material, it is necessary to modify the mechanical properties. The introduction of fibers of various sizes into the polymeric matrix is known to be very effective. In order to preserve the main advantages of PLA - its biodegradability and renewable resources basis, biodegradable composites of either micrometer or nanometer sized fillers based on renewable resources are attractive. A study presented recently by Huda et al demonstrated the beneficial effects of cellulose fibers embedded in a PLA matrix by strictly mechanical mixing [3]. The glass transition temperature as well as the modulus improved depending on the fiber loading level, which reached values up to 30% by weight. SEM micrographs presented in the study indicated a fairly good dispersion of the cellulose fibers in the polymer matrix. However, agglomerates can still be identified, and in general material derived by purely mechanical mixing tends to lack an intense interaction at the interface between the two components, which is a key parameter for performance and stability of fiber-reinforced composites.

A possible way to increase the degree of dispersion is attempted in this study, which takes advantage of the well accepted fact that hydroxyl groups act as initiator during lactide polymerization in systems using tin-2-ethylhexanoate (Sn-octoate) as a polymerization catalyst. As shown in Figure 1, the molecular structure of cellulose contains a large number of hydroxyl groups, which are available on the fiber surface to initiate the polymerization reaction. By this process it is possible to not only mix the two components mechanically, but also by the means of chemical bonding. It can be assumed that PLA chains initiated from the fiber surface support the individualization of the fibers and increase the mixing behavior of the two components.



**Figure 1.** Molecular structure of cellulose showing the hydroxyl groups available for reactive compatibilization.

This approach opens up various ways to modify the properties of the resulting material by either blending pre-formed PLA with the material obtained by reaction compatibilization of fibers and lactide, or by a one-step process in which lactide is polymerized in the presence of the fibers alone or while being blended with pre-formed high molecular weight polymer.

## Materials and Methods

L-lactide and preformed polylactide used in this study were purchased from Cargill Dow (Minnetonka, MN) and used without further purification. Lactide was dried under vacuum (22 inch Hg) at 70°C for at least 8 hours prior to use. PLA was dried under vacuum at 80°C for at least 14 hours before being processed.

A special catalysts package was employed. Stannous octoate  $\text{Sn}(\text{Oct})_2$  was obtained from Sigma Aldrich and used as received. The ratio, R, of lactide to Stannous octoate for all reactions was 2500. The co-catalyst triphenylphosphine  $\text{P}(\phi)_3$  has a beneficial effect on the kinetics of polymerization of L,L-Lactide when polymerized with  $\text{Sn}(\text{Oct})_2$  as catalyst [4].  $\text{P}(\phi)_3$  was purchased from Sigma Aldrich and added without further purification in an equimolar amount to  $\text{Sn}(\text{Oct})_2$ . Titanium(IV)isopropoxid TIP was used as transesterification agent in samples containing pre-formed polymer (0.1 wt% of PLA). For handling purposes, solutions of the catalyst and co-catalyst, as well as the transesterification agent were prepared in dried toluene. The catalyst was deactivated using poly(acrylic acid) PAA [5] (0.25 wt% of lactide) purchased from Sigma Aldrich and dissolved in dioxane for transfer purposes.

The fibers used in this study (TC2500) were supplied by CreaFill Fibers Corp (Chestertown, MD). These fibers have an average length of 900  $\mu\text{m}$  and an average width of 20  $\mu\text{m}$  (L:D ratio=45). In order to remove surface impurities and increase reproducibility the fibers were pretreated; 10 g fibers were suspended in 500 ml 8 wt% NaOH. The solution was placed in a sonicator for 6 hours at slightly elevated temperature (about 37°C). The fibers were then filtered and washed with distilled water until neutrality. This washing step was determined to be important in order to remove low molecular weight components formed during alkalization. The washed and filtered fibers were dried in a convection oven at 70°C for 24 hours.

Samples were mixed and polymerized in a Haake Rheomix 600. Polymerizations were performed at 200°C for 25 minutes at 100 rpm. The molecular weight of homopolymer samples was determined by Schultz-Blaschke 1-Point Test Method at 30°C using solutions in THF ( $k_{SB}=0.298$ ,  $K=0.0174$ ,  $a=0.736$ ).

