

# Improving Mechanical Performance of Injection Molded PLA by Controlling Crystallinity

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**ABSTRACT:** Currently, use of poly(lactic acid) (PLA) for injection molded articles is limited for commercial applications because PLA has a slow crystallization rate when compared with many other thermoplastics as well as standard injection molding cycle times. The overall crystallization rate and final crystallinity of PLA were controlled by the addition of physical nucleating agents as well as optimization of injection molding processing conditions. Talc and ethylene bis-stearamide (EBS) nucleating agents both showed dramatic increases in crystallization rate and final crystalline content as indicated by isothermal and nonisothermal crystallization measurements. Isothermal crystallization half-times were found to decrease nearly 65-fold by the addition

of only 2% talc. Process changes also had a significant effect on the final crystallinity of molded neat PLA, which was shown to increase from 5 to 42%. The combination of nucleating agents and process optimization not only resulted in an increase in final injection molded crystallinity level, but also allowed for a decreased processing time. An increase of over 30°C in the heat distortion temperature and improved strength and modulus by upwards of 25% were achieved through these material and process changes. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 2246–2255, 2008

**Key words:** crystallization; injection molding; nucleation; biopolymers

## INTRODUCTION

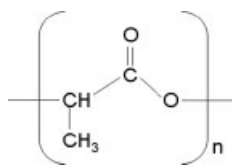
Poly(lactic acid) (PLA) is a compostable polymer that can be derived completely from renewable resources. The repeating chemical structure of PLA is shown in Figure 1. Annual crops, such as corn and sugar beets, are currently utilized as feedstock in the commercial production of PLA resin. PLA is an aliphatic polyester thermoplastic with high strength and stiffness, but low impact strength. These properties are significantly affected by the morphology, which can be controlled stereochemically to yield semicrystalline or amorphous forms. Degradation of PLA occurs primarily through hydrolysis of the ester bond, and is highly dependent on temperature, moisture, microbial environment, morphology, as well as thickness and geometry of the article.<sup>1,2</sup>

Homopolymer PLA can be processed into fibers, textiles, films, and molded objects with standard polymer processing equipment. Its initial uses were for medical and dental applications due to its biocompatibility and biodegradability. Applications range from sutures to drug delivery systems.<sup>3,4</sup> More recently, however, its usage has extended to packaging materials for food and consumer goods; applications in which the polymer film is typically discarded

after use. These applications utilize the amorphous form of PLA and take advantage of its ability to decompose relatively quickly in landfill or compost environments. Films, blow molding, and paper coating (for water resistance) are processing methods that have been commercialized for the packaging industry. Fiber and textile applications have also been investigated and commercialized to a limited extent. Clothing and upholstery for office furniture are available in Japan, while bedding and linen applications are the sole commercial textile applications in the US. Other than the early medical applications, injection molded applications that require high mechanical and durability requirements have not yet been reported.

Only limited research on injection molded PLA for structural parts, such as those found in automotive applications, exists in the literature.<sup>5</sup> Although PLA can have good mechanical properties, its use in structural applications demands tight tolerances, good impact performance, and high durability; properties that current materials lack. Improvements in mechanical properties need to be made, while preserving the overall compostability of the materials before more widespread use is possible. This can be achieved through control of the polymer crystallinity, by optimization of the processing parameters, and/or changes in the formulation of the material.<sup>6</sup> Thus, an understanding of the crystallization behavior and its effects on physical properties and performance is essential.

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**Figure 1** Repeat unit of the chemical structure of poly(lactic acid).

It is well known that PLA crystallinity can play a significant role in the mechanical and durability performance in rigid molded applications.<sup>2,3,7–10</sup> An increase in the polymer's overall crystallinity can lead to improvements in stiffness, strength, heat deflection temperature and chemical resistance. Obtaining a highly crystalline, injection molded article of PLA remains difficult, however, due to the slow crystallization rate. The crystallization half time,  $t_{1/2}$ , of a pure sample of PLA is reported in the literature to be in the range of 17–45 min, depending on crystallization temperature, stereochemistry, and molecular weight, whereas polypropylene homopolymers have half times that can be faster by an order of magnitude at similar degrees of undercooling.<sup>1,11–13</sup> To obtain a component with sufficient crystallinity to maximize physical property enhancements during injection molding, the cycle time would be extremely long—or a post-annealing step would have to be added.<sup>14</sup> Since a typical injection molding cycle time is  $\sim 60$ – $90$  s, this would be impractical and economically unrealistic for high volume automotive use.

Crystallization behavior has been found to depend on the stereochemistry of PLA. Two optically active forms of lactic acid exist: L-lactic acid and D-lactic acid. Lactic acid derived from petrochemical feedstock results in a racemic mixture of D- and L- isomers, while optically pure lactic acid can be selectively produced through fermentation with suitable micro-organisms. These can be synthesized to form various copolymers (poly(DL-lactic acid), PDLLA), homopolymers (poly(L-lactic acid), PLLA and poly(D-lactic acid), PDLA), or blends, each with unique properties. Crystallization behavior of the homopolymers has been studied extensively over the past several decades.<sup>15–18</sup> Blends of optically pure PDLA and PLLA have been found to form a stereocomplex with a melt temperature  $\sim 50^\circ\text{C}$  higher than either pure homopolymer.<sup>2,12,19,20</sup> PDLLA copolymers will remain amorphous if the polymerization of D- and L- motifs is random. Use of certain initiators during the polymerization of a racemic mixture, however, can result in long isotactic sequences in the polymer chains, allowing for crystallization over a broad range of optical purities of copolymer.<sup>21,22</sup> As the optical purity decreases, however, the crystallization rate also decreases.

