Investigation of crystalline structure of plasticized poly (lactic acid)/ Banana nanofibers composites

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Abstract. Polylactic acid (PLA) is a promising biodegradable candidate to replace synthetic commodity plastics in many applications. However, this polymer shows high brittleness, slow rate and lower degree of crystallization. The addition of plasticizing agents can enhance the toughness, but its effects on the crystallization behavior remain inconclusive. Therefore, this research is aiming to cast light on this area. Using differential scanning calorimetry (DSC) at a 2°C/min cooling rate, extruded neat PLA samples showed lower degree of crystallinity and thermal stability. This material shows cold crystallization upon heating and does recrystallize prior melting. These results indicate a clear instability in the crystalline state are confirmed by the crystallographic results by the X-ray diffractions (XRD) pattern and atomic force microscopic imagery. The addition of around 20 wt% of glycerol triacetate (GTA) with 1wt% of banana nanofibers (BNF) almost doubled the crystallinity. This modification is believed to occur through a dilution mechanism in order to increase crystallization rate yielding a more stable crystalline structure as shown by the XRD. However, the dynamic mechanical thermal analysis (DMTA) showed a 30 to 50% reduction in the room temperature storage modulus (stiffness) is in plasticized samples when compared to neat 100% PLA. Although these results shows the possibility to enhance the crystallization through a combination of plasticizing and nanoreinforcing effects, further studies is still needed to optimize the material formulation in order to find the best ratios to secure both a good crystallization and mechanical properties. This will definitively result in a new material that can be used for current and futuristic applications.

1. Introduction
The negative environmental impact of oil based plastics motivates scientists to search for eco-friendly substitutes. The biodegradable polymers like Agro-polymers and Biopolysters seemed a suitable candidate since they possess many attractive characteristics like renewability, sustainability and compostability [1-11]. Intensive investigations of bio-polyesters revealed the potentials of polylactic acid (PLA) as a replacement for commodity plastics and as an interesting material in many fields like biomedical [12,13], pharmaceutical [14] and packaging [15,16]. Similar to commodity plastics, PLA shows appealing characteristics such as good mechanical properties [17,18], high clarity [19] and simple processability [20,21]. However, its intrinsic brittleness [18], low melt strength [22,23], low thermal stability [24] and slow crystallization [25] prevent its domination over oil based plastics in many applications [26-30].
During the last decade, many studies on the morphology and structure of PLA tried to improve its fragility and poor crystallinity. Different strategies have been adopted for this purposes such as blending with softer polymers [31,32], chemical modification and copolymerisation [33,34] and heterogeneous crystallization through using steroecomplex and other polyesters [35-44].

Currently, PLA is intensively used with nanocellulose reinforcement in order to make biodegradable nanocomposites. The results showed an overall improvement in the mechanical, optical and thermal properties of these materials [45-47]. Unexpectedly, the Triacetin plasticizer which was primarily intended to ensure good dispersion of nanoreinforcements, showed the potential of improving PLA crystallinity. This surprising result needs clarification through understanding the origin of this behavior as well as the mechanism by which it works. The aim of this work is to answer these questions by a thorough experimental investigation.

2. Experimental

2.1. Materials
Polylactic acid made by FUTERRO (Escanaffles, Belgium) is used in this work. The data sheet showed that this high molecular weight L-PLA which is primarily used for extrusion has a glass transition temperature (Tg) of 56 ± 4°C and a crystallisation temperature (Tc) of 160±15°C. The glycerol triacetate (GTA) is purchased from Sigma-Aldrich (Stockholm). This high purity liquid plasticizer has a molecular weight of 218 g/mol. The Banana nanofibers (BNF) were prepared from bleached banana waste pulp using mechanical fibrillation method using Masuko super mass collider [47]. These nanofibers have diameter that varies from 10 to 60 nm.

The samples were prepared using a liquid feeding extrusion process in similar manner as reported by Oksman et al 2006 [48].

The formulation of each material is given in table 1. Neat PLA is used as a reference, whereas plasticized and reinforced PLA samples are used to study the impact of the plasticizer and the reinforcing agents on the crystallinity.

2.2. Thermal transitions (DSC)
A Mettler Toledo DSC822e (Schwerzenbach, Switzerland) is used to study different thermal transitions within the materials. Samples weighting 6 mg were cut from each extruded material and placed in an aluminum pan to be thermally scanned under N₂ atmosphere from 30 to 200°C at a heating rate of 10°C/min. In order to thoroughly investigate the crystallization process, two cooling rates of 20°C/min and 2°C/min are used.

2.3. Crystal structure (XRD)
A Siemens D5000 Diffractometer (Berlin) with a CU-Kα radiation source (λ=0.154 nm) was used to study the internal crystalline structure in these materials. The tests were performed on thin films made from extruded samples. The equipment was operated at 40 KV and 45 mA.