## Results

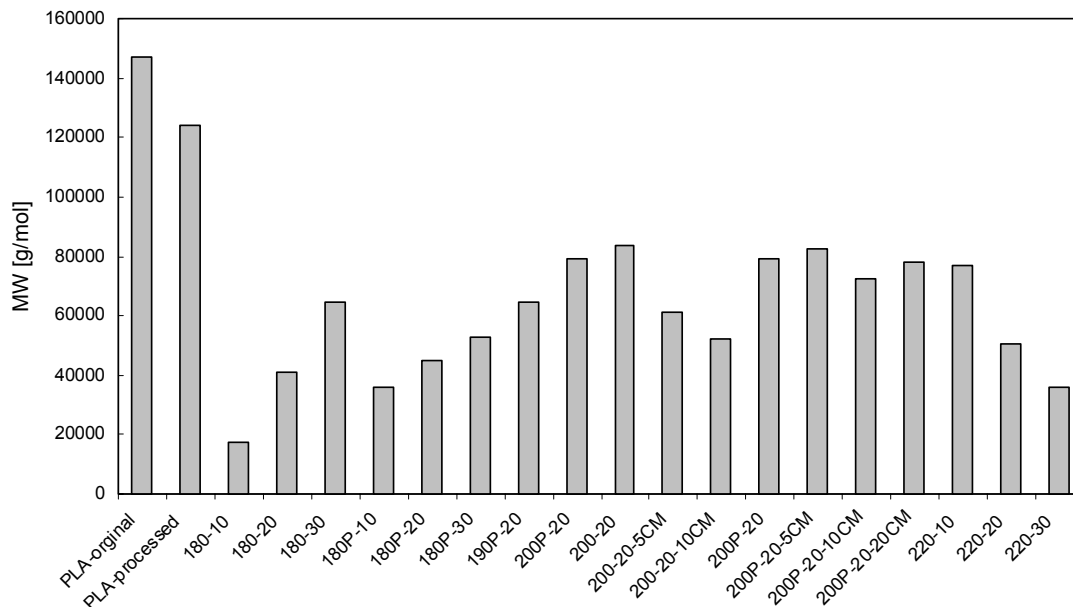
In order to determine optimal polymerization conditions a set of samples of various experimental parameters was prepared and the molecular weight determined (Table 1). The effect of PAA addition was investigated by compression molding the material for 5, 10 or 20 minutes at 180°C, followed by determining the molecular weight. It was observed that samples containing PAA showed better molecular weight stability (see Figure 2). The addition of PAA in order to deactivate the catalyst does not affect the molecular weight during the polymerization.

**Table 1.** Summary of homo-polymer samples prepared at 100 rpm (R=2500, 0.1 wt% TIP, 0.25 wt% PAA for catalyst deactivation)

Sample ID#	T [°C]	time [min]	CM [min]	
PLA-original	-	-	-	as obtained
PLA-processed	180	20	-	pre-formed PLA with 0.1 wt% TIP
180-10	180	10	-	
180-20	180	20	-	
180-30	180	30	-	
180P-10	180	10	-	catalyst deactivation
180P-20	180	20	-	catalyst deactivation
180P-30	180	30	-	catalyst deactivation
190P-20	190	20	-	catalyst deactivation
200P-20	200	20	-	catalyst deactivation
200-20	200	20	-	
200-20-5CM	200	20	5	
200-20-10CM	200	20	10	
200-20P-5CM	200	20	5	catalyst deactivation
200-20P-10CM	200	20	10	catalyst deactivation
200-20P-20CM	200	20	20	catalyst deactivation
220-10	220	10	-	
220-20	220	20	-	
220-30	220	30	-	

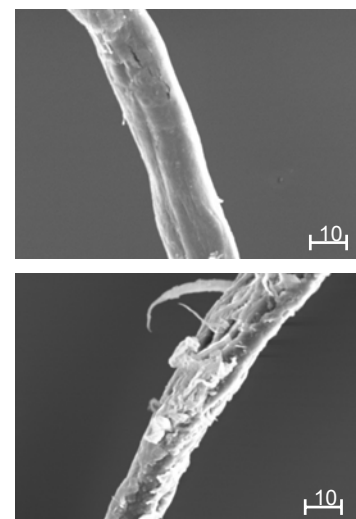
Figure 2 also verifies that increasing reaction temperature results in increasing molecular weight at the specified experimental conditions. However, at a polymerization temperature of 220°C the molecular weight decreases rapidly at reaction times greater than 10 minutes. Comparison of the molecular weight of unprocessed PLA to material mixed with TIP at 180°C for 20 minutes, a decrease in MW occurred due to degradation of the polymer as observed in many previous studies.

Mwaikambo and Ansell [4] observed an increase in surface roughness when natural fibers were treated with NaOH. A similar effect was observed in this study as shown in Figure 3. However, it should be noted that the pretreatment effect was not equally strong for all individual fibers.



**Figure 2.** Molecular weight of various PLA samples listed in Table 1

Using the system conditions determined by examining the molecular weight of various poly(lactic acid) samples a set of materials with different fiber contents ranging from 0-30 wt% and varying lactide/PLA content was prepared. Mechanical and thermal measurements demonstrate that these reactively compatibilized PLA-cellulose composites are a promising new class of renewable materials.



**Figure 3.** SEM micrographs of untreated fibers (left) compared to alkali treated (right) fibers

## References

- [1] Vink, E. et al "Applications of life cycle assessment to NatureWorks PLA production", *Polymer Degradation and Stability*, 80(2003) 403-419
- [2] Degee, P. et al "Beneficial Effect of Triphenylphosphine on the Bulk Polymerization of L,L-Lactide Promoted by 2-Ethylhexanoic Acid Tin(II) Salt", *Journal of Polymer Science: Part A: Polymer Chemistry*, 37 (1999) 2413-2420
- [3] Huda, M.S. et al "Effect of Processing Conditions on the Physico-Mechanical Properties of Cellulose Fiber Reinforced Poly(Lactic Acid)", ANTEC 2004, May 16-20, Chicago, Illinois
- [4] Mwaikambo, L.Y., Ansell, M.P. "The effect of chemical treatment on the properties of hemp, sisal, jute and kapok for composite reinforcement", *Die Angewandte Makromolekulare Chemie*, 272 (1999) 108-116
- [5] "Lactic acid residue containing polymer composition and product having improved stability, and method for preparation and use thereof", US Patent No. 6,353,086