

DETERMINATION OF THE POLY(LACTIC ACID) CRYSTALLIZATION THROUGH A SYNERGISTIC APPROACH, CONTAINING A BIOBASED CARBON NUCLEANT

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ABSTRACT

This research discusses poly(lactic acid) based composites prepared through melt blending and injection molding with the plasticizer poly(ethylene glycol) (PEG), and a biobased carbon-rich pyrolyzed biomass char residue with industrially available microcrystalline talc as a comparative nucleating agent. The molding temperature was varied by using a low and high mold temperature to determine the effect of processing conditions on the crystallinity, along with the presence of plasticizer and nucleating agents. The thermal properties of the different composites were tested, including the heat deflection temperature (HDT), coefficient of linear thermal expansion (CLTE), and crystallinity. Several mechanical properties were also investigated such as the tensile, flexural and impact performance of the samples. To visibly identify the differences between PLA composites, morphological characterization was performed by means of optical microscopy, and scanning electron microscopy (SEM).

Results showed that the biobased carbon was beneficial in establishing nucleation sites for the poly(lactic acid) upon cooling, which caused an increase in the crystallization relative to the neat PLA, as was also evident with the talc samples. In the case of the nucleating agent samples with the inclusion of PEG, the crystallization occurred rapidly and was not observable at the isothermal crystallization temperature, unlike the neat PLA that took 15 minutes to crystallize. These tertiary samples also demonstrated a significant reduction in spherulitic size, as the nucleation density was drastically increased. Upon utilizing the higher mold temperature, the PLA crystallinity surpassed 40% for the multi component formulations. This increase helped retain good thermal stability at high temperature conditions as seen in the HDT of the samples surpassing 100°C and CLTE reduction of up to 35%. The biocarbon based samples showed good performance comparable or exceeding the general talc samples and provide a less dense and greener alternative to the common nucleating agent for PLA.

1 INTRODUCTION

Biobased and biodegradable polymeric materials continue to be a fundamental step towards achieving an environmentally-friendly society. Therefore, poly(lactic acid) (PLA) being one of the most common biodegradable thermoplastic biopolymer in the industry today is useful as the base component in the formation of future compostable consumer products. The current downsides of PLA being its toughness and low thermal stability are the key cause for its limited applications.[1] Part of the reasoning behind the latter issue is the slow crystallization rate of PLA, especially under high cooling rates. This results in a greater amount of amorphous phase and low glass transition temperature.[2]

One method to improving the heat tolerance of PLA is by enhancing the crystallinity of the material, which increases the stiffness and structural rigidity when above the glass transition point (~60°C).[3] Since the crystalline phase is capable of a greater contribution to the strength of the

material compared to the amorphous regions. Commonly, three methodologies are available to obtain an improvement in the crystallinity for a thermoplastic. They are the inclusion of a nucleating agent, a plasticizer or altering the processing parameters.[4] Depending on the strategy the crystal nucleation and or growth rate may be increased to establish higher crystallinity of the molded part and a major focus for research and optimization.

For poly(lactic acid), the common plasticizer is polyethylene glycol, (PEG), as it is known to provide chain mobility during crystallization. Similarly, talc has been extensively used as a nucleating agent in PLA to reduce crystallization times and establish higher crystallinities under fast cooling conditions. Therefore, this work aims to determine the performance of an under-valued biobased carbon particle as a nucleating agent, in relation to talc and its implication with a plasticizer.

2 METHODOLOGY

2.1 Material Formation

Poly(lactic acid) (PLA) pellets, injection grade Ingeo 3251D, a product of NatureWorks LLC (USA) was utilized in this study. It has a density of 1.24 g/cm³ and contains 1.4% D-isomer. Poly(ethylene glycol) (PEG) 4000 with a Mw from 3.6-4.4 kg/mol from Sigma-Aldrich was included in the investigation, having a melting range of 58 – 61 °C. A *Miscanthus* based biochar having a particle size less than 400 µm (Competitive Green Technologies, ON, Canada) produced under slow pyrolysis conditions at a temperature of 700°C was also implemented in the composites. Alternatively, talc with a grade name of Mistron Vapor R (Imerys Talc) with a mean particle size of 2.0 µm was tested for comparison to the biocarbon.

The polymer pellets of poly(lactic acid) were initially dried in an oven set at 80°C for a duration of 4 hours before being utilized, reaching a moisture content below 1 wt.%. Similarly, the biocarbon was also kept in an oven ahead of processing at a temperature of 105°C for 24 hours to maintain a minimal moisture content of less than 1.5 wt.%. The polymer compounding was done in a DSM Xplore (Netherlands) 15 mL micro compounder co-rotating twin screw extruder. The polymer and additives were melt blended at a temperature of 180°C for a duration of 2 minutes at a screw speed of 100 rpm. The resulting molten polymer was then transferred at 180°C to a 12 mL micro injection molding machine DSM Xplore with a mould temperature of 48°C or 90°C and removed immediately afterwards. The low mold temperature of 48°C was used to ensure removal of the rigid composite samples without fracture from the mold. The solidified samples were then used for characterization purposes. See Table 1 for the weight ratios of the plasticizer and nucleating agent additions to PLA matrix.

Sample	Mold Temp. (°C)	PLA (wt.%)	PEG (wt.%)	Biocarbon (wt.%)	Talc (wt.%)
1		100	-	-	-
2	48 / 90	80	10	10	-
3		80	10	-	10

Table 1: Composition based on weight of the PLA samples at low and high mold temperature conditions.

2.2 Measurements

2.3 Tensile Properties

An Instron 3382, Universal testing machine, was utilized to measure the strength and moduli of all formulations. The tensile properties were performed following ASTM D638 with type IV specimens at

a testing speed of 5 mm/min in ambient conditions. All the values presented are the averages of five or more replicates for each formulation. Analysis of the collected data was performed with Bluehill 3 software (Instron).

2.4 Heat deflection temperature (HDT)

The heat deflection temperatures (HDT) of the samples were carried out according to the standard ASTM D648 with a 0.455 MPa load in a DMA Q800 (TA Instruments). The samples were measured in three point bending mode at a heating rate of 2°C/min starting from 30°C up to 150°C. Universal Analysis 2000 software (TA Instruments) was used for analysis.

2.5 Coefficient of linear thermal expansion (CLTE)

A thermomechanical analyzer (TMA) Q400 (TA Instruments), was used to measure the coefficient of linear thermal expansion of the samples. The experiment was conducted following ASTM E831 with the specimen tested orthogonal to the injection molded direction using an expansion probe. The data was obtained at a heating rate of 5°C/min from room temperature up to 150°C at a constant force of 0.1 N, with the CLTE calculated in the linear region between 80 and 130°C. The thermal-mechanical analyses were conducted using Universal Analysis 2000 software (TA Instruments).

2.6 Differential scanning calorimeter (DSC)

A differential scanning calorimeter (DSC) Q200 (TA Instruments), was utilized to study the thermal behaviour of the samples. Samples of 5-10 mg were heated at a ramp rate of 10°C/min, starting at 0°C and finishing at 240°C. The temperatures corresponding to the melt (T_m), cold crystallization (T_{cc}), and glass transition (T_g) were measured along with the calculated crystallinity, χ , based on the analysis of the first heating cycle using Universal Analysis 2000 software (TA Instruments).

2.7 Polarized optical microscopy

A Nikon universal design microscope was used for polarized optical microscopy with a controllable hot stage (Linkam LTS 420) for temperature control. The microscope is equipped with a DS-2Mv camera and controlled using NIS-Elements microscope imaging software. The samples were prepared between two microscope glass coverslips and melted at 180°C. The samples were then cooled at a rate of 25°C/min to an isothermal temperature of 120°C, where photos were taken of the growth of the crystal spherulites over time.

3 RESULTS AND DISCUSSION

3.1 Differential scanning calorimetry

To monitor the changes that occur as a result of the nucleants, biobased carbon and talc, the plasticizer, PEG, and mold temperature on the crystallinity of the injection molded samples, DSC thermograms were analyzed. Table 2, shows the glass transition, cold crystallization, melt temperature and crystallinity for all the samples. When analyzing the neat PLA, the sample showed the common glass transition range of 55-60°C, with a low crystallinity of 13%. Upon examination of the ternary composites, the plasticizer and nucleants together showed a synergistic combination of nucleation sites and maneuverability of the polymer chains, to increase the crystallinity above that of the neat PLA, while reducing the T_g and T_{cc} because of the inclusion of the low molecular weight plasticizer.[5]

For the same neat PLA, prepared at high mold temperature, there remained little difference with minimal increase in its crystallinity. As for the ternary composites however, the cold crystallization was completely removed. For these two cases, the samples have reached their maximum crystallinity (>40 %) for the semi-crystalline PLA and are therefore more thermally stable above the glass transition temperature, even with the lower T_g relative to the neat PLA.

Sample	Mold Temp. (°C)	T _g (°C)	T _{cc} (°C)	T _m (°C)	χ (%)
1	48	62	101	169	13
2		42	74	168	32
3		42	72	168	37
1	90	63	101	170	19
2		54	-	169	47
3		47	-	170	41

Table 2: The glass transition, cold crystallization, melt temperature and crystallinity of PLA and ternary composites analyzed from first heating scan of DSC.

3.2 Tensile Properties

The mechanical performance of the neat PLA and ternary composites were measured as seen in Figure 1. The neat PLA had the greatest tensile strength and modulus compared to the ternary samples at both low and high mold temperatures. When both the PEG and the nucleant were added into the PLA matrix, a decrease in strength by upwards of 33-43 % from the neat PLA was evident. The same trend in tensile was prevalent for the high mold temperature samples as well. The reason behind the loss of strength is due to the nucleants acting primarily as a filler, with no compatibility with the PLA. This lack of affinity between the particles and polymer cause high stress concentrations at the irregular shaped edges with no significant stress-transfer.[6] Along with this, the plasticizer having a low molecular weight reduces the overall strength of the material and reduced the intermolecular bonding of the PLA chains.[7]

Regarding the moduli of the samples, there is a small reduction in moduli for the ternary composites at low mold temperature, which is further reduced at high mold temperature. The decrease in modulus of these composites is associated with the PEG, being a softer and flexible material. However, the reduction is hindered by the addition of the stiff nucleants which provided some support in offsetting the plasticizer.

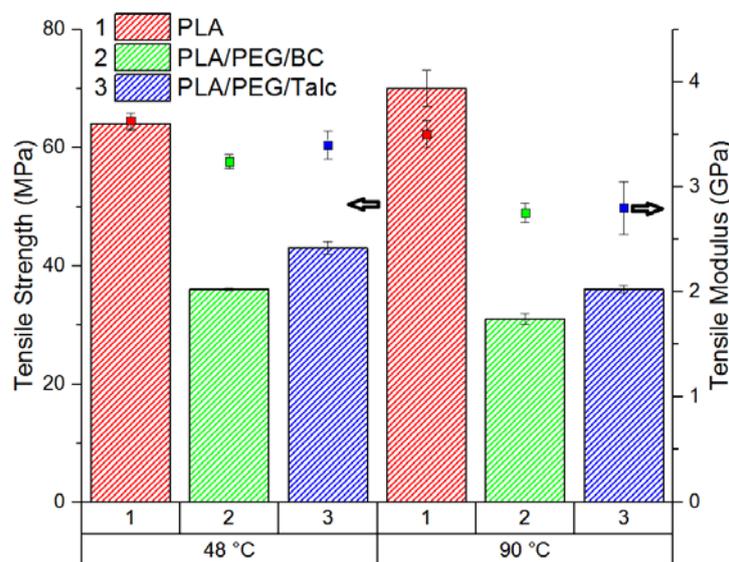


Figure 1: Tensile strength (bars) and tensile modulus (scatter points) of PLA and ternary composites containing plasticizer and nucleating agent.

3.3 Heat deflection temperature

When it comes to thermal properties of polymeric materials, the softening point known as the heat deflection temperature (HDT) is used to establish the viable thermal application window and processing limitations.[8] Figure 2, depicts the HDT results for the samples investigated. The neat PLA had an HDT value of 57 °C, close to its glass transition temperature. The tertiary composites at low mold temperatures showed HDTs below the neat polymer, as the plasticizer enhanced flexibility and lowered the glass transition. Regarding the high mold temperature samples, there is a distinct improvement in the HDT for the tertiary composites unlike the lack of change observed for the PLA. The combination of the plasticizer, nucleating agent, and mold temperature provided the proper conditions for elevated crystallinity that resulted in an enhancement of the HDT. The talc and biocarbon tertiary composites showed a percent increase of 140 and 174%, respectively, when changing from low to high mold temperature.

3.4 Coefficient of linear thermal expansion

When the polymeric material is in use, the dimensional stability of the product may be important in very precise designs, therefore the implication of thermal fluctuations on the dimension of the material can be measured through the coefficient of linear thermal expansion, CLTE. Figure 2, shows the CLTE values for the PLA samples at both low and high mold temperature. The neat PLA had a value of 152 $\mu\text{m}/(\text{m}\cdot^{\circ}\text{C})$. Next, the tertiary composite containing both PEG and biocarbon at the low molded temperature the CLTE is highest at 205 $\mu\text{m}/(\text{m}\cdot^{\circ}\text{C})$ relative to the rest of the samples. It has been shown that fillers with a high thermal conductivity will provide quicker cooling rates and reduce the crystallinity of the composite.[9] However, in the case of the talc based tertiary composite the CLTE remained within standard deviation of the PLA as the talc is a dense filler at 2.8 g/cm^3 , compared to the 1.4 g/cm^3 for the biocarbon, that can provide reinforcement with a low coefficient of thermal expansion. Following the difference in mold temperature, the PLA alone did not show a substantial change in dimensional stability. Though, unlike the low molded samples, both the tertiary blends had an improved thermal stability with the CLTE lowering to 111 $\mu\text{m}/(\text{m}\cdot^{\circ}\text{C})$ for both the biocarbon and talc composites. The biocarbon composite had the largest change, with a 46% reduction in CLTE from low to high mold temperature. This reduction is imparted by the high crystallinity of the PLA, which is thermally stable over the heating range unlike the amorphous portion of the polymer. The amorphous PLA available for expansion was therefore impeded by the crystal regions and stiff fillers in both instances.

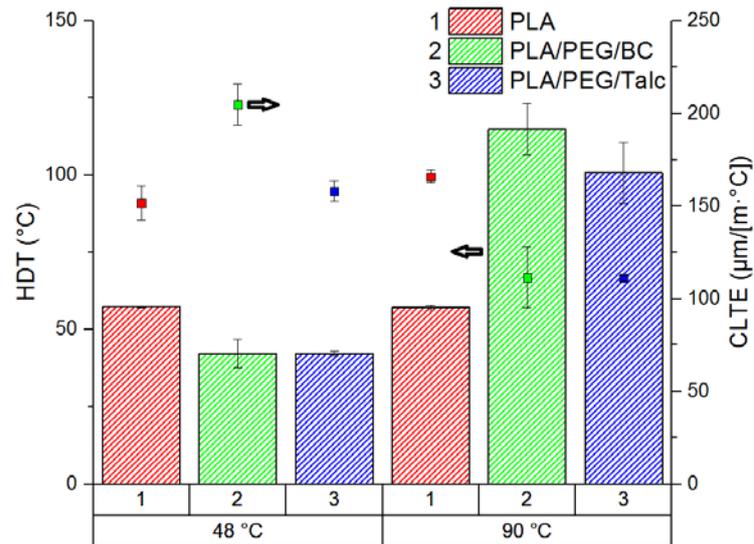


Figure 2: Heat deflection temperature (bars) and coefficient of linear thermal expansion (scatter points) of PLA and ternary composites containing plasticizer and nucleating agent.

3.5 Polarized optical microscopy

The isothermally crystallized neat PLA and the composites containing plasticizer and nucleants are shown in Figure 3. The polarized optical microscopy images show the spherulitic morphology of the different samples. These results were able to provide a visual representation of the crystal structure forming under high mold conditions, as under very fast cooling rates with the low mold temperatures, the percent of crystallinity is lower and have reduced crystallites sizes.[10] For the neat PLA the spherulites are still growing after 2 minutes and have not reached complete crystallinity. When continuing the isothermal crystallization, the PLA finally reached maximum crystallization after 15 minutes. This was considered when the spherulites had filled all the gaps between adjacent spherulites. However, for the case of the ternary composite systems, the crystal formation occurred less than a second of reaching 120°C. This is because the combination of the plasticizer and nucleating agents allow for chain mobility and nucleation sites, respectively. The growth rate of the PLA is enhanced along with the nucleation density. The resulting spherulitic size is reduced as there is less space available for growth when there is an abundance of nuclei present in the composite.[11]

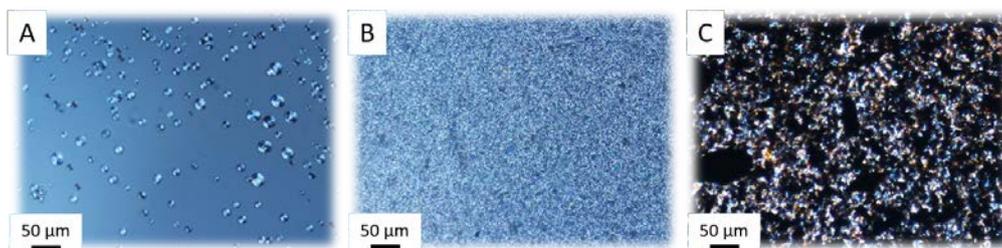


Figure 3: Crystallization of (A) PLA, (B) PLA/PEG/Talc (80/10/10), and (C) PLA/PEG/Biocarbon (80/10/10) samples after 2 minutes at 120°C captured using an optical microscope.

4 CONCLUSIONS

This research evaluated how well the inclusion of various crystallization promoters affected the PLA crystallinity under injection molding conditions. The results demonstrated that the plasticizer

poly(ethylene glycol) was helpful in providing greater ease of movement for the PLA chains to form crystals. In a similar manner, the biobased carbon strengthened the crystallinity when in conjunction with the PEG. The talc nucleating agent showed an enhancement in thermal characteristics at high mold temperatures. The ternary composites enabled PLA to reach its maximum crystallinity with no cold crystallization seen in the DSC. Though it was feasible to reach these properties, only high mold temperature of 90 °C was able to do so with a loss in mechanical strength. Overall, these ternary composites with the crystallinity above 40% had an HDT value greater than 100°C and CLTE that was reduced by upwards of 35 %. The biobased carbon structure was capable of establishing comparable nucleating agent properties to talc, while being a less dense substitute under high mold temperatures conditions with a plasticizer.

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