The presence of additives in a pristine polymer resin can influence the crystalline morphology and

kinetics by providing nucleating sites for crystallization to initiate. Nucleating agents can be chemical or physical in nature. Kolstad, and others tested several types of common physical nucleating agents for PLA, including talc and nanoclays.<sup>13,14,23–31</sup> Although not always the most efficient when compared with chemical nucleating agents, talc is often chosen due to both its low cost as well as its additional reinforcement effect. Schmidt and Hillmyer investigated self-nucleation of PLA, in which small crystallites of the stereocomplex were formed from blending up to 15% PDLA into PLLA.<sup>11</sup> They compared the effectiveness of self-nucleation with the heterogeneous nucleation obtained from the addition of talc, finding self-nucleation more efficient. Self-nucleation reduced the crystallization half time by nearly 40-fold, in the best case, while a similar loading of talc only decreased the half time by just over 2-fold under the conditions they studied. Although the research on PLA materials to date have yielded thorough information on the effects of nucleation on the crystallization kinetics, microstructure, and in a few cases the mechanical properties, they do not relate these further to the final processing steps.

In the current investigation, we have studied the relationship between crystallinity level and mechanical performance in injection molded specimens of PLA. Furthermore, the addition of physical nucleating agents, post-processing, and the optimization of injection molding processing parameters were studied to increase final crystallinity, while speeding the crystallization rate. Isothermal and nonisothermal crystallization experiments, including final crystalline content, were evaluated by differential scanning calorimetry (DSC). Optical microscopy was also performed to investigate the morphology of injection molded specimens. Mechanical performance was assessed through flexural and heat distortion measurements. These measurements show for the first time that an increase in the crystallinity through an optimized injection molding process and the addition of nucleating agents can result in a direct and significant improvement in mechanical performance of a commercial grade of PLA.

## EXPERIMENTAL

### Materials

Commercially available, injection molding grade PLA (NatureWorks<sup>®</sup> 3001D) was purchased from NatureWorks LLC (Minnetonka, MN). The PLA had high optical purity, containing mainly L-lactic acid, with  $1.4\% \pm 0.2\%$  D-lactic acid. A general purpose talc filler was obtained from Basell USA. (Lansing, MI). A completely vegetable-based ethylene bis-stearamide (EBS) was purchased from Acme-Hard-

esty (Blue Bell, PA), in an attempt to keep the entire composite bio-derived.

### Sample preparation

The composites in this study were prepared by melt extrusion. Prior to extrusion, the resin and the EBS were 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 nominal filler loadings ranging from 2 to 20 wt %) and then melt extruded using a Thermo Haake Rheomex PTW25 twin screw extruder. The extruder barrel was operated at a temperature range of 165 to 190°C and a screw speed of 230 rpm. The dry mixture was starve-fed into the extruder from a K-Tron feeder operating at a screw speed of 70 rpm. 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.

Dry extruded and neat pellets were injection molded using a lab scale injection molding machine (Mini-Jector Machine Co., Newbury, OH, Model No. 55). The injection molding machine barrel temperature ranged from 190 to 196°C. Both neat PLA and PLA composites were molded into flexural bars (per ASTM D790). Extruded composites at 20 wt % nominal filler loading were let down with neat PLA at the injection press to produce samples with lower filler loadings.

To evaluate the effect of crystallinity on the mechanical performance of PLA samples, specimens injection molded into a room temperature mold were annealed at 80°C for 15, 45, and 60 min. Annealing produced samples with spatially uniform crystallinity. Crystalline content was also varied in the PLA samples directly by injection molding into a preheated mold, at temperatures ranging from 60 to 110°C. The mold was kept at a constant set temperature through use of heating elements connected to a temperature controller.

### Characterization

#### Thermal properties

Degree of crystallinity ( $X_c$ ), melt temperature ( $T_m$ ), cold crystallization temperature ( $T_{c1}$ ), and glass transition temperature ( $T_g$ ) were determined during the heating scan for the PLA materials before and after composite preparation using a DSC (Mettler Toledo DSC30 with TC15 TA Controller). Crystallization temperature from the melt ( $T_{c2}$ ) was determined during the cooling scan. Unless otherwise noted, DSC samples ranged from 4 to 10 mg in mass and were taken from cross sections at the center of injection

molded flexural bars. The specimens were placed in aluminum pans and run under a flow of nitrogen. The following equation was used to calculate the degree of crystallinity within the samples:

$$\% \text{ Crystallinity} = X_c = 100 \times \frac{\Delta H_m - \Delta H_c}{\Delta H_m^\infty}, \quad (1)$$

where  $\Delta H_m$  is the measured endothermic enthalpy of melting and  $\delta H_c$  is the exothermic enthalpy that is absorbed by the crystals formed during the DSC heating scan. The theoretical melting enthalpy of 100% crystalline PLA was taken to be  $\Delta H_m^\infty = 93 \text{ J/g}$ .<sup>2</sup> The DSC was calibrated periodically with indium standards.

#### Optical microscopy

To observe the morphology of injection molded bars, samples were microtomed into 5  $\mu\text{m}$  thin sections and mounted between glass slides in type A Cargille immersion oil (formula code 1248). Optical microscopy was then carried out under polarized light (Nikon Microphot FX) to observe the presence and size of the spherulitic structure.

#### Mechanical properties

Injection molded flexural specimens (nominal dimensions 3.2 mm  $\times$  12.6 mm  $\times$  125 mm) underwent quasi-static three-point bend testing according to ASTM method D790 at a crosshead speed of 1 mm/min at room temperature on an Instron Model 3366. The heat distortion temperature (HDT) testing was carried out according to ASTM method D648 under a stress of 0.455 MPa applied to the midsection of the samples. The samples were positioned edgewise in the test apparatus so that the direction of the testing force was perpendicular to the direction of the molding flow. Injection molded flexural specimens were used for HDT testing. Results from flexural and HDT testing were reported as averages from five specimens per sample.

#### Gel permeation chromatography

Molecular weights ( $M_w$ ) of PLA before and after processing were measured using gel permeation chromatography (GPC) (Waters 2695 Separations Module, Styragel guard, Styragel HR4E, and Styragel HR5 columns, with a Waters 2410 RI detector). Monodisperse polystyrene (PS) standards (Polymer Laboratories, Amherst, MA) were used for the calibration with tetrahydrofuran (THF, Fisher Scientific, Hampton, NH) as the eluent at 30°C and a flow rate of 1 mL/min. Because optically pure PLA homopolymers are insoluble in THF, samples were first dis-

solved in a small amount of chloroform (Fisher Scientific) and then diluted with THF. Because of the small ratio of chloroform to THF, the refractive index increment ( $dn/dc$ ) and solvent quality parameters for the mixed solvent were assumed to be close to those of pure THF. Mark-Houwink parameters for PS and PLA in THF at 30°C, were obtained from literature.<sup>1,32</sup> Molecular weights of PLA specimens were determined through universal calibration using the Mark-Houwink relationship:

$$[\eta] = KM^a, \quad (2)$$

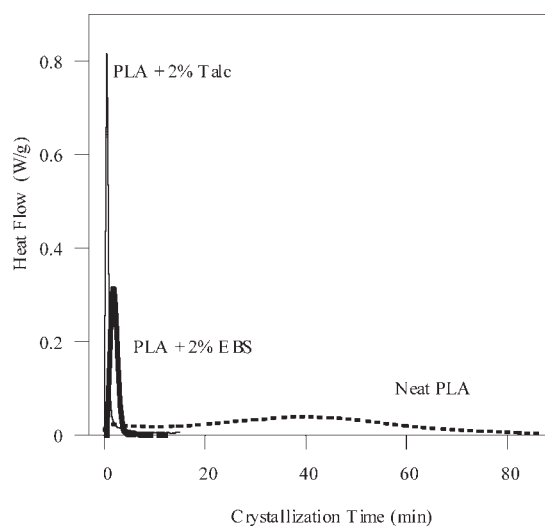
where  $K_{PS} = 1.4 \times 10^{-4}$  dL/g and  $a_{PS} = 0.7$  for PS in THF, while  $K_{PLA} = 1.74 \times 10^{-4}$  dL/g and  $a_{PLA} = 0.736$  for PLA in THF.

## RESULTS AND DISCUSSION

### Crystallization of PLA

#### Isothermal crystallization

The effects of talc and EBS on the crystallization kinetics of PLA were compared through crystallization half times obtained during isothermal crystallization experiments. Using DSC, the PLA samples were heated to 200°C at a rate of 10°C/min, held for 10 min to erase thermal history, and then cooled at 200°C/min to the iso-crystallization temperature of interest, here 115°C, and held for up to 90 min.<sup>30</sup> Crystallization exotherms were measured from the isothermal temperature program as a function of time. Figure 2 shows the DSC traces of neat PLA, as well as the PLA samples nucleated with 2% talc and



**Figure 2** DSC curves of the isothermal crystallization of for neat PLA, PLA + talc, and PLA + EBS samples cooled from the melt at 115°C. Note that the signal for neat PLA has been magnified by a factor of two for ease of comparison.

**TABLE I**  
Isothermal Crystallization Half Times,  $t_{1/2}$ , at 115°C

Samples	$t_{1/2}$ (min)
Neat PLA	38.2
PLA + 2% EBS	1.8
PLA + 2% talc	0.6

EBS. The neat PLA trace is magnified by a factor of two to show more clearly the comparison with the nucleated samples. Both nucleated samples show extremely sharp and intense peaks, while the neat PLA has a much broader exotherm.

