

INJECTION MOLDED POLYLACTIDE (PLA) COMPOSITES FOR AUTOMOTIVE APPLICATIONS

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Abstract

Poly lactide (PLA) is a biodegradable, compostable, thermoplastic polymer produced from corn, an annually renewable resource. In moving towards developing a sustainable vehicle, use of materials such as PLA could greatly contribute to the goal of a more environmentally friendly vehicle. To date, several non-automotive applications of PLA have been commercialized. These include PLA fiber/textile applications for clothing, carpeting, and linens; as well as blow molded articles for food packaging. Thus far for automotive use, a single niche application of compression molded PLA has been developed. Here, we seek to optimize the injection molding process conditions and composition of PLA composites for automotive interior applications. The effects of adding various reinforcements to the PLA resin for property improvements were assessed. Crystallinity, modulus, and strength properties were evaluated by differential scanning calorimetry (DSC), tensile and flexural testing.

Introduction

Over recent years, much attention has been given to potential applications of polylactide (PLA) as a replacement for petroleum based polymers. Polylactide is currently one of the most promising bio-based resins commercially available. PLA is made entirely from corn and is compostable. Dextrose is processed from the corn starch which is then fermented to produce lactic acid. The lactic acid can then be polymerized to produce polylactide. The PLA can be processed into a part, fabric, fiber or film. At the end of the product's life the product can be composted and will degrade to produce energy, carbon dioxide, and water. See Figure 1 below for the life cycle of PLA material.

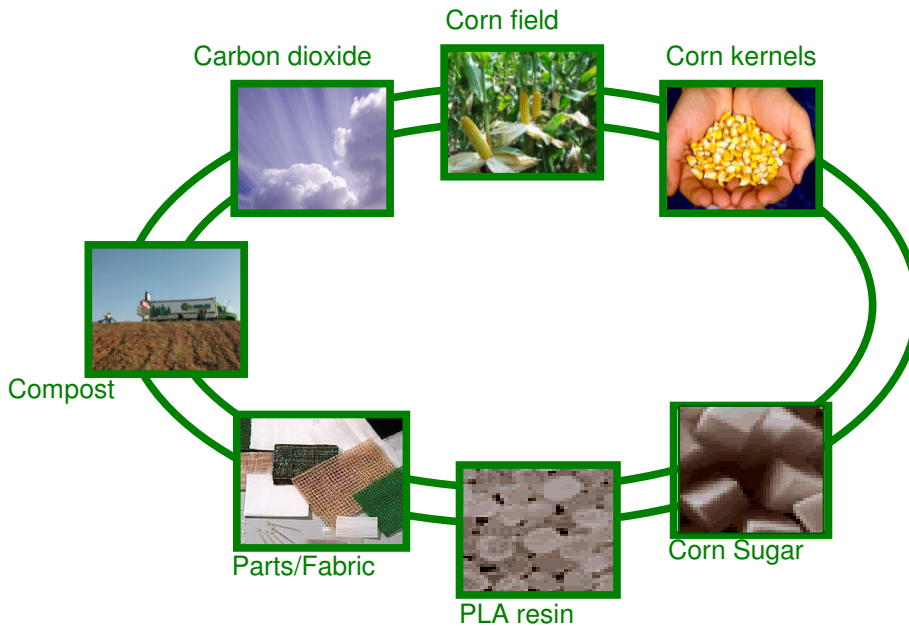


Figure 1: Life Cycle of PLA Material (photos courtesy of Cargill Dow)

Due to its good mechanical properties, PLA has various end use applications. Several non-automotive applications of PLA have been commercialized. These include PLA fiber/textile applications for clothing, carpeting, and linens; as well as blow molded articles for food packaging. PLA has been commercialized for film applications such as grocery bags, waste composting bags, and film envelope windows. For automotive use, a single niche application of compression molded PLA has been developed by Toyota for spare tire covers. (Sekito et al., 2006).

In this study we focus on injection molding PLA material for automotive applications. The main performance requirements for injection molded parts are flexural properties, resistance to impact, heat distortion temperature, long term durability, and formability during the molding process. Currently, unfilled injection molded PLA material does not have high enough performance to meet automotive specifications in some of these property areas. Use of the injection molding process for PLA is also a concern because PLA has a comparatively slow crystallization rate (Nam et al., 2003). However, by adding a filler material to the PLA matrix, we believe improvements in mechanical properties and overall crystallization rate can be made, since fillers can often act as nucleating agents.

Crystallization and microstructure are extremely important in determining the overall mechanical performance of semi-crystalline polymers. For example, it has been shown by several authors that an increase in PLA crystallinity results in improved stiffness (see for example Ray et al., 2003; Sarasua et al., 2005; Sekito et al., 2006). Furthermore, when various crystal forms are present in PLA, hybrid effects can occur. For example, Sarasua and Arraiza (Sarasua et al., 2005) showed that a stoichiometric blend of poly (L-lactide) (PLLA) and poly (D-lactide) (PDLA) yields an increase in the stiffness by approximately 20% over optically pure PLLA. This was attributed to the formation of a stereocomplex, which can have improved properties over homocrystallites.

For this study, we evaluated three different fillers: an organically modified silicate clay, a general purpose talc and corn starch. It has been shown in previous work that the addition of nano clay to polyolefins greatly improves the mechanical properties of the material (Ray et al., 2003). Also, the nano clay is environmentally benign and will not adversely affect the overall bio-degradation of the PLA. Corn starch was also evaluated as a filler because it is inexpensive, readily available, and also will not negatively affect the biodegradation of the composite. It has also been shown that with the addition of corn starch the biodegradation properties of the PLA can be improved. PLA/corn starch composites have received recent attention because they are a totally bio based-composite system (Ohkita et al., 2005). Comparisons of the PLA/nano and PLA/corn starch composites with a PLA/talc composite were made since talc is a commonly used filler for commercial polyolefin composites.

Experimental

Materials

Pellets of injection molding grade 3001D polylactide were purchased from NatureWorks®. The nano-clay filler used in this study was supplied by Nanocor®. This nano-clay is from the I.30 series, and is a high purity, surface compatibilized montmorillonite designed primarily for polyolefin applications. The talc used was a general purpose talc filler from Basell. Corn starch, with high amylose content was purchased from Sigma Aldrich.

Sample Preparation

The composites in this study were prepared using melt extrusion. Prior to extrusion, the resin was dried in an oven at 60 °C for a minimum of 3 days to remove any moisture present in the sample. The PLA (resin form) and fillers (powder form) were first dry mixed together (at a nominal filler loading of 20 weight %) and then melt extruded using a Thermo Haake Rheomex twin screw extruder. The extruder barrel was operated at a temperature range of 165 °C to 190 °C and a screw speed of 230rpm. The dry mixture was starve fed into the extruder from a K-Tron feeder operating at a screw speed of 70rpm. Post-extrusion steps consisted of a water bath and pelletizer. The extruded pellets were dried at 60 °C for at least 3 days to remove any moisture present before injection molding.

The dried, extruded pellets were then injection molded using a lab scale injection molding machine (Mini-Jector Machine Co. Model No. 55). The injection molding machine barrel temperature ranged from 190 °C to 200 °C. Both neat PLA and PLA composites were injection molded into tensile bars (ISO 527 type 5A – identical to ISO 37 specimen type 2) and flexural bars (ASTM D790). The composites were molded at 20 weight % nominal filler loading, and also let down with neat PLA to produce samples of 5% and 10% nominal loadings.

Characterization

Thermal Properties

Degree of crystallinity (χ_c), melt temperature (T_m), crystallization temperature (T_c) and glass transition temperature (T_g) were determined for the PLA before and after composite preparation using a differential scanning calorimeter (Mettler Toledo DSC30 with TC15 TA Controller). The differential scanning calorimeter (DSC) scans were performed from -50 °C to 220 °C at a heating rate of 10 °C/min. DSC samples were prepared by taking cross sections from the neck region of injection molded tensile bars. To calculate the degree of crystallinity of the samples, the energy absorbed by the crystals formed during heating had to be subtracted from the total endothermic heat flow due to the melting of the crystals. The theoretical melting enthalpy of 100% crystalline PLA was taken to be $\Delta H^0_m = 93$ J/g. (Ray et al., 2003).

Mechanical Properties

Injection molded tensile bars were tested according to the ISO 527 method (Model 3366, Instron with a 1" gauge length extensometer) at a strain rate of 50 mm/min at room temperature. Due to minimum sample availability, both the tensile modulus and tensile strength were determined in a single experiment. Injection molded flexural specimens (3.2 mm x 12.6mm x 125mm) underwent quasi-static three-point bend testing according to the ASTM D-790 method at a strain rate of 1 mm/min at room temperature. Flexural modulus and strength were also calculated from a single experiment.