2.4. Thermomechanical properties (DMTA)
The thermomechanical properties were investigated using a QA 800 analyzer from TA instruments (USA). The analysis was conducted in tensile mode under 3°C/min heating rate and 1Hz frequency. The temperature scan ranges from 30°C to 200°C in air.
2.5. Atomic force microscopy (AFM)
The morphology and structure of PLA samples was investigated using a Nanoscope V AFM. From extruded materials, rectangular samples (2 mm×10 mm) were cut and fixed on an AFM specimen holder (Insert 16702448). The samples was placed on the Leica EM UC7 ultramicrotome to prepare a rectangular flat surface (400 µm × 600 µm) for Tapping mode™ AFM imaging. In order to visualize the spherulitic structure, the scanning was performed on large area (120 µm × 120 µm). The morphology was characterized by measuring the average spherulites size which was calculated from the diameter (cross-section) of at least 9 different spherulites.

2.6. Optical microscopy
Samples weighting around 5 mg from neat, plasticized and reinforced PLA were cut and placed on rectangular (75 mm × 25 mm) glass microscope slide (Vista Vision™). The slide was heated at 190°C for 10 min before placing another slide on the top to cover the molten matter. In order to create a very thin film, the sandwich was pressed gently then left to cool down in air. A second heating cycle at 190°C for 5 min was used to release any stress that might be induced during the compression and to prepare the thin film for morphology investigation.

Using Nikon’s inverted optical microscope (Eclipse MA 200™), thin films were observed under polarized light to visualize the spherulitic morphology. In addition, dark field mode was also used to clearly observe the spherulites since a good contrast between the high refractive crystalline spherulites and the amorphous region is expected in this mode [49,50].

3. Results and discussion

3.1. Thermal analysis
Thermal transition curves of neat, plasticized and reinforced PLA measured using differential scanning calorimetry are shown in figure 1. Neat PLA shows a clear second order transition (Tg) at 64°C, after which it goes through two cold crystallization stages at T_{cc1}= 100°C and T_{cc2}=161°C before melting (T_m) at 178°C. Plasticized and reinforced PLA materials showed the absence of the glass transition and cold crystallization peaks. Thermal properties such as the melting enthalpy, thermal transitions and degree of crystallinity estimated from the DSC thermograph are presented in table 2.

Figure 1. DSC thermograph of different materials.
Table 2. DSC thermal properties of Neat, Plasticized and reinforced PLA.

| Material        | Cold crystallization | Melting | Glass transition | Crystallinity |
|-----------------|----------------------|---------|------------------|--------------|
|                 | $T_{CC1}$ ($°C$)     | $\Delta H_{cc1}$ (J/g) | $T_{CC2}$ ($°C$) | $\Delta H_{cc2}$ (J/g) | $T_m$ ($°C$) | $\Delta H_m$ (J/g) | $T_g$ ($°C$) | $X_c$ (%) |
| Neat PLA        | 100                  | 22.7    | 161              | 5            | 178          | 48               | 64            | 22       |
| Plasticized PLA| -                    | -       | -                | -            | 167          | 39               | -             | 41       |
| Reinforced PLA  | -                    | -       | -                | -            | 170          | 35               | -             | 37       |

The absence of the glass transition ramp in plasticized and reinforced PLA can be attributed to the lack of sensitivity in the DSC. Previous studies showed a 20° C decrease in the glass transition temperature when adding GTA to neat PLA which is a clear indication of the plasticizing ability of GTA [51-53].

At 100°C, neat PLA chains gain enough mobility to disentangle from the amorphous phase and rearrange in an ordered 3-D crystallites. The exothermic peak at 161°C is due to melt-recrystallization of early formed crystallites since they possess low thermal stability therefore they recrystallize at the vicinity of the melting temperature. The recrystallization peak indicate that previously formed crystallites did not assume the stable orthorhombic $\alpha$-crystal form [54, 55]. The thermographs of plasticized and reinforced PLA (in contrary to neat PLA) showed no signs of cold crystallization which proves that their crystallites are made of thermally stable $\alpha$-form.

The crystallites size distribution can be also estimated since it is directly proportional to the width of the melting peak [56]. Plasticized PLA with a melting peak span $\Delta T_m=29° C$ has the largest crystallites size distribution whereas, neat PLA with $\Delta T_m=20° C$ has the narrowest size distribution. Reinforced PLA has a melting temperature of 169°C and a peak span of 26°C indicating a slightly narrower crystallite size distribution compared to plasticized PLA.

The highest melting temperature in these three samples is observed for the neat PLA ($T_m=178° C$). This indicates that Neat sample has the highest crystallite average size, whereas plasticized PLA has the lowest crystallites average size since it has the lowest melting temperature $T_m= 167° C$.

![Figure 2. DSC thermograph for cooling cycle at 2°C/min.](image)

During the cooling cycle at 20°C/min (figure 1), these materials showed no crystallization peaks which would indicate the formation of amorphous materials. The PLA crystallization process is known
to be slow and at this cooling rate, the crystal growth will decrease drastically since PLA molecules do not possess enough mobility to diffuse to the crