Overcoming the Fundamental Challenges in Improving the Impact Strength and Crystallinity of PLA Biocomposites: Influence of Nucleating Agent and Mold Temperature

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S *Supporting Information*

ABSTRACT: Poly(lactic acid) (PLA), one of the widely studied renewable resource based biopolymers, has yet to gain a strong commercial standpoint because of certain property limitations. This work is a successful attempt in achieving PLA biocomposites that showed concurrent improvements in impact strength and heat deflection temperature (HDT). Biocomposites were fabricated from a super toughened ternary blend of PLA, poly(ether-*b*-amide) elastomeric copolymer and ethylene-methyl acrylate-glycidyl methacrylate and miscanthus fibers. The effects of varying the processing parameters and addition of various nucleating agents were investigated. Crystallinity was controlled by optimizing the mold temperature and cycle time of the injection process. With the addition of 1 wt % aromatic sulfonate derivative (Lak-301) as a nucleating agent at a mold temperature of 110 °C, PLA biocomposites exhibited dramatic reduction in crystallization half

time to 1.3 min with crystallinity content of 42%. Mechanical and thermal properties assessment for these biocomposites revealed a 4-fold increase in impact strength compared to neat PLA. The HDT of PLA biocomposites increased to 85 °C from 55 °C compared to neat PLA. Crystallization behavior was studied in detail using differential scanning calorimetry and was supported with observations from wide-angle X-ray diffraction profiles and polarized optical microscopy. The presence of a nucleating agent did not alter the crystal structure of PLA; however, a significant difference in spherulite size, crystallization rate and content was observed. Fracture surface morphology and distribution of nucleating agent in the PLA biocomposites were investigated through scanning electron microscopy.

KEYWORDS: *poly(lactic acid), impact strength, heat deflection temperature, injection molding, crystallization, nucleating agent, mold temperature*
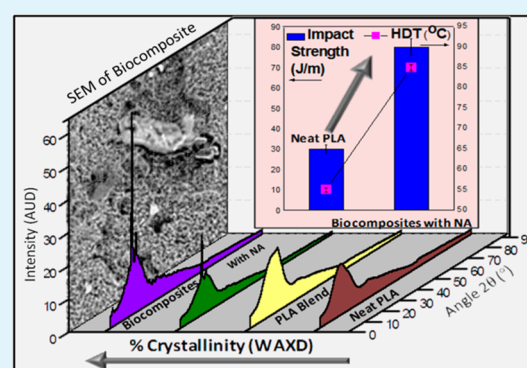
■ INTRODUCTION

Poly(lactic acid) (PLA) is an aliphatic thermoplastic polymer obtained from renewable resources. PLA has high strength, modulus, biocompatibility and transparency. PLA is superior to many petroleum based polymers based on its compostability, energy consumption, CO_2 emissions and end of life standpoints. Large scale availability of PLA at a reasonable price has opened up more common application areas like packaging, fiber materials and other commodity materials.[1−3] Wide scale applications of PLA are, however, significantly hindered by its poor impact resistance, slow crystallization rate and low heat deflection temperature (HDT), especially in areas that require high levels of mechanical strength, high resistance to temperature and sudden impact.[2,3]

Only the crystalline PLA phase that exists above the glass transition (T_g) temperature, around 55 °C, is known to impart useful mechanical properties.[4] The crystalline form of PLA is therefore important to achieve required improvements in the

HDT. On the other hand, the impact strength of semicrystalline polymers like PLA usually varies inversely with the percent crystallinity.[5] Attempts to enhance the performance of PLA beyond standard levels, so far, for injection molded applications, have generated formulations with either higher HDT or greater impact strength, but not both. Huda et al.[6,7] described the effect of untreated and silane treated talc on the mechanical properties of PLA hybrid composites with newspaper fibers. Stiffness and HDT of PLA were improved with talc; however, a drastic decrease in impact strength and increase in the density of the composites were observed. Liu et al.[8,9] studied the blends containing PLA, ethylene/butyl acrylate/glycidyl methacrylate and a zinc ionomer of ethylene/methacrylic acid copolymer as additives in an attempt to

Table 1. Differential Scanning Calorimetry Data

formulation	percentage crystallinity, χ_c		melt temp, T_m (°C)		cold crys temp, T_{cc} (°C)		melt crys temp, T_{mc} (°C)	glass trans temp, T_g (°C)		
	1st cycle	3rd cycle	1st cycle	3rd cycle	1st cycle	3rd cycle		1st cycle		3rd cycle
composites without nucleating agent at different mold temps										
PLA1 blend-MS (90/10) @ 190c, 30c, 30s	17.22	8.02	170.23	170.45	93.93	116.54	96.05	44.53	60.55	61.9
PLA1 blend-MS (90/10) @ 190c, 110c, 30s	31.35	15.27	168.84	170.30	99.31	114.2	--	45.97	62.22	62.14
composites with nucleating agent at different mold temps and diff loading levels										
PLA1 blend-MS-Lak (89/10/1) @ 190c, 30c, 30s	14.94	49.01	170.06	170.14	94.85		133.86	44.96	60.96	62.05
PLA1 blend-MS-Lak (89/10/1) @ 190c, 60c, 60s	19.08	51.04	172.63	171.63	96.51		134.97	44.08	62.29	61.28
PLA1 blend-MS-Lak (89/10/1) @ 190c, 90c, 60s	27.09	52.17	170.41	170.71	91.31		135.04	42.95	60.85	61.92
PLA1 blend-MS-Lak (89/10/1) @ 190c, 110c, 60s	42.25	58.94	171.61	169.77			134.33	43.94	63.47	61.71
PLA1 blend-MS-Lak (89/10/1) @ 190c, 120c, 60s	41.11	57.38	167.26	169.41			133.76	43.53	62.18	62.14
PLA1 blend-MS-Lak (88/10/2) @ 190c, 110c, 60s	43.98	47.68	172.59	169.55			135.27	44.72	61.96	62.39
composites with nucleating agent at different melt temps										
PLA1 blend-MS-Lak (89/10/1) @ 180c, 110c, 60s	41.88	58.73	174.24	171.78			135.24	45.29	62.36	61.68
PLA1 blend-MS-Lak (89/10/1) @ 170c, 110c, 60s	31.34	56.57	169.88	169.68			134.19	43.91	61.98	61.89
composites with other nucleating agents										
PLA2 blend-MS (90/10) @ 190c, 110c, 60s	39.42	54.71	179.14	177.42			104.23	43.17	63.78	63.5
PLA1 blend-MS-HPR (89/10/1) @ 190c, 110c, 60s	18.00	5.60	170.23	170.68	98.36	116.56		45.09	61.05	61.94
PLA1 blend-MS-Emf (89/10/1) @ 190c, 110c, 60s	22.52	9.71	169.27	170.17	97.05	113.68		44.47	60.93	62.05

improve impact strength. However, the HDT of these blends remained nearly same as that of neat PLA. Numerous approaches and techniques like block copolymerization, chemical modification, nucleation, plasticization and blending with suitable polymers[5,10] have been explored to increase the crystallization and toughness of PLA. Chemical modification is typically complex, technically demanding and expensive due to the cost of required catalysts and/or monomers. Combining nucleating agents with plasticizers has showed an improvement in PLA mechanical properties and crystallization kinetics. However, plasticizers have a tendency to leach out over long-term use, thereby causing embrittlement of the polymer.[5,10] Furthermore, lowering of the glass transition temperature (T_g) may affect the production process of commercial products made from the plasticized PLA.[5,10]

Blending of polymers is an alternate economical and effective way of achieving new materials with desired properties. Mechanical and physical properties that are usually absent in individual polymers can be obtained by blending. However, the toughness improvements achieved in binary blends are usually accompanied by the reduction in tensile strength and modulus; therefore, the addition of compatibilizers that make up ternary or multicomponent blends are gaining research attention.[8,11] In our previous work,[12] super toughened PLA ternary blends were formulated by adding a functionalized polyolefin, ethylene methyl acrylate glycidyl methacrylate (EMA-GMA) to a PLA and polyether block amide (PEBA) blend. Reactive functional groups on the EMA-GMA reacted with carboxyl and hydroxyl end groups present in the PLA and PEBA, thereby improving the toughness of the ternary blend dramatically. Although a nonbreak impact behavior was observed in the PLA ternary blends, the HDT remained typically the same as that of neat PLA.

An increase in PLA's total percentage crystallinity can effectively improve HDT, stiffness and chemical resistance.[13] Due to high crystallization half time resulting from the slow crystallization rate of PLA, obtaining an injection molded article with high crystallinity remains a challenge. Therefore, to obtain a molded component with increased crystallinity and

maximized mechanical and physical performance, Harris and Lee[14] increased the mold temperature during injection molding to over 100 °C. However, the problem with this step is that a higher cycle time of ~2 min would be required. Demolding of the processed components would be difficult in a short cycle time due to the higher cooling time required.

The presence of nucleating agents in a virgin polymer can have a positive effect on crystallization kinetics and morphology by offering nucleating sites for initializing the crystallization process. Lowering of crystallization half time achieved with the presence of a nucleating agent can help in shortening the molding cycle times.[15] Another approach to increase crystallinity is by adding natural fibers to the polymer matrix. This approach serves dual purposes: they can increase the stiffness and heat resistance of a polymer while decreasing the cost of resulting composite materials as they replace a certain percentage of relatively expensive matrix material. Miscanthus, a perennial grass, has been recently studied as an effective filler in biopolymers[16,17] owing to its multiple advantages including availability at very low cost. Besides increasing the crystallinity and heat resistance, natural fibers and nucleating agents can curtail the toughness of PLA, as these properties negatively impact each other. But by using super toughened ternary PLA blends as a matrix material, the resulting biocomposites would still have higher impact strength and HDT compared to neat PLA. This paper therefore proposes a novel combination of PLA ternary blends, nucleating agents and natural fibers to formulate PLA biocomposites that are injection molded at different mold temperature to accomplish the desired results. The effect of adding different nucleating agents and the effect of varying the process parameters on the PLA biocomposites are summarized by investigating the mechanical, thermal, thermomechanical properties and morphology by various characterization techniques.

■ MATERIALS AND METHODS

Materials. PLA, Ingeo 3001D with approximately 95% of L-lactide content was purchased from NatureWorks LLC, USA. PLA 3100 HP with increased crystallizability was also purchased from NatureWorks

LLC, USA. Polyether block amide (PEBA), Pebax Rnew 35R53 having renewable carbon content of 28−32% was purchased from Arkema Company. EMA-GMA terpolymer containing 8% of glycidyl methacrylate, commercially available as Lotader AX 8900 from Arkema Company, was obtained from Quadra Chemicals, Canada. Nucleating agents used are (1) aromatic sulfonate derivative (potassium salt of 5-dimethyl sulfoisothalate), commercially available as Lak-301 from Takemoto Oil & Fat Co., Japan, (2) magnesium oxysulfate, sold as HPR-803i by Milliken Chemical. Ltd., USA and (3) precipitated calcium carbonate sold by Specialty Minerals Inc., as Emforcebio. Miscanthus fibers were supplied by New Energy Farms, Leamington, ON, Canada. Polymers, nucleating agents and fiber will henceforward be abbreviated in the text and figures as noted: PLA 3001D as PLA1; PLA 3100HP that is said to contain about 1% of Lak-301 as PLA2 and blends containing these PLAs will be referred to as PLA1 blend and PLA2 blend. Miscanthus will be abbreviated as MS, Lak-301 as Lak, HPR-803i as HPR and Emforcebio as Emf. At a few places for brevity, nucleating agents will be abbreviated as NA.

Biocomposite Fabrication. The matrix material was a blend of PLA/EMA-GMA/PEBA (70/20/10), and optimization of the blend ratio was done in our earlier work. The details can be found in our previous publication.[12] Based on preliminary examinations, weight percentage of miscanthus in the biocomposite was decided to be 10%, beyond which it is difficult to achieve required impact strength in the biocomposites. PLA and miscanthus were dried in an oven for at least 12 h at 80 °C whereas PEBA and EMA-GMA were dried at 60 °C. A micro 15 cc corotating twin screw extruder and micro 12 cc injection molder from DSM Research, The Netherlands were used to fabricate all the test samples. Biocomposites were extruded and injection molded at 190 °C; however, to investigate the effect of varying the processing temperature, 170 and 180 °C were also used. Residence time and screw RPM was maintained at 2.5 min and 100, respectively. A preheated collector connected to the injection molder was used to transfer the extrudate for molding. Injection pressure used for first and second stage are 3 and 6 bar, respectively.

It is known from the wealthy of literature that the crystallization temperature for PLA is approximately around 105 to 130 °C; therefore, different mold temperatures (30, 60, 90, 110 and 120 °C) were adopted and the properties were examined systematically at these molding temperatures. A cooling time of 30 s was adopted for a 30 °C mold temperature and 60 s for higher temperatures to facilitate complete cooling before demolding of the samples without distortion. To provide a comparison with non-nucleated biocomposites and to emphasize the individual effect of high mold temperature and presence of nucleating agents, PLA1 blend/MS (90/10) was molded at low and high temperatures (30 and 110 °C). Furthermore, to investigate the effect of other nucleating agents such as HPR and Emf in comparison with Lak, the performance of PLA1 blend/MS/HPR, PLA1 blend/MS/Emf was studied at 110 °C. Results of varying the concentration of Lak in the biocomposite between 1 and 2% are also reported, as no significant difference was observed in the intermediate concentrations. For the list of formulations, please refer to Table 1 (column 1) on DSC data.

Testing and Characterization Methods. Properties were tested after the molded specimens were conditioned according to ASTM D618-08, Procedure A: 40 h, 23 °C and 50% relative humidity. Mechanical properties reported are an average result of five samples. Differential scanning calorimetry (DSC) was performed with a DSC 200 from TA Instruments. 5 mg of sample was prepared by cutting a thin slice from molded sample conditioned at laboratory atmosphere. Heat−cool−heat cycles with the following conditions were used: heat cycle, −50 to +190 °C at 10 °C/min; cool cycle, +190 °C to −50 °C at 5 °C/min. The first heat cycle was followed by a 3 min isothermal step to erase the thermal history. The glass transition temperature (T_g), crystallization temperature (T_{mc}), cold crystallization temperature (T_{cc}) and melting temperature (T_m) were determined from the DSC graphs. Percentage crystallinity (χ_c) was calculated using the using the equation $\chi_c = ((\Delta H_m - \Delta H_{cc})/(f \cdot \Delta H_m^0))$, where ΔH_m is the enthalpy of melting, ΔH_c is enthalpy of cold crystallization, ΔH_m^0 is the enthalpy of melting of 100% pure PLA, 93.7 J/g as mentioned in the

literature,[18] and f is the weight fraction of PLA in the composite. Wide-angle X-ray diffraction (WAXD) profiles were obtained at room temperature using a SuperNova Agilent single-crystal diffractometer equipped with a microfocus Cu Kα (λ = 1.541 84 Å) radiation source and Atlas CCD detector. X-ray diffraction images were collected from four different angular positions of the goniometer using φ-scans to generate a 1D powder pattern within 2θ range of 5−100°. The images were processed using CrysAlisPro software. Steps of 0.02° in 2θ were used to generate powder pattern plots.

An Instron Instrument Model 3382 was used to measure the tensile and flexural properties by adapting ASTM standards D638 and D790, respectively. Tensile test conditions: gauge length, 50 mm; crosshead speed, 50 mm/min for the blends and 5 mm/min for the biocomposites. Flexural test of blends and composites were done at a crosshead speed of 14 mm/min and span length of 52 mm. A TMI 43-02 monitor impact tester with a 5 ft-lb pendulum was used to measure the notched Izod impact strength (ASTM D 256) at room temperature. Dynamic mechanical properties (storage and loss modulus and tan δ) were studied using a DMA Q800, TA Instruments (temperature range, −50 to +130 °C; ramp rate, 3 °C/min). HDT was also measured in with the DMA Q 800 with a three-point bending clamp in DMA controlled force mode at a stress of 0.455 MPa and ramp rate of 2 °C/min. Deflection was evaluated at 250 μm (0.1889% strain). Thermal stability of biocomposites in nitrogen atmosphere was accomplished using a TGA Q 500, TA Instruments (experimental temperature range, 25 ± 3 to 600 °C; heating rate, 20 °C/min). A fractured surface morphology was observed by scanning electron microscopy (SEM, Inspect S 50, FEI, The Netherlands). Samples were gold coated for 30 s under an argon atmosphere using a Cressington sputter coater 108. A Phenon ProX SEM (Phenon World BV, The Netherlands) instrument equipped with a back scattering electron (BSE) detector and energy dispersive spectroscopy (EDS) was used to illustrate the composition of different nucleating agents. SEM images were captured at an accelerating voltage of 10 keV. A polarized optical microscopy (POM) instrument equipped with a hot stage (Nikon Instruments Inc., Canada, Linkam Scientific Instruments Ltd., UK) was used to perform a qualitative analysis of the crystallization process.

■ RESULTS AND DISCUSSIONS

Crystallization Behavior. *Nonisothermal Crystallization.* The nonisothermal crystallization behavior of neat polymers and PLA biocomposites was studied using differential scanning calorimetry (DSC) to investigate the effect of processing parameters and effect of different nucleating agents in promoting the crystallinity. DSC melting curves for neat PLA, PEBA, EMA-GMA and PLA blends are presented in the Supporting Information (Figure S1). PLA exhibited its characteristic cold crystallization and melting peaks and glass transition temperature (T_g). PEBA is seen to melt at 140 °C with a shallow melting peak; the T_g was around −15 °C. EMA-GMA also showed a very shallow melting peak at 60 °C, seen mostly as a flat line in Figure 1a. Several trends were noticed from the first heating scans obtained from DSC for PLA biocomposites with and without nucleating agents at different mold temperatures. The first heating scan is preferred here, as it best reflects the effect of different processing temperature profiles used for processing the samples on the resulting crystallinity content. The first obvious observation from Figure 1 is the cold crystallization peak that reflects the materials ability to crystallize below the melting temperature. The cold crystallization peak was present in all the composites except the ones containing Lak molded at temperatures higher than 90 °C. This indicates that some of the semicrystalline chains were still capable of rearranging or recrystallizing before melting and that the particular processing parameter used did not allow complete reorganization of the chains while processing. The
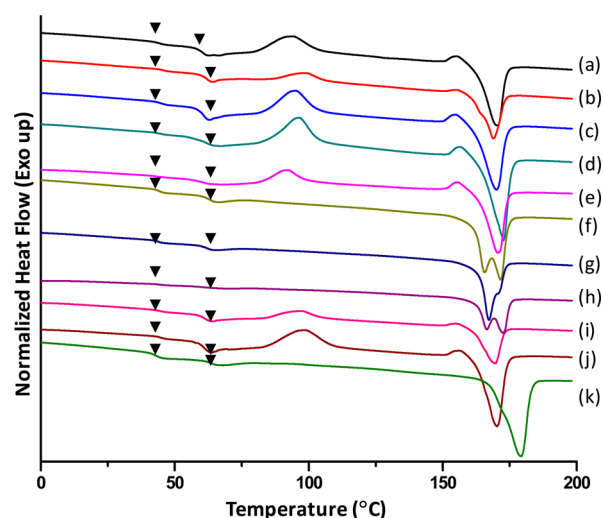
Figure 1. DSC thermograms of first heating scans. PLA1 blend-MS (90/10) molded at (a) 30 °C and (b) 110 °C; PLA 1 blend-Ms-Lak (89/10/1) molded at (c) 30 °C, (d) 60 °C, (e) 90 °C, (f) 110 °C and (g) 120 °C; (h) PLA 1 blend-MS-Lak (88/10/2) molded at 110 °C; (i) PLA 1 blend-MS-HPR (89/10/1) molded at 110 °C; (j) PLA 1 blend-MS-Emf (89/10/1) molded at 110 °C; (k) PLA2 blend-MS (90/10) molded at 110 °C.

general trend noted here was the decrease in T_{cc} values of biocomposites with Lak as the molding temperature increased. The absence of cold crystallinization peak in PLA1 blend/MS/Lak (89/10/1) at 110 °C, 120 °C and PLA2 blend/MS (90/10) at 110 °C is a good indication that Lak at higher molding temperatures acts as an effective nucleating agent in promoting the crystallization process compared to other nucleating agents (HPR, Emf). From observations noted on T_{cc}, individual effects of high mold temperature and presence of Lak at 30 °C molding were not sufficient in eliminating the process of cold crystallization. This emphasizes the combination effect of having high mold temperature and the presence of effective nucleating agent like Lak in facilitating crystallization such that the crystal are in a stable form and does not show any recrystallization.

The percentage of crystallinity could be used to quantify the effectiveness of different nucleating agents in combination with elevated mold temperatures, which is discussed in subsequent paragraphs. From Figure 1, several peculiarities were noticeable in the melting peaks of the first heating scan. A small exothermic peak just before the melting peak was noticed in all the biocomposites, except the one containing Lak molded at higher mold temperatures. Another event is the occurrence of double melting peaks, which was distinct in PLA biocomposites with Lak (1 and 2%) molded at 110 °C, where the small exothermic peak was absent. Multiple melting peaks usually indicates the presence of imperfect crystals that have the tendency to melt at lower temperatures.[18] In fact, the phenomenon of multiple melting peaks is attributed to a variety of factors including the presence of different crystal morphologies and modifications, possibility of crystallization induced molecular segregation, the orientation and reorganization process occurring during DSC and the heating rates of the DSC experiment.[18−23] Detailed analysis of multiple melting peaks in PLA by several researchers reveals that these phenomena can be correlated with crystallization condition requirements for the formation of α' and α crystal.[20−22] When

the PLA biocomposite crystallizes at temperatures below 120 °C, α' crystals are formed, which are disordered crystals with the same conformation as the α form but with loose packing. The exothermic peak appearing just before the melting peak in our results can be associated with the transformation of disordered α' crystals to more ordered α crystals. When the PLA biocomposite crystallizes at temperatures that favor the simultaneous formation of α' and α crystals, a double melting peak appears. Single melting peaks are associated with the formation of α crystals alone at higher crystallization temperatures.[20] This behavior can also be explained in terms of low and high melting temperature crystallites. The presence of low melt temperature crystallites in larger quantities reduces the fraction of material competing with the formation of high temperature crystallites, at least within the temperature zone where the low temperature crystal phase is stable and there is potential to nucleate the high temperature crystal phase. As a result, increasing the molding temperature would increase the concentration of the low temperature crystallites and thus the lower melting peak has a more significant presence on the DSC thermogram. Slight reduction in melting temperature of PLA biocomposites containing Lak molded at higher temperatures supports the imperfection in crystal structure. PLA2 containing Lak in the master batch has a high melt temperature and a single melting peak, indicating the presence of stable crystal structure. Ke and Sun[24] have also noticed similar behaviors in their work on PLA and starch composites. They have attributed the appearance of small exothermic peak to the additional crystallization that had occurred at a higher temperature during the DSC heating scan than the initial temperature at which the first crystallization occurred, which is quite possible in our case as well.

Melting temperature (T_m), melt crystallization and cold crystallization temperature (T_{mc} and T_{cc}), percentage crystallinity (χ_c) and glass transition temperature (T_g) data are provided in Table 1. Two different glass transition temperatures were observed for PLA biocomposites under the first heating cycle (represented by inverse triangles in Figure 1). The first T_g appeared at around 42−45 °C, which was manifested by a typical inflection in the baseline toward the endothermic side. The second T_g, noticed around 60 °C, showed a very sharp transition almost like an endothermic melting peak in some of the biocomposite formulations. The sharpness observed is often related to the relaxation kinetics of the polymer chains subjected to heating at a constant rate.[25] This phenomena of double T_g has been reported previously for PLA based materials and are attributed to the presence of some of the amorphous polymer chains of the PLA being located in two different regions, one region is where all the amorphous polymer chains are situated far from the crystalline ones and the next region is where the immobilized polymer chains are situated closer to the crystallites.[25] The double Tg behavior disappeared in the second heating scan suggesting that the relaxation behavior of the samples could have changed by erasing the thermal history.

Dramatic difference in melt crystallization temperature was observed with the addition of Lak, which shifted the T_{mc} from ~96 to ~134 °C. The T_{mc} peak was absent in biocomposites containing HPR and Emforce, due to inability of the material to crystallize at the programmed cooling rate (5 °C/min), an indication of the material being in an amorphous state when cooled down from the molten state. Similar observations have been reported previously by Jiang et al.[26] and Suskut et al.[19] in the PLA/CaCO$_3$ system. A difference of ~40 °C in T_{mc} of

biocomposites with Lak strongly suggests that there is an increase in the concentration of nucleation sites induced by the addition of nucleating agent, Lak. However, PLA2 blend/MS biocomposites showed only ∼8 °C improvement in crystallization temperature.

Isothermal Crystallization. Degree of crystallinity relative to the maximum achievable crystallinity level is referred to as relative crystallinity.[23] It is often more desirable to know the rate at which crystallization occurs at a fixed temperature and a measure of which is crystallization half time. It is the time taken by a sample to reach half the final crystallinity. Crystallization behaviors of composites with different nucleating agents were studied under two different temperatures. Figure 2 is a plot of
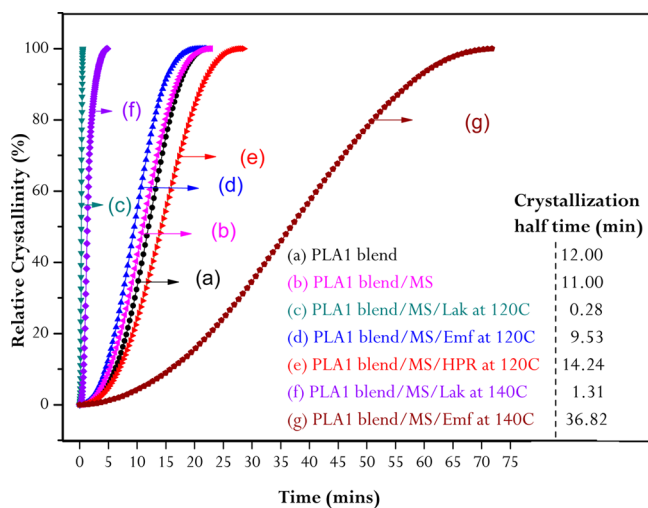

Figure 2. Plot of relative crystallinity vs time and crystallization half time of composites with different nucleating agents at two different temperatures.

relative crystallinity against time. It shows the crystallization behavior and half time of PLA biocomposites with different nucleating agents (Lak, Emforcebio and HPR803i).

Nonisothermal crystallization revealed that Lak was increasing the crystallization temperature significantly; therefore, 140 °C was selected for the isothermal crystallization study but this temperature was very high that no crystal formation was observed in composites containing other nucleating agents even when subjected to isothermal conditions for more than 3 h. Therefore, efficiency of other nucleating agents was analyzed at 120 °C. This temperature is not very appropriate for Lak as most of the crystals would have formed by the time the samples are quenched to 120 °C; however, a comparison is provided in Figure 2.

Many studies have reported the strong dependence of crystallization rate on the selected isothermal crystallization temperature. Neat PLA is known to have a very slow crystallization rate, and depending on the temperature selected in the range of 105 to 130 °C, PLA has shown to have crystallization half times between 5 and 40 min.[14,27,28] As listed in Figure 2, crystallization half time for PLA blend was noticed to be 12 min and with the addition of fibers, it slightly decreased to 11 min, which could be attributed to the presence of miscanthus. Multiple studies have reported the ability of cellulose in natural fibers to act as nucleating agents, and sometimes the presence of fibers can promote transcrystallinity.[29,30] A striking difference in crystallization rate was observed

in the case of Lak with a ∼40-fold increase at 120 °C and a ∼10-fold increase at 140 °C. A very low half time of 0.28 min for composites containing Lak isothermally crystallized at 120 °C could be an indication that crystal formation might have already started while cooling down from the melt temperature. HPR had increased the half time to 14.24 min, indicating that addition of HPR actually hindered the crystallization process and is not effective in offering nucleation sites for the polymer to crystallize. The Emf nucleating agent decreased the half time to 9.33 min; however, it was not as effective as Lak. In comparison, it can be said that Lak is very efficient in imparting a desired level of crystallinity within a short period of time, which is of great value to maintain short cycle times during the injection molding.

The effectiveness of different nucleating agents tested here can mainly be attributed to their physical nature and the nucleation mechanism. HPR (magnesium oxysulfate) and Emf (precipitated calcium carbonate) are inorganic materials, which when added as nucleating agents, act as heterogeneities on which the crystallizing polymer crystallizes when cooled down from unoriented molten state giving rise to a heterogeneous nucleation mechanism.[31] On the other hand, Lak is a salt of organic sulfonic acid, which makes it an organic nucleating agent. A chemical nucleation behavior is mostly favored by organic NAs, where they are said to cause the chain scission in polyesters and form ionic chain ends and then ionic clusters that act as the true nuclei.[32] Under the conditions studied in this work, organic nucleating agent (Lak) has been found to impart high level of crystallization in PLA.

Wide-Angle X-ray Diffraction (WAXD). To obtain further information on crystallization, the crystalline nature of matrix, fiber and biocomposites were analyzed with WAXD. Figure 3
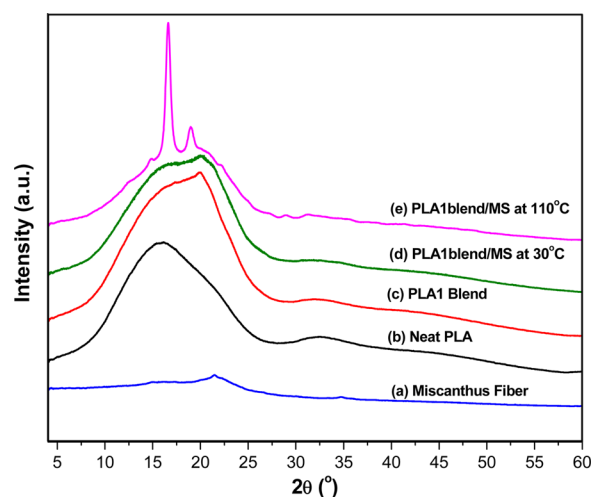

Figure 3. WAXD profile of raw materials and biocomposites without nucleating agents molded at low and high mold temperatures.

demonstrates the profiles obtained for neat PLA, PLA blend matrix, miscanthus and biocomposites at low and high mold temperatures (30 and 110 °C). Neat PLA exhibited a broad hollow ascribed to the amorphous nature and a weak reflection peak at 2θ = 16.84, revealing the semicrystalline nature. In addition to the above characteristic peaks, blends and composites molded at 30 °C exhibited a small diffraction peak at around 2θ = 20.8, which could be ascribed to poorly formed crystals of PEBA.[33] On the other hand, a broad hollow

of PLA was noticed in biocomposites molded at 30 °C, indicating the inability of PLA to form perfect crystals at this molding temperature. However, when molded at 110 °C and in the absence of a nucleating agent, the intensity of the PLA characteristic peak at $2\theta = 16.84$ strongly increased and a shoulder appeared at $2\theta = 19.13$, indicating the increase in crystallization of PLA under this molding condition. These peaks are two strong reflections of 200/110 ($2\theta = 16.84$) and 203 ($2\theta = 19.13$). These peak values are in accordance with values reported in the literature.[22,34,35]

Therefore, the two same reflections seen in our WAXD profile, along with DSC data, support the formation of mixture of α' and α crystal phases in our biocomposite system. Figure 4
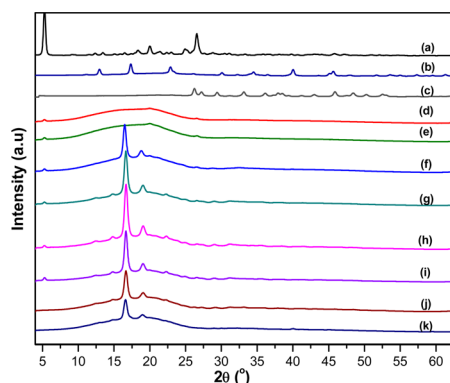

Figure 4. WAXD profile of different nucleating agents and their composites molded at different temperatures: (a) Lak-301, (b) HPR 803i, (c) Emforcebio; PLA1 blend/MS/Lak (89/10/1) at (d) 30 °C mold, (e) 60 °C mold, (f) 90 °C mold, (g) 110 °C mold and (h) 120 °C mold; (i) PLA1 blend/MS/Lak (88/10/2) at 110 °C mold; (j) PLA1 blend/MS/Emf (89/10/1) at 110 °C mold; (k) PLA1 blend/MS/HPR (89/10/1) at 110 °C mold.

compares the X-ray diffraction profiles of different nucleating agents, PLA biocomposites nucleated with Lak at different mold temperatures and biocomposites with HPR and Emf molded at 110 °C. The PLA1 blend/MS/Lak (89/10/1) at low mold temperatures (30 and 60 °C) was similar to the patterns of biocomposites without a nucleating agent at low mold temperatures except for the peak at $2\theta = 5.37$ m, which comes from the characteristic peak of Lak. With the increase in mold temperature from 90 to 120 °C, the crystalline peak intensity of PLA increased significantly and the highest intensity was recorded for the biocomposites molded at 120 °C. With the increase in content of Lak from 1 to 2%, the peak intensity was not significantly affected and it was much similar to the one containing 1% molded at 110 °C. Comparing PLA1 blend/MS/Lak molded at 110 °C with HPR and Emf, again the ones with Lak showed higher intensity of reflection associated with the crystalline part. Approximate peak maxima, 2θ (d spacing) values obtained for PLA1 blend/MS/Lak (89/10/1) molded at 110 °C are 5.37 (16.46), 12.35 (7.16), 14.80 (5.98), 16.84 (5.26), 19.13 (4.64) and 22.33 (3.98). In all of the above-discussed biocomposites, the 2θ values for the crystalline peak remained the same, indicating that the addition of nucleating agent and the increase of mold temperature has increased the crystallizability of PLA without affecting its inherent crystal structure. A similar result has been previously reported by Xiao et al.[36] in PLA with triphenyl phosphate and talc as nucleating agents.

Mechanical Properties and Heat Deflection Temperature (HDT). As discussed previously, impact strength and HDT are the two most important deciding factors for commercializing PLA for wide scale applications. Therefore, the effect of nucleating agents and processing parameters on the impact strength and HDT were first determined and the optimizations were done based on the balance of these two properties.

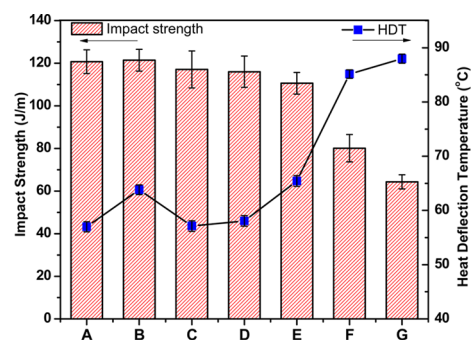Figure 5 shows the trend in impact strength and HDT of PLA biocomposites with and without nucleating agents at

Figure 5. Impact strength and HDT of PLA biocomposites with and without Lak molded at different mold temperatures and injection cycle times: A, PLA1 blend/MS (90/10) at 30 °C, 30 s; B, PLA1 blend/MS (90/10) at 110 °C, 60 s; C, PLA1 blend/MS/Lak (89/10/1) at 30 °C, 30 s; D, PLA1 blend/MS/Lak (89/10/1) at 60 °C, 60 s; E, PLA1 blend/MS/Lak (89/10/1) at 90 °C, 60 s; F, PLA1 blend/MS/Lak (89/10/1) at 110 °C, 60 s; G, PLA1 blend/MS/Lak (89/10/1) at 120 °C, 60 s.

various mold temperatures. Neat PLA has an impact strength of 20 J/m and HDT of 55 °C. PLA blends containing PEBA and EMA-GMA showed a nonbreak behavior, which was attributed to the unique morphology development in this particular blend formulation as noted in our previous publication.[12] However, the HDT of blends remained the same as that of neat PLA. From Figure 5, it is noticeable that the addition of 10% miscanthus reduced the impact strength to ca. 120 J/m. This is considered to be common, as the ductility of the matrix is reduced by the addition of fibers that restrict the molecular mobility of the polymer chains. Nagarajan et al.[16] have previously reported such reduction in impact strength with the addition of miscanthus fibers in a different matrix system. Nonetheless, the level of impact strength is still 300% higher compared to the neat PLA. But the HDT of this formulation was found to be at 58 °C, meaning the incorporation of natural fiber alone in the blend matrix system did not help in increasing the HDT tremendously mainly because there was no significant change in crystallinity as discussed in the 'Crystallization Behavior section. Nyambo et al.[37] studied the effect of adding agricultural residues in PLA and noticed no improvement in HDT, even at 30 wt % fiber loading.

Increasing the mold temperature is one of the effective and proven strategies to improve the crystallizability of PLA. Vadori et al.[38] have recently published an investigation on the effect of mold temperature on the performance of PLA where a 90 °C mold temperature was found to impart maximum crystallinity. In our study, when the PLA biocomposites without any nucleating agent were molded at a high mold temperature of 110 °C, the impact strength was maintained while the HDT increased from 58 to 64 °C, which was only a limited

improvement. This observation revealed that incorporation of fiber and high mold temperature alone is not sufficient to achieve the required balance of properties, which can again be well supported with crystallinity results from DSC experiments. Hence, addition of nucleating agents becomes important.

The effectiveness of a nucleating agent, Lak-301, was studied by varying the mold temperature from 30, 60, 90, 110 and 120 °C. From Figure 5, it can be said that an increase in mold temperature in the presence of Lak has minor influence on the impact strength up to a temperature of 90 °C, but the HDT improved to 65 °C at a molding temperature of 90 °C. Once the temperature was increased beyond 90 °C, a drastic difference in both impact strength and HDT was noticed. This could be well related to the marked improvement in crystallinity achieved at different mold temperatures. This result is also an indication of nucleated material having faster crystallization rates. Once the percentage crystallinity of PLA in the biocomposites is over 40%, it plays a dramatic role in influencing the material properties. Although the HDT reached a plateau over the 110 °C mold temperature, the impact seemed to reduce further with the increase in mold temperature. Therefore, depending on the property requirements, the crystallinity level needed to achieve those requirements can be controlled by selecting appropriate mold temperatures. Another noteworthy point here is demolding of the samples at high mold temperatures; without the nucleating agent, the samples were hard to remove from the mold in spite of having miscanthus fibers, which imparted a certain amount of stiffness to the composites. However, with the addition of Lak, the samples did not warp and were easy to remove from the mold without causing any potential deformation. This factor is important from an industrial processing point of view because cooling times exceeding 60 s would not be preferred, as they would affect the overall production efficiency and cost, defeating the very purpose of making these materials available at an affordable cost. Suryanegara et al.[15] have also made similar observation where the presence of combination of micro-fibrillated cellulose and phenyl phosphonic acid zinc (NA) helped in easy demolding of the samples processed with a 90 °C mold temperature.

The effectiveness of two other additives as nucleating agents (HPR 803i and Emforcebio) and PLA containing Lak-301 nucleating agent, (PLA 3100 from Natureworks, referred as PLA2) in providing the required balance of impact strength and HDT was tested at a mold temperature of 110 °C and has been compared with biocomposites containing Lak; the results are shown in Figure 6. Addition of HPR and Emfocebio nucleating agents did not influence the properties significantly: the impact strength remained same as that of biocomposites without any nucleating agents molded at higher mold temperatures and the HDT increased to just above 60 °C. On the other hand, the PLA2 system already containing the Lak additive showed better performance compared to the other two additives but was still lower than that of adding Lak separately during processing as in the PLA1 system. Depending on the property requirements and to achieve the cost vs performance balance, using PLA containing the Lak additive might be a better choice.

Yu et al.[39] studied the effect of adding talc on thermal and mechanical properties of PLA. They have reported that talc did not bring about any significant difference in HDT until 5 wt % loading, and the maximum increment achieved was 3 °C at 18 wt % talc loading, beyond which the HDT plateaued. Sinha et al.[40] have reported a significant enhancement in HDT of PLA
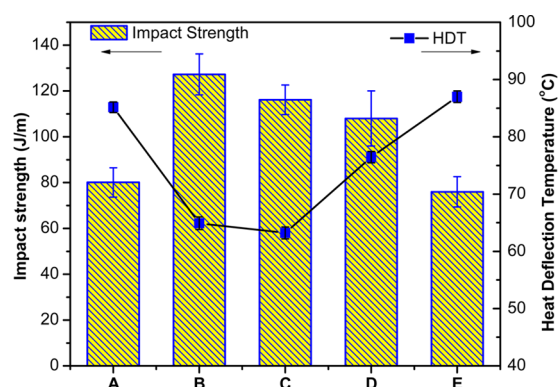

Figure 6. Impact strength and HDT of PLA biocomposites with different nucleating agents molded at a 110 °C mold temperature: A, PLA1 blend/MS/Lak (89/10/1); B, PLA1 blend/MS/HPR (89/10/1); C, PLA1 blend/MS/Emf (89/10/1); D, PLA2 blend/MS (90/10); E, PLA1 blend/MS/Lak (88/10/2).

when organically modified synthetic fluorine mica was added and when the injection-molded specimens were annealed at 120 °C for 30 min. Therefore, on the basis of the literature and experimental evidence, we can conclude that organic nucleating agents, in combination with high temperature molding, are very efficient in crystallizing PLA and increasing the HDT effectively. Our results suggest that the crystallinity strongly dictates the balance that could be achieved between impact strength and HDT. In other words, by controlling the crystallinity through mold temperature and the type of nucleating agents, control of impact strength and HDT could be achieved. Increase in HDT with increase in crystallinity has also been reported by Tang et al.[41] They noted that the crystallinity threshold for achieving improvements in HDT is about 20−25%. With the increase in content of Lak from 1% to 2%, improvement in properties seems to reach a plateau, as only a slight increase in HDT and a slight decrease in the impact strength was noticed; therefore, we can conclude that 1% was sufficient to impart the required level of crystallinity that positively changed the impact strength and HDT.

Tensile strength, tensile modulus, flexural strength and flexural modulus were also investigated. Figure 7 shows the results obtained for selected PLA biocomposites with and without nucleating agents at different mold temperatures. Tensile modulus was found to increase slightly with increase in mold temperature, immaterial of the nucleating agent being present in the composite and this trend was more prevalent in flexural modulus.

Most studies have also reported an increase in modulus with increase in the degree of crystallinity.[42] The differences in tensile strength between different mold temperatures and nucleating agents are considered to be within the standard deviation. However, a slight increase in flexural strength is seen with increases in mold temperature in biocomposites with and without Lak, which can be correlated with the increase in percent crystallinity. In the case of biocomposites with HPR and Emf, the observed increase in flexural cannot be correlated with crystal formation; therefore, it is postulated to be due to the possible reinforcing effect offered by these additives.

Optical Microscopy. In the case of PLA1 blend/MS (90/10) biocomposites, spherulite growth was difficult to observe at temperatures higher than 120 °C, whereas in the case of biocomposites with the Lak nucleating agent, the crystals were already formed at 120 °C as we discussed in previous results
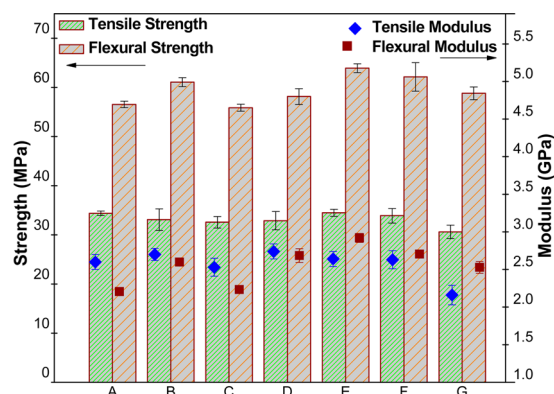
Figure 7. Tensile and flexural properties of selected PLA biocomposites: A, PLA1 blend/MS (90/10) at 30 °C, 30 s; B, PLA1 blend/MS (90/10) at 110 °C, 60 s; C, PLA1 blend/MS/Lak (89/10/1) at 30 °C, 30 s; D, PLA1 blend/MS/Lak (89/10/1) at 110 °C, 60 s; E, PLA1 blend/MS/HPR (89/10/1) at 110 °C, 60 s; F, PLA1 blend/MS/Emf (89/10/1) at 110 °C, 60 s; G, PLA2 blend/MS (90/10) at 110 °C, 60 s.

that Lak has effectively increased the crystallization temperature of PLA. Therefore, the optical microscopy images of biocomposites with and without Lak are compared at different temperatures. PEBA and EMA-GMA present in the matrix as dispersed particles were clearly visible along with a large fiber particle when the composites without Lak were melted at 200 °C. In the case of biocomposites with Lak, the dispersed phase was noticeable, however, not very clear, as observed in composites without Lak. A main observation was regarding the crystalline content. In the absence of Lak, the spherulite size was very large and the rate at which they were forming was relatively slow. This is clearly visible from the images in Figure 8. In the case of PLA1 blend/MS/Lak (89/10/1), densely packed spherulites impinged on one another were observed and the spherulite formation occurred at a much faster rate. The crystallization process was almost complete in 1.5 min, as shown in Figure 8. Although both samples with and without nucleating agent exhibited a spherulitic morphology, there was a dramatic difference in spherulite size, crystallization rate and content. Tang et al.[41] have also reported such reduction in average diameter of the spherulites when ethylenebishydroxystearamide (EBH) was added as a nucleating agent for PLA.

Morphology of Optimized PLA Biocomposites. The mechanical properties of composites largely depend on phase morphology; therefore, SEM was employed to study the phase structure. Figure 9 shows impact fractured surface morphology of biocomposites with and without Lak nucleating agent. The micrographs of impact fractured surface of the biocomposites largely showed ductile fracture, evident from rough fracture surface and the presence of longer fibrils and cavitations, indicating matrix deformation. The energy dissipation process in biocomposites can be grouped into matrix related (microvoiding or cavitation, crazing, shear bending and yielding) and fiber related (debonding, fiber pullout and breakage).[43]

The toughening mechanism observed in the super toughened PLA ternary blend used as a matrix here has been reported in detail in our previous work.[12] The synergistic effect of good interfacial adhesion and cavitations followed by massive shear yielding of the PLA matrix was said to have contributed to the enormous toughening effect observed in the ternary blends.[12] Fiber pull-out and debonding was also observed on the impact fractured surfaces of the biocomposites mainly because of the absence of any compatibilizer that could improve the interfacial adhesion between the fiber and the matrix. In the presence of Lak, PLA was expected to be well nucleated; however, the spherulitic morphology was not noticeable in the SEM micrograph but the number of voids or cavitation was found to be higher in the nucleated matrix. The reduction in impact strength with the simultaneous increase in mold temperature and addition of nucleating agent could be attributed to the enhanced crystallization ability of the well nucleated samples which diminished the capability of PLA in the blend matrix to accommodate the interfacial debonding.

Composition, Particle Size and Dispersion of Nucleating Agents in PLA Biocomposites. SEM with EDS data for biocomposites with different nucleating agents are shown in Figure 10 and Table 2. Intensity of the back scattered electron (BSE) signal which is related to the atomic number of the material, can provide meaningful insight on chemical composition and distribution of various elements. Compositions of nucleating agents were identifiable through EDS. As mentioned before Lak-301 is potassium salt of dimethyl 5-sulfoisophthalic acid, hence a strong peak for potassium and sulfur was observed.

The particle size of Lak in PLA1 blend/MS/Lak composites was fairly high, between 10 and 20 μm. The surface of Lak particles was noticed to be very rough. In the case of the PLA2 blend/MS system, Lak particles were of 1−2 μm and were hard to spot. Also, when scanned for composition, only the
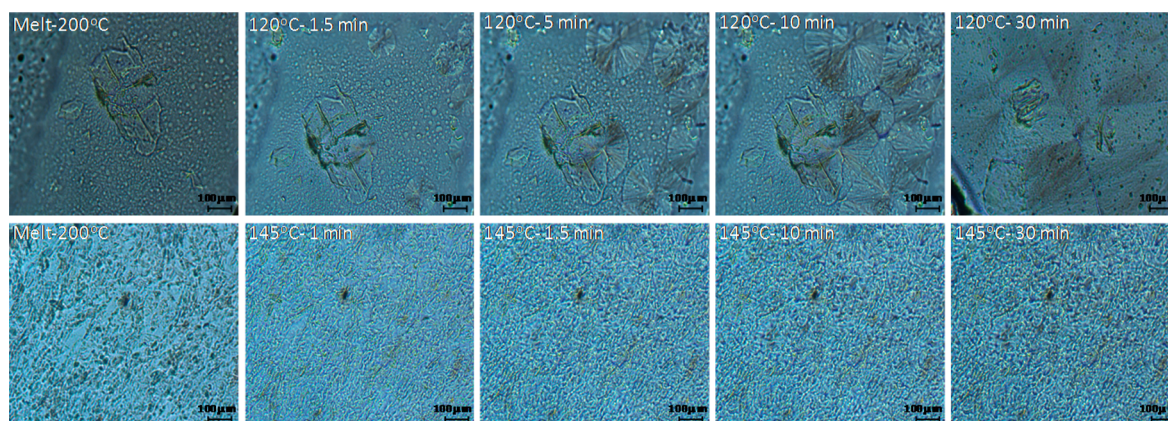

Figure 8. Optical microscopy images (50× magnification): top row, PLA1 blend/MS (90/10); bottom row, PLA1 blend/MS/Lak (89/10/1).
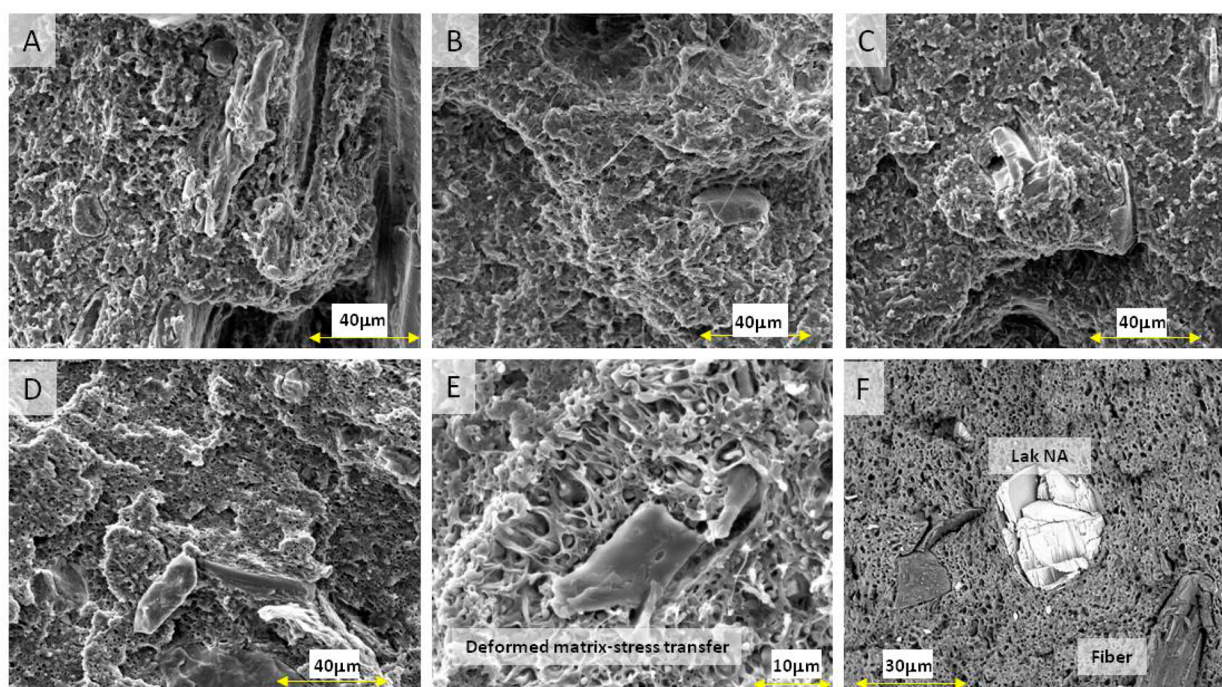
Figure 9. SEM images of PLA biocomposites with and without NA. PLA1 blend/MS (90/10) at (a) 30 °C mold temperature and (b) 110 °C mold temperature; c, PLA2 blend/MS (90/10) at 110 °C mold temperature; d and e, PLA 1 blend/Ms/Lak (89/10/1) at 110 °C with different magnifications; f, PLA 1 blend/MS/Lak (89/10/1) at 110 °C from SEM with back-scattering electron (BSE) detection. Magnifications: a−d, 2000×; e, 5000×; f, 2500×.
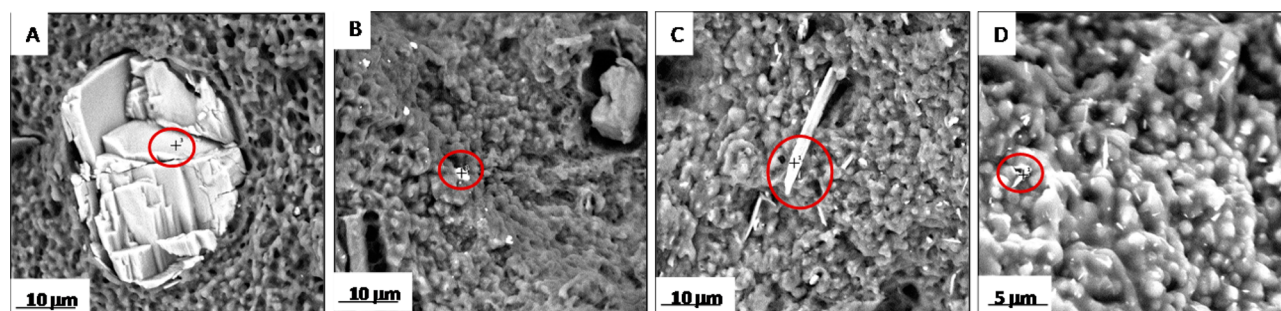

Figure 10. SEM with EDS points of (A) PLA1 blend/MS/Lak, (B) PLA2 blend/MS and (C) PLA1 blend/MS/HPR at a magnification of 5000× and (D) PLA 1 blend/MS/Emf at a magnification of 12000×. All biocomposites molded at 110 °C mold temperature.

Table 2. Elemental Composition of Different Nucleating Agents

element number, symbol, name	% atomic concentration, error			
	PLA1 blend/MS/ Lak Lak-301	PLA2 blend/MS Lak-301	PLA1 blend/ MS/HPR HPR-803i	PLA 1 blend/ MS/Emf Emforcebio
6, C, carbon	59.5 (0.9)	62.8 (0.8)	45.1 (0.9)	66.8 (0.9)
8, O, oxygen	26.8 (0.2)	30.7 (0.0)	45.7 (0.0)	28.1 (0.0)
12, Mg, magnesium			8.2 (0.0)	
16, S, sulfur	4.6 (0.1)		1.0 (0.1)	
19, K, potassium	9.0 (0.0)	6.6 (0.0)		
20, Ca, calcium				5.1 (0.1)

concentration of potassium was obtainable. This could be because of the fairly small particle size, making it difficult to detect. X-rays usually come deeper from the surface; therefore,

the concentration of other elements could have masked the insignificant amount of sulfur in the Lak at the particular scanned point. A rod-like morphology was observed for HPR (magnesium oxysulfate) and Emf (precipitated calcium carbonate). HPR seemed to possess the highest aspect ratio, which supports our previous claims of it acting more as a reinforcing agent. Emf was hard to visualize at the same magnification used for other composites; therefore, a comparison is provided at higher magnification. The particle size of Emf was measured to be around 1−3 μm. No agglomerates were noticed in biocomposites with different NAs, they were all well distributed.

In addition to the difference in nucleating agent nature, i.e., organic or inorganic, particle size and shape could also have an effect on the nucleation efficiency. Nucleation density, distribution and size of spherulites are dependent on the particle size of NA, and a fine particle size is known to possess higher nucleation tendency.[44] However, in our case, Lak with a larger particle size has been the efficient nucleating agent,

leading us to postulate that there is a factor that is outplaying the effect of particle size of NA. To increase the rate of crystallization, molecular interactions between polymer and surface of NA are important.[45] From our investigation and experimental results, we can conclude that Lak was efficient in reducing the interfacial free energy barrier for nucleation and hence increased the crystallization rate significantly.

Dynamic Mechanical Analysis (DMA). The effect of mold temperature and different nucleating agents on the storage modulus and tan δ of the PLA biocomposites are presented in Figures 11 and 12a,b. With the increase in mold
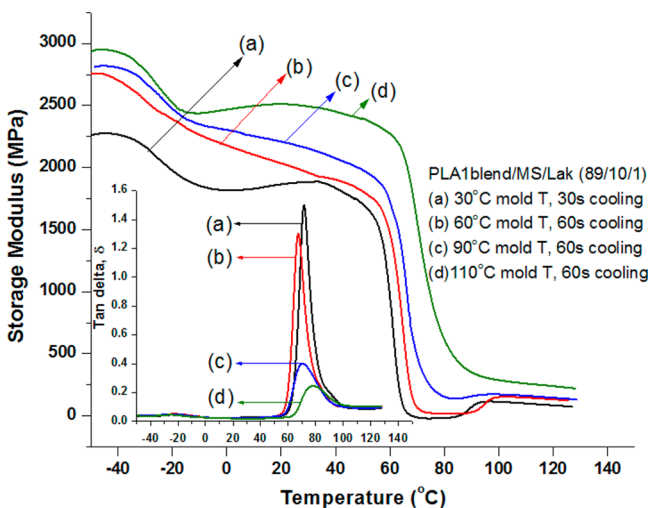

Figure 11. Effect of mold temperature on the storage modulus and tan δ of the PLA biocomposites.

temperature from 30 to 110 °C for PLA1 blend/MS/Lak composites, a significant increase in storage modulus was noticed and the increase was observed to be a gradual step increase between the mold temperatures due to the increase in crystallinity. At room temperature, the maximum storage modulus obtained for the biocomposites molded at 110 °C was found to be 2458 MPa. At sub-zero temperatures, the

storage modulus for the biocomposites with Lak nucleating agent molded at 110 °C was distinctly higher. Comparing the storage modulus of biocomposites with different NA values, PLA1 blend/MS/Lak composites still performed significantly better. The maximum storage modulus at room temperature for PLA1 blend/MS composites molded at 110 °C without any nucleating agent was 2103 MPa whereas, for the rest of the biocomposites with different NA values , the storage modulus was ca. 2120 MPa, which is only a slight increase compared to the one without any nucleating agent processed at the same molding temperature. The increase in storage modulus trend can be well correlated with the crystallinity results from DSC, as the crystalline structures in combination with fibers decrease the mobility of the chains in the amorphous region, thereby increasing the composite stiffness.[46]

A sharp reduction in storage modulus was noticed at the glass transition zone that is associated with the softening of the composites. Almost all samples touched a zero value except for PLA1 blend/MS/Lak molded at 90 and 110 °C and PLA2 blend/MS. This is because the large amount of amorphous region in the composites having low crystallinity is not capable of storing energy above the glass transition zone[47] and a similar behavior has been reported in neat PLA molded at different mold temperatures by Vadori et al.[38]

In most of the biocomposites with and without NA processed at different mold temperatures, the storage modulus was noticed to increase after 90 °C, which was typical of recrystallization.[47] In the case of PLA1 blend/MS/Lak molded at 110 °C, the modulus was deteriorating throughout the investigated range of temperature without touching zero. This indicated that there was no amorphous region incapable of storing energy and the crystal structures are already in a stable state therefore there was no apparent increase in storage modulus due to recrystallization. The temperature at which maximum of tan δ occurs is referred to as dynamic T_g of the system. In our case, we noticed two tan δ peaks: one occurred at low temperatures corresponding to the rubbery components present in the matrix whereas the other peak at high temperatures corresponds to the PLA matrix. The magnitude
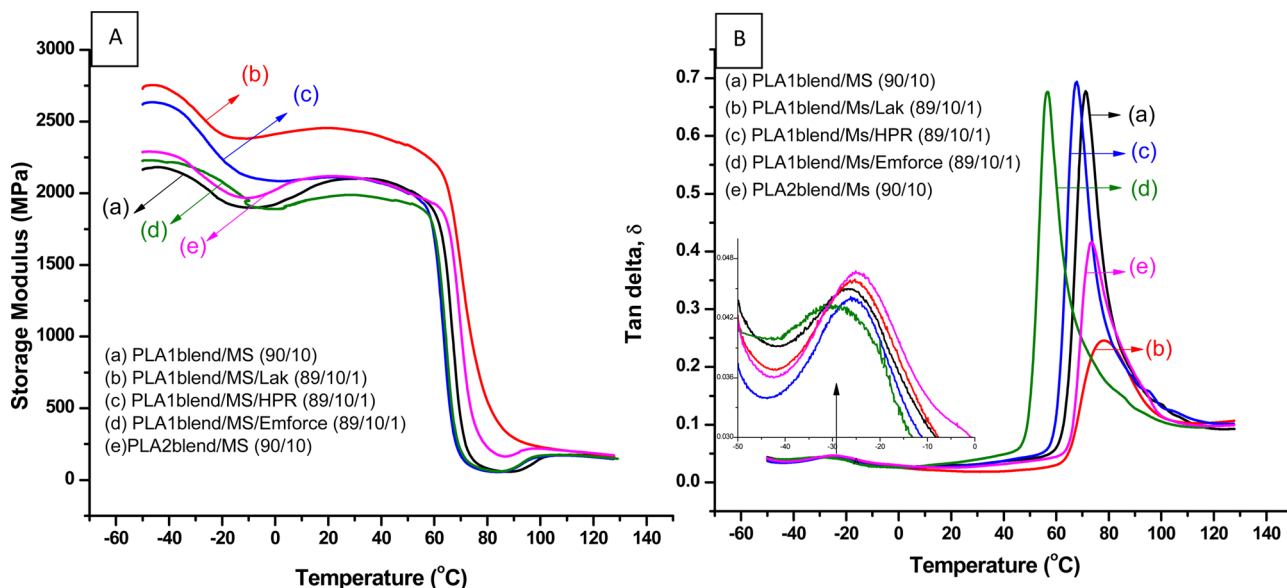

Figure 12. Effect of different nucleating agents on the (A) storage modulus and (B) tan δ of the PLA biocomposites molded at 110 °C.

of the tan δ peak depends essentially on two factors: the relative concentration of the components and the nature of the phase, whether dispersed or continuous.[47] In the low temperature range, the smaller tan δ peak denotes the component with lower T_g to be in the dispersed phase, which is true in our case.

From the tan δ curve shown in the inset graph in Figure 11, it is clear that the damping peak height is significantly reduced and the peak temperature, dynamic T_g has shifted significantly from 71.5 °C for samples molded at 30 to 78.1 °C for samples molded at 110 °C. Comparing the tan δ graphs of biocomposites without NA and with different NA values, the peak height is almost the same for all biocomposites except for the one containing Lak at mold temperatures higher than 90 °C. However, the peak temperature values are significantly different. Interestingly, the T_g values from tan δ peak for biocomposites with HPR and Emforce NA were noticed to be less than those of the biocomposites without any NA. This behavior could again be related to the difference in crystallinity content observed for these biocomposites and the resulting restriction in molecular movement that lowered the damping in transition zone. The DMA results corroborate well with the results obtained from mechanical properties and DSC, thus showing the effectiveness of Lak in providing required performance.

CONCLUSIONS

PLA biocomposites with significantly high impact strength and HDT have been successfully developed. Such marked improvements in the mechanical performance of injection molded PLA biocomposites were accomplished using a super toughened blend system as a matrix and by enhancing the crystallinity using nucleating agents and preheated mold during injection molding.

Compared to neat PLA, a 4-fold increase in impact strength and a HDT of 85 °C were observed for PLA biocomposites. Lak-301 was found to be an effective nucleating agent compared to others used in this work. The combined effect of appropriate nucleating agents and optimized process parameters not only increased the crystallization rate and content but also reduced the molding time. The fastest crystallization rate was achieved in the case of biocomposites with 1 wt % Lak molded at 110 °C. Also, the molded PLA biocomposite samples were able to be ejected without any distortion. Compared to HPR and Emf, Lak was efficient in reducing the free energy barrier for nucleation. DMA results clearly indicated the increase in crystallinity through a gradual step increase in storage modulus as the mold temperature was varied from 30 to 110 °C for PLA1 blend/MS/Lak biocomposites. A densely packed spherulitic morphology of the nucleated biocomposites was clearly observed under optical microscopy. The increase in the HDT was moderate whereas PLA2 (PLA 3100 HP containing 1% Lak, from NatureWorks) was used in the blend matrix; however, our results suggest that based on the property requirements set for the final molded part, Lak-301 could either be added separately during processing to PLA or PLA 3100HP could be used. SEM with EDS was helpful in analyzing the distribution and size of nucleating agents in the composite system. Lak was found to possess larger particle size compared to other nucleating agents.

This study has effectively demonstrated that PLA biocomposites with improved impact and heat resistance, possessing sufficient moldability can provide a solution to overcome the impediments in adapting PLA for a variety of commercial applications. Biocomposites showing a higher level of crystallinity, enhanced mechanical and thermal performance are expected to show improvements in durability as well. This is the subject of our current investigation and future publication.

ASSOCIATED CONTENT

Supporting Information

DSC thermograms of neat polymers and PLA1 blend and discussion on thermal stability of biocomposites containing different nucleating agents investigated using thermogravimetric analysis (TGA). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b01145.

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Notes

The authors declare no competing financial interest.

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