Results and Discussion

To determine the actual amount of inorganic filler present in the compounded samples, burn-off experiments were performed at 600 °C. The results from these experiments are recorded below in Table I. Because the actual filler loading of corn starch could not be determined by burn off, the loading in these composites was estimated by evaluation of the injection molded specimens specific gravities. Estimates for two filler loadings are also shown in Table I.

Table I: Actual Wt %

Sample	Filler Loading (wt %)	Actual Filler Loading (wt %)
PLA/ Nano	5	3.6
PLA/ Nano	10	6.1
PLA/ Nano	20	12.2
PLA/ Talc	5	7.0
PLA/ Talc	10	8.2
PLA/ Talc	20	16.9
PLA/ Corn Starch	5	6.5
PLA/ Corn Starch	20	9.7

Table II below shows the thermal properties of the neat PLA and the PLA composites. All of the samples exhibit an exothermic crystallization peak (T_c) and an endothermic melting peak, (T_m). For the talc- and nano-reinforced samples, the crystallization peak appears at a much lower temperature than for neat PLA. This fact, combined with the increase in crystallinity for the composite samples seems to indicate that the addition of talc or nano-clay enhances both the crystallization kinetics as well as the overall crystallinity of PLA. For the PLA corn starch composites, there is a much lesser shift in the crystallization temperature compared to the nano and talc composites. For a starch loading of 6.7%, there is only a slight increase in the crystallinity compared to the neat PLA. These two results indicate that the corn starch does not enhance the crystallization as well as the talc or the nano fillers. A comparison of the DSC scans for the PLA composites at similar loading levels is shown in Figure 2. All samples shown in the scans were prepared from specimens that were injection molded at room temperature.

Table II: Thermal Properties of PLA and PLA Composites

Samples	Filler (wt%)	T_g (°C)	T_c (°C)	T_m (°C)	χ_c (%)
PLA	0	63.0	113.2	172.3	3.6
PLA/ Nano	3.6	64.7	97.6	172.6	13.6
PLA/ Nano	6.1	61.5	96.3	172.0	13.6
PLA/ Nano	12.2	56.4	96.3	171.2	14.5
PLA/ Talc	7.0	62.7	95.2	171.5	15.4
PLA/ Talc	8.2	63.4	95.2	171.5	12.3
PLA/ Talc	16.9	60.8	92.9	171.6	20.8
PLA/ Corn Starch	6.5	63.0	107.5	172.5	6.7
PLA/ Corn Starch	9.7	60.8	101.1	171.5	15.4

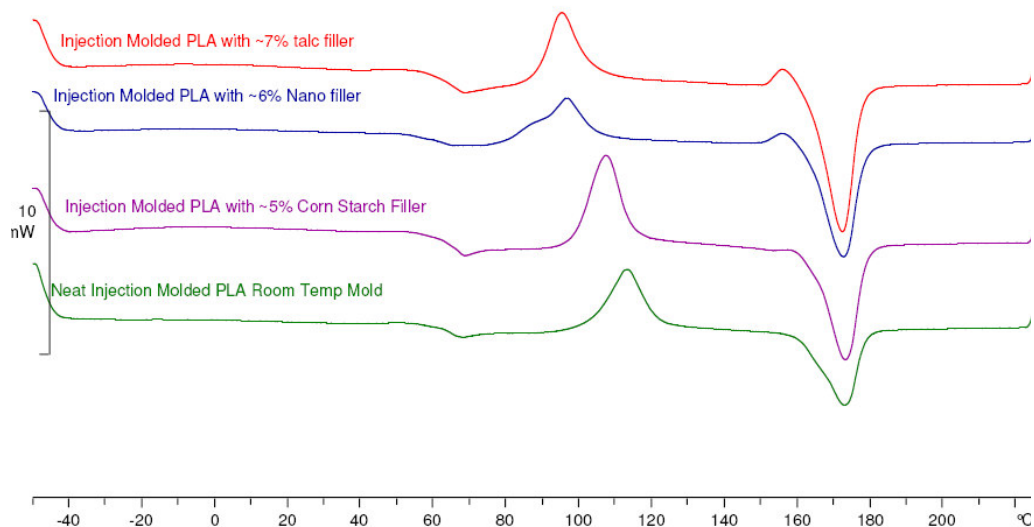


Figure 2: DSC Traces of Injection Molded PLA and PLA Composites

The tensile modulus of neat PLA and various composites are illustrated in Figure 3. In this graph, it is shown how the modulus is affected by the type of filler as well as the amount of filler present in the sample. There is a significant increase in the tensile modulus for the nanocomposite samples. For an actual loading level of 6.1% by weight of nano-clay, the modulus increased by 48%, whereas for a similar loading level of talc, 7.0 wt%, the modulus only increased by 15%. As expected, the modulus continues to increase as the amount of filler increases. However, the PLA corn starch composites do not exhibit an increase in tensile modulus. This is most likely due to poor mixing and dispersion of the uncompatibilized corn starch composites. In addition, some degradation may have occurred due to the heat from the extrusion and injection molding processes.

The flexural moduli of neat PLA and various composites are illustrated in Figure 4. In this graph, the flexural modulus is shown as a function of the type of filler as well as the amount of filler present in the sample. There is an increase in the flex modulus for the nanocomposite and talc composite samples. For an actual loading level of 6.1% by weight of nano-clay the modulus increased by 43%, where as for a similar loading level of talc, 7.0 wt%, the modulus only increased by 22%. The modulus continues to increase as the amount of talc and nano filler increases.

A decrease in both the flex modulus and flex strength was also observed with the addition of corn starch as the filler. Again, this is attributed to poor mixing and dispersion of the starch due to the lack of compatibilizer or coupling agent to improve adhesion between the PLA and the corn starch phases, as well as possible degradation.

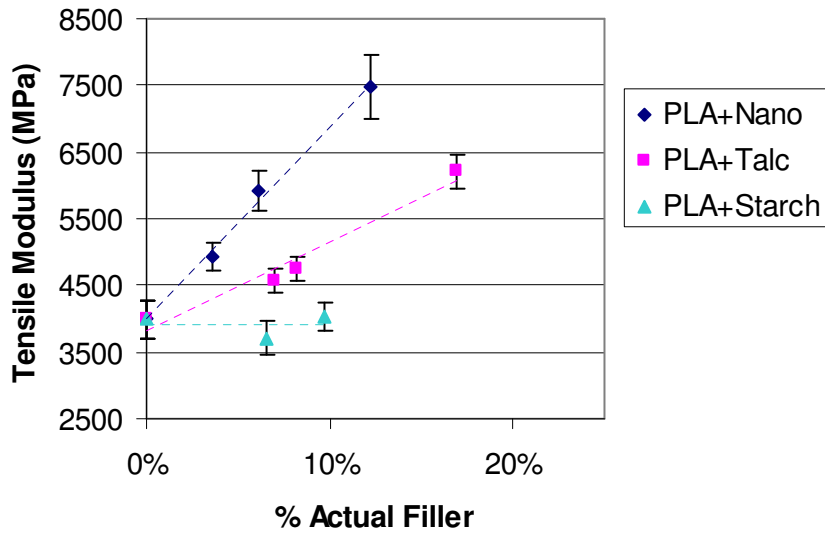


Figure 3: Tensile Modulus Dependence on Filler Type and Filler Amount

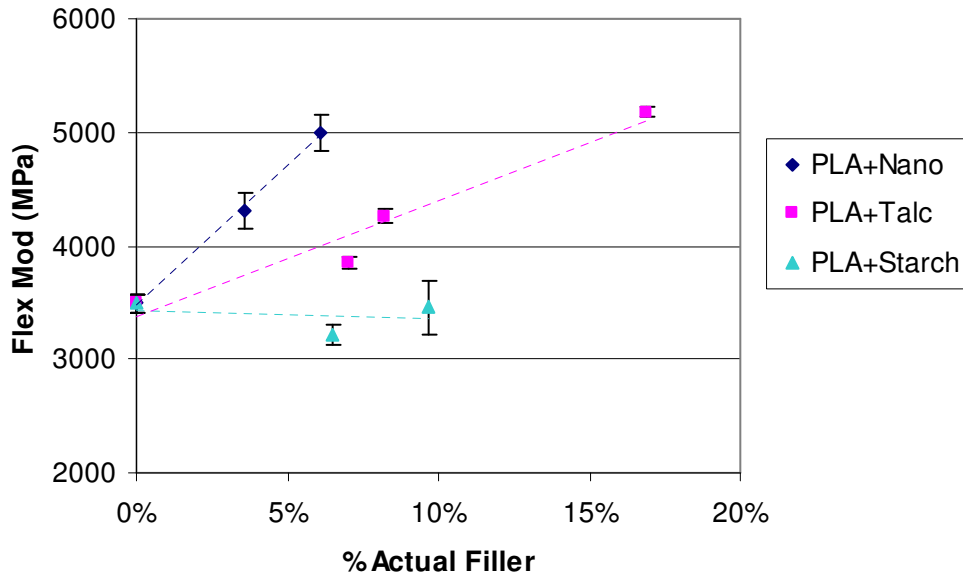


Figure 4: Flexural Modulus Dependence on Filler Type and Filler Amount

Although the flexural modulus of the nanocomposite samples significantly increased with filler loading, the flexural strength decreased for the nanocomposite samples (as shown in Figure 5). This behavior is likely due to the brittleness of the material. The nano material at a loading level of 20% was too brittle to even mold the flex bars, hence the lack of flexural data at that loading amount.

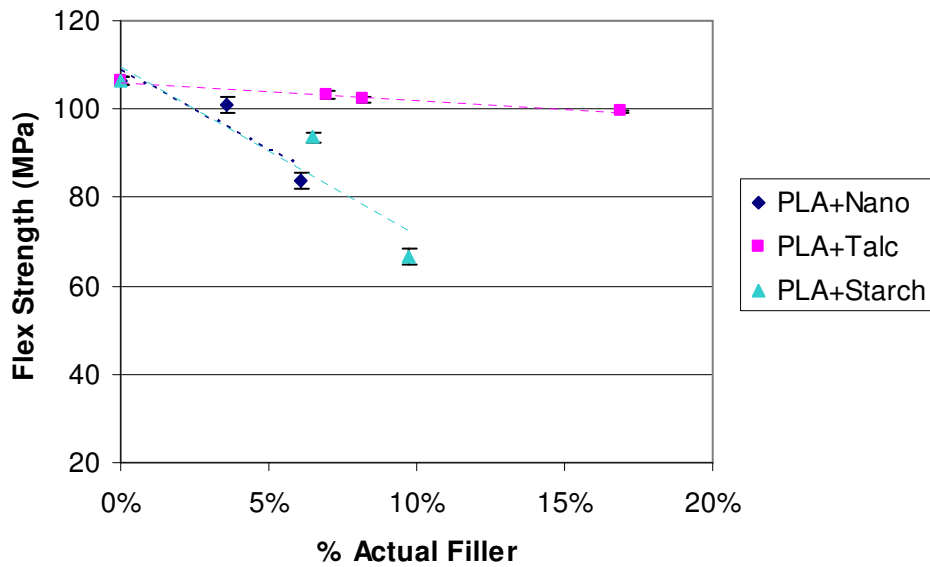


Figure 5: Flexural Strength Dependence on Filler and Filler Amount

Conclusion

The current work shows that the microstructure and mechanical properties of PLA can be controlled as both a function of composite formulation and processing conditions. By increasing the crystallinity of the PLA composites, both durability and mechanical properties can be improved for automotive applications.

Crystallization kinetics and overall crystal microstructure were significantly altered by addition of nano and talc reinforcements. Room temperature molding of these composite materials yielded stiffer materials than neat PLA molded under the same conditions. In addition, the overall crystallinity was reached more quickly due to the increase in crystallization kinetics. The increased kinetics can translate both to reduced cycle time in injection molding processing, as well as increased mechanical properties through the size and morphology of the crystallites. Although not shown here, we also observed an increase in the crystal content for injection molded neat PLA samples as the tool temperature was increased from room temperature to 110 °C. A combination of reinforcement and processing conditions can result in materials that have sufficient formability and durability for commercial use.

The variations in microstructure can play a significant role in determining the mechanical performance of these composites. A thorough investigation of the crystal structure is currently underway in our laboratory.

This study has shown that the mechanical performance of PLA composites can be optimized through reinforcement and processing conditions. However, in order to extend the performance to automotive usage, the durability must be improved. Obviously, a trade off between durability and compostability must be found. Future work will include the evaluation and enhancement of material durability in environments with elevated heat and humidity. The

effects of filler level and type on the compostability of the composites will also be studied. Furthermore, as a result of increased brittleness through filler reinforcement, impact modifiers and compatibilizers will be examined in order to improve on the impact performance of the PLA composites.

Acknowledgments

The authors would like to acknowledge Mark Nichols for thoughtful discussions and insights regarding the art of differential scanning calorimetry.

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