The relative crystallinity was calculated by integrating each exotherm from  $t = 0$  to  $t$  and dividing by the total area under the curve. The crystallization half time,  $t_{1/2}$ , was taken to be the time at which the relative crystallinity was equal to 0.5, and are reported in Table I. Neat PLA had a crystallization half time of 38.2 min, which is in good agreement with values reported in the literature.<sup>11–13,15,16,33</sup> Differences in crystallization half times can result from differences in molecular weight, optical purity (stereochemistry), as well as crystallization temperature.<sup>17,22,29</sup> Half times for melt crystallization have also been shown to depend on the melt temperature and hold time in the melt.<sup>11,29</sup> The nucleated materials containing talc and EBS show striking reductions in crystallization half times. The addition of nucleating agents speeds the crystallization rate by over 20-fold for EBS and nearly 65-fold for talc over neat PLA. Day and coworkers report similar increases in crystallization rate for PLA nanoclay composites compared with neat PLA at crystallization temperatures of 120, 125, and 130°C. In agreement with literature,<sup>13</sup> we see that talc seems to be an extremely effective nucleating agent in isothermal crystallization.

With just 2% talc loading, the crystallization half time was decreased to 0.6 min, which was near the lower limit measurable by our instrumentation. Higher loadings of talc were also prepared, but were only examined by nonisothermal crystallization measurements. Half time measurements for these materials would require faster methods such as light scattering, X-ray scattering, or optical microscopy.<sup>1,34</sup>

#### Nonisothermal crystallization

The injection molding process is more closely described by a nonisothermal crystallization experiment. The effect of nucleating agent type was therefore also examined in a series of nonisothermal experiments, summarized in Table II. In these experiments, samples that were injection molded at room temperature were heated at 10°C/min from  $-50^\circ\text{C}$  to  $220^\circ\text{C}$ . After holding at  $220^\circ\text{C}$  for 20 min to erase thermal history, the samples were cooled to

TABLE II  
Effects of Nucleating Agents on Thermal Properties of Injection Molded PLA

Samples	Additive weight (%)	$T_g^a$ (°C)	$T_{cl}^a$ (°C)	$T_m^a$ (°C)	$T_{c2}^b$ (°C)	$X_c^a$ (%)
Neat PLA	0	64.3	115.9	172.4	n/a	10.0
PLA + EBS	2	63.6	93.2	169.4	97.4	18.5
PLA + talc	2	64.8	99.6	172.1	106.9	17.9
PLA + talc	5	62.7	95.2	171.5	110.9	15.4
PLA + talc	10	63.4	95.2	171.5	111.1	12.3
PLA + talc	20	60.8	92.9	171.6	112.6	20.8

Samples molded at room temperature.

<sup>a</sup> DSC program: Heat at 10°C/min to 220°C.

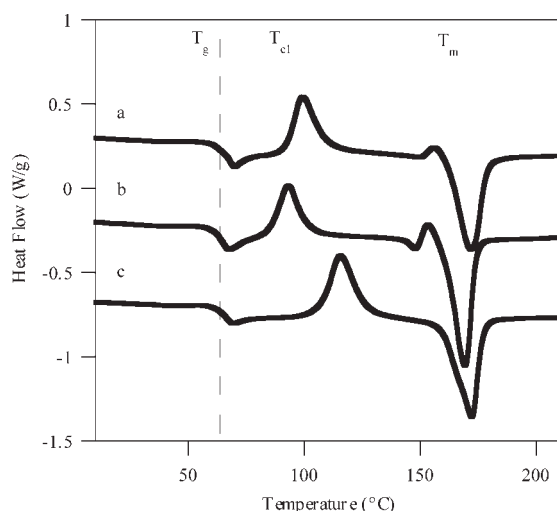
<sup>b</sup> DSC program: Heat at 10°C/min to 220°C, hold for 20 min, cool at 10°C/min to 25°C.  $T_{c2}$  was determined from the final cooling ramp.

25°C at 10°C/min to observe the nonisothermal crystallization. Because the samples did not reach maximum crystallinity during the injection molding process, even for the nucleated samples, a cold crystallization exotherm was observed prior to the melting endotherm during the heating ramp. The peak of the crystallization exotherm was denoted as  $T_{cl}$ , while the melting endotherm was denoted  $T_m$  (see Fig. 3). On cooling from the melt, some samples showed a sharp crystallization exotherm, which was denoted  $T_{c2}$  (see Fig. 4).

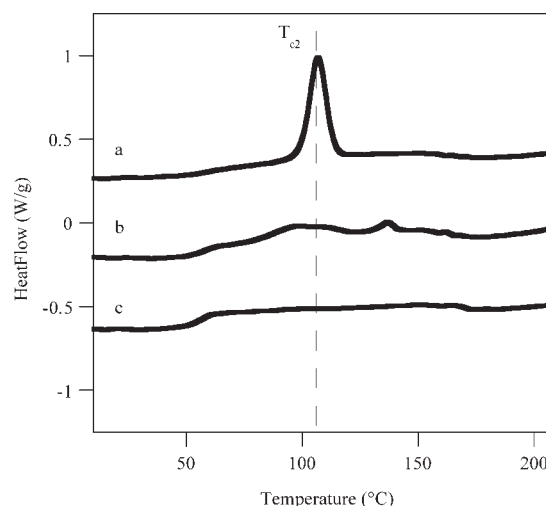
A comparison of the 2% loadings of talc and EBS against neat PLA show the most significant effect on  $T_{c2}$ . In agreement with the isothermal experiments, the 2% talc nucleated sample showed the fastest crystallization rate. The talc sample started to crystallize much sooner and more quickly than either 2% EBS nucleated or neat PLA materials. This was shown by the sharp peak seen in Figure 4 for the talc nucleated sample, compared with the broad hump for PLA. The EBS nucleated sample showed several broad peaks, and the  $T_{c2}$  value was 97.4°C. A

small, sharper peak was observed at 142°C, which was attributed to the crystallization of EBS itself. Also of significance was the cold crystallization of the amorphous regions during the heating ramp (see Fig. 3).  $T_{cl}$  was found to shift to lower temperatures for the nucleated samples (samples a and b) when compared with neat PLA (sample c). In this case, however, the EBS nucleated sample seems to crystallize sooner than the talc nucleated sample. Again, the neat PLA was the slowest to crystallize the amorphous portion of the injection molded specimen. Finally, small crystallization exotherms were observed immediately preceding the melting endotherm for the nucleated specimens, which were not seen in the neat PLA specimen. This unusual behavior is the subject of further investigation in our laboratory, but is beyond the scope of the current study.

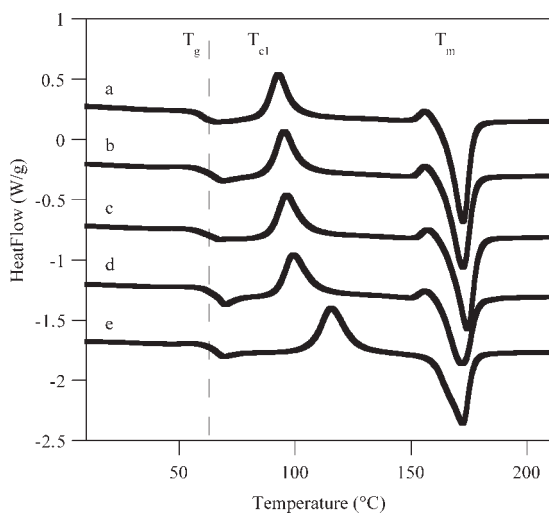
In addition to the nucleating efficiency of different agents, the effect of loading was also studied for the talc nucleating agent, as summarized in Table II. Figure 5 shows the DSC scans of a homologous series of PLA with talc loadings from 2 to 20%. In addition



**Figure 3** DSC heating scans of injection molded specimens of (a) PLA + 2% talc, (b) PLA + 2% EBS, and (c) neat PLA.



**Figure 4** DSC cooling scans of injection molded specimens of (a) PLA + 2% talc, (b) PLA + 2% EBS, and (c) neat PLA.



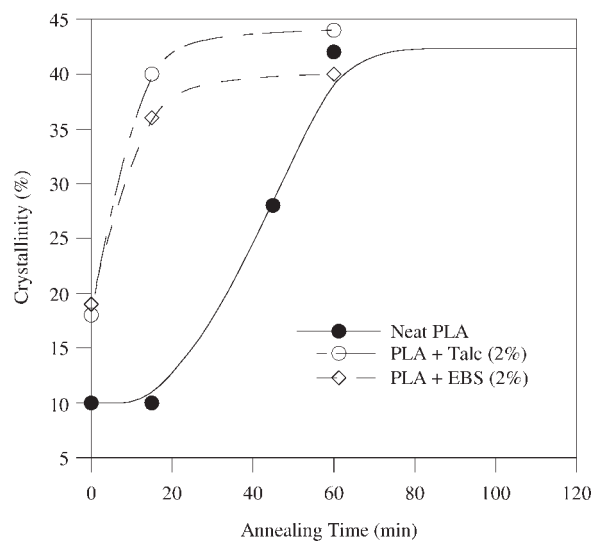
**Figure 5** DSC heating scans of injection molded specimens: (a) PLA + 20% talc, (b) PLA + 10% talc, (c) PLA + 5% talc, (d) PLA + 2% talc, and (e) neat PLA.

to the same trends in  $T_{c1}$  and  $T_{c2}$  observed for the improved nucleating efficiency of 2% EBS and talc loadings, the  $T_g$  was also found to decrease as the talc loading was increased. Furthermore, for the highest loading of 20%, the specimen which was injection-molded into a room temperature mold had a crystalline content of almost 21%.

### Annealing

Post-annealing of specimens, which had been injection molded into a room temperature mold, was performed to increase the crystalline content of neat and nucleated PLA samples. To fully understand the dependence of crystalline content on the mechanical performance, molded specimens were annealed for increasing durations, as shown in Figure 6. Note that in this and remaining figures, lines have been added to guide the eye for observation of trends in the data. Annealing at 80°C, neat PLA reached its maximum crystallinity of 42% by 60 min. Although long time measurements are not shown in Figure 6, annealing for longer periods of time did not further increase the crystallinity.

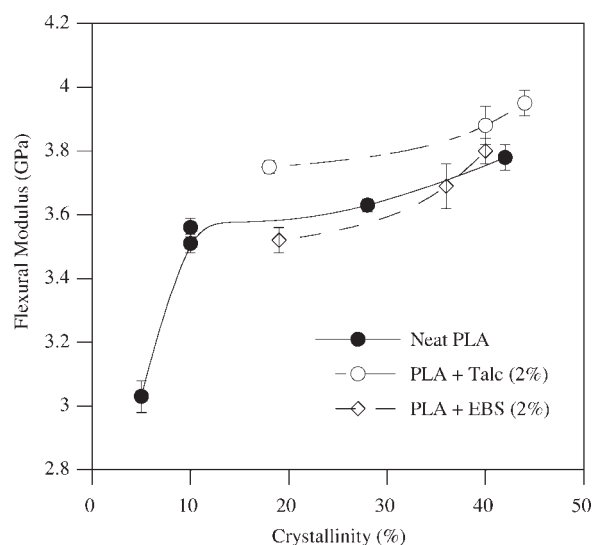
PLA composites containing 2% nucleating agent were also subjected to post-annealing experiments. We see that the addition of a nucleating agent not only results in an increased level of crystallinity for samples molded into a room temperature mold (~20% vs. ~10%), but also a faster annealing process. Both talc and EBS samples have reached maximum crystalline content at ~30 min while after the same duration, the neat PLA has not yet reached 20%. The PLA containing talc shows slightly higher crystalline content than the EBS sample as a function



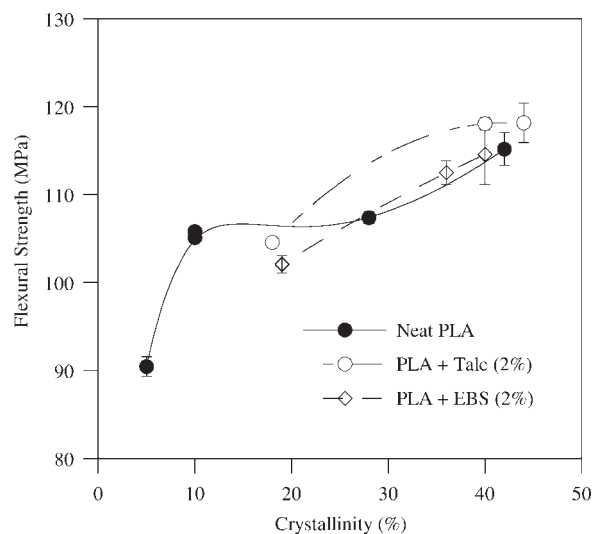
**Figure 6** Crystallinity versus annealing time at 80 °C for neat PLA, PLA + talc, and PLA + EBS samples.

of annealing time, in agreement with the measurements of nucleation efficiency.

The effect of crystallinity level on mechanical performance was measured through flexural and HDT testing. Figures 7 and 8 show that the modulus and strength improved by 25% when a nearly amorphous sample was compared with a highly crystalline sample in neat PLA. Similarly, enhancements in crystallinity also resulted in improvements in mechanical performance for the nucleated samples. Although the EBS nucleated sample showed very similar values of modulus and strength to the neat PLA, the talc nucleated sample showed an additional improvement. At 2% loading level, the contribution to the flexural modulus from particle rein-



**Figure 7** Dependence of flexural modulus on crystalline content for neat PLA, PLA + talc, and PLA + EBS samples.



**Figure 8** Dependence of flexural strength on crystalline content for neat PLA, PLA + talc, and PLA + EBS samples.

forcement should be negligible, so the additional increase in properties over the neat PLA was attributed to differences in crystal structure. Unfortunately, due to the opacity of the talc nucleated samples, optical microscopy was not possible. The HDT was also found to increase by upwards of 30°C with an increase in PLA crystallinity for both neat and nucleated materials (see Fig. 9). Furthermore, a significantly shorter annealing time was required for the nucleated samples to reach the same level of improvement in flexural and HDT performance.

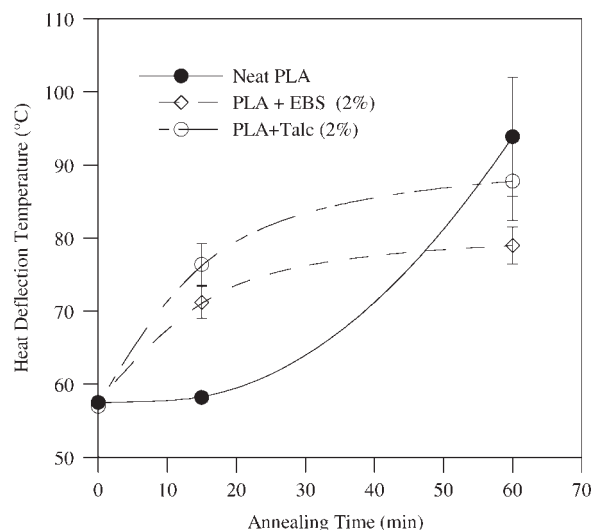
It is well known that the addition of fillers and reinforcements can have a negative effect on the toughness of polymer composites. Although reinforcements loading levels are typically on the order of 20–40% by weight, very modest concentrations of nucleating agents are used to affect crystallinity. Our observations of the tensile elongation revealed that the presence of just 2% nucleating agent had no deleterious effect on PLA toughness.

### Injection molding

Percent crystallinity was also controlled directly by injection molding into a preheated mold. Injection molding neat PLA samples into a room temperature mold generally yields an amorphous or very low crystallinity sample because of the slow crystallization rate. A highly crystalline injection molded sample was produced by injecting the polymer into a mold, which had been held at an increased temperature of 110°C and holding in the mold for several min, allowing crystals to fully form. Table III summarizes the physicochemical properties of unprocessed PLA (PLA pellet) and injection molded neat PLA by DSC and GPC. Amorphous and crystalline

injection molded specimens were prepared by molding into room temperature and preheated molds, respectively. Note that both the unprocessed pellet and the crystalline injection molded sample showed no measurable cold crystallization temperature ( $T_{cl}$ ), indicating maximum crystallinity level. The residence time of the plasticized melt in the barrel during injection molding into a room temperature mold did not have a significant effect on the molecular weight, as shown by the molecular weight of the unprocessed PLA pellet compared with the amorphous injection molded sample. The residence time was measured to be 100 s for the process of molding into a room temperature mold. A slight decrease in molecular weight did occur, however, when the mold temperature was elevated to 110°C and the cycle time increased. This is likely due to the additional residence time the melt experienced in the injection molding barrel from the increased mold cycle time. Because the molded bar was held in the mold for several min, the residence time was increased from 100 s to over 4 min. There does not appear to be any dependence of the melting temperature ( $T_m$ ) on the overall crystallinity or molecular weight of the samples.

The morphology of the injection molded samples was investigated by optical microscopy. Optical micrographs of neat PLA injection molded at two different mold temperatures are shown in Figure 10(a,b). As expected for injection molded specimens, a variation in the morphology from the surface to core was observed. The ratio of the skin to core thicknesses was found to be extremely small, as is typical for conventional injection molding grade resins. Since the morphology at the core controls bulk



**Figure 9** Dependence of heat deflection temperature (HDT) on annealing time at 80 °C for neat PLA, PLA + talc, and PLA + EBS samples.

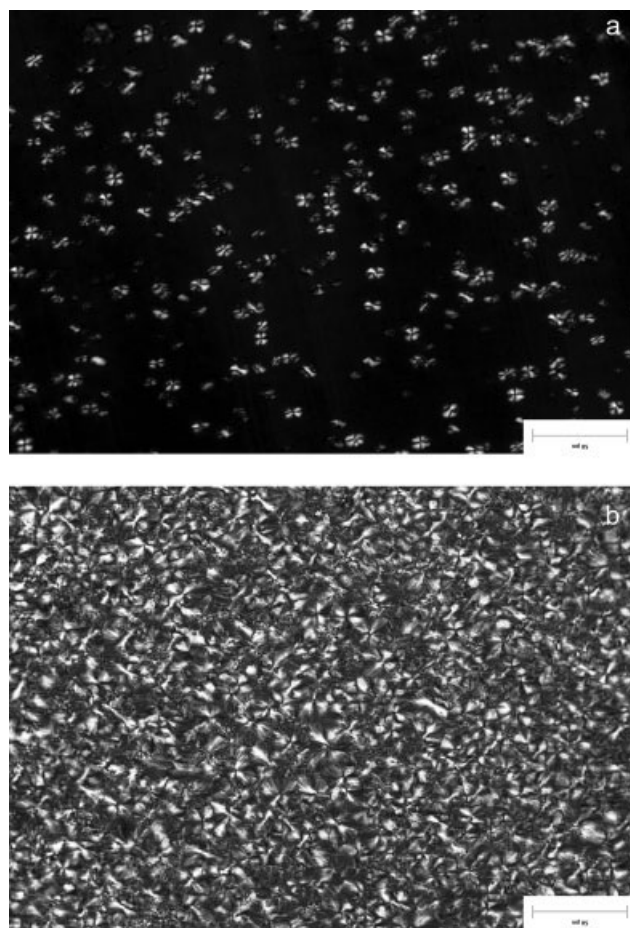
**TABLE III**  
Effects of Processing on Thermal Properties and Molecular Weight

Samples	Residence Time (min)	$T_{\text{mold}}$ ( $^{\circ}\text{C}$ )	$T_g$ ( $^{\circ}\text{C}$ )	$T_c$ ( $^{\circ}\text{C}$ )	$T_m$ ( $^{\circ}\text{C}$ )	Mw (g/mol)	$X_c$ (%)
PLA Pellet	n/a	n/a	n/a <sup>a</sup>	n/a	171.9	$1.0 \times 10^5 \pm 1\%$	41
Amorphous injection molded PLA	1.67	25	64.3	115.9	172.4	$1.0 \times 10^5 \pm 1\%$	10
Crystalline injection molded PLA	>4	110	n/a <sup>a</sup>	n/a	172.3	$9.4 \times 10^4 \pm 1\%$	43

DSC program: Heat at  $20^{\circ}\text{C}/\text{min}$  from  $-50$  to  $220^{\circ}\text{C}$ , hold for 20 min, cool at  $10^{\circ}\text{C}/\text{min}$  to  $25^{\circ}\text{C}$ .

<sup>a</sup>  $T_g$  could not be measured accurately due to high crystalline content of the samples.

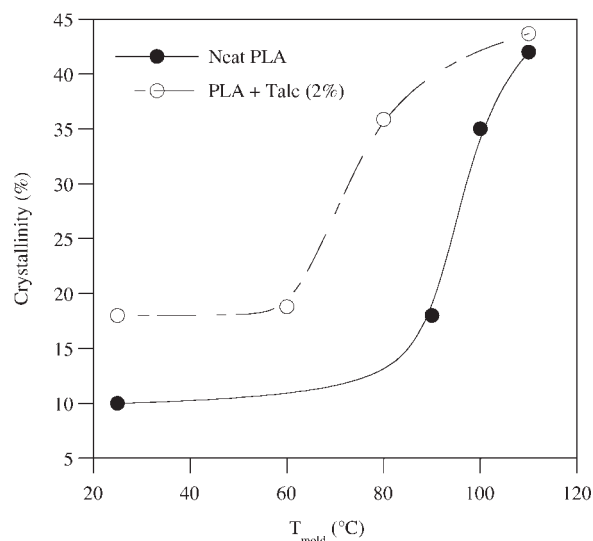
properties, micrographs shown in Figure 10 were from samples taken from the core. Both samples exhibited a spherulitic morphology, but dramatic differences in crystalline content can be seen. The increase in spherulite number and size are both clearly observed when the mold temperature is raised from 100 to  $110^{\circ}\text{C}$ . The sample molded at  $110^{\circ}\text{C}$ , with a crystallinity of 42%, shows densely packed spherulites that have impinged on one another. No differences in optical birefringence or orientation were observed for the various samples.



**Figure 10** (a) Core, injection molded bar,  $T_{\text{mold}} = 100^{\circ}\text{C}$ ,  $X_c = 35\%$ . (b) Core, injection molded bar,  $T_{\text{mold}} = 110^{\circ}\text{C}$ ,  $X_c = 42\%$ .

Figure 11 shows the increase in overall crystallinity of neat injection molded PLA as a function of mold temperature. The mold temperature was held at a constant set temperature and the specimen was held in the mold for  $\sim 3$  min. The crystallinity of PLA was maximized when the mold temperature was held at  $110^{\circ}\text{C}$ . At this mold temperature, the crystalline content begins to plateau to just under 45%. This is in agreement with maximum crystallinity values found in literature for isothermally crystallized PLA.<sup>35</sup> Above  $110^{\circ}\text{C}$ , the specimens were difficult to demold without distortion.

The crystalline content of injection molded PLA with 2% talc nucleating agent was also investigated as a function of mold temperature, from 60 to  $110^{\circ}\text{C}$ . A significant increase in crystallinity was achieved at each mold temperature when compared with neat PLA, again indicative of faster crystallization rates for the nucleated material. Furthermore, at similar temperatures, the nucleated specimens were easier to demold. It is interesting to note that the curves shown in Figure 11 are similar in shape to those for post-annealing (Fig. 6).



**Figure 11** Crystallinity as a function of injection molding mold temperature for neat PLA and PLA + talc samples.



Both neat and nucleated PLA were found to plateau to a crystallinity level just below 45% at the highest mold temperature. The overall temperature dependence of the nucleated sample, however, has significant implications for an industrially viable injection molding process. The target crystalline content can be achieved in a nucleated sample at a lower mold temperature, which will result in a reduction in energy requirements. For the neat PLA, while an elevation in mold temperature did increase the overall crystallinity, the cycle time was still not practical for an industrial process. The samples had to be held in the mold for several minutes to allow for the crystallization process to be completed and for the sample to fully form. Although an optimization of the injection molding cycle time was not performed as a part of the current investigation, our findings indicate that the cycle time of the nucleated sample could be reduced significantly due to the increased crystallization rate.

## CONCLUSIONS

Significant improvements in mechanical performance of PLA were achieved by increasing the overall material crystallinity. This was accomplished in several ways including: the addition of nucleating agents, post-annealing of injection molded specimens, and direct enhancement of crystallinity by injection molding into a preheated mold. The highly crystalline samples formed by these methods were shown to have enhanced flexural stiffness, strength, and HDT.

The addition of just 2% of either nucleating agent had a considerable effect on both the isothermal and nonisothermal crystallization behavior, as shown by the lower cold crystallization temperatures as well as lower crystallization half-times. An increase to 20% loading of the talc nucleating agent had a correspondingly larger effect. These findings were in agreement with data reported in the literature.

The optimization of processing conditions, especially of the nucleated samples, was found to be effective in increasing the crystallinity and thus mechanical performance of the PLA samples. Post-annealing processing of both nucleated and neat PLA materials was found to increase the crystallinity of PLA to its maximum level of 42%. In agreement with the findings from the crystallization measurements, the addition of nucleating agents accelerated the annealing process of PLA dramatically. Injection molding the PLA materials into a preheated mold was also found to significantly increase the crystalline content of the molded specimens to their maximum level in both neat and nucleated PLA materials. Furthermore, the same crystallinity was reached

at a lower temperature in the nucleated samples than for neat PLA.

The current study shows that PLA materials can have sufficient formability for commercial use in durable goods such as those used in the automotive components or appliances. The increased crystallization rates achieved here can translate both to reduced cycle times and reduced energy requirements in the injection molding process. The materials with higher crystallinity showed correspondingly increased mechanical properties and are thought to have improved durability. Durability and degradation rate measurements are currently being investigated in our laboratory and are the subjects of future publications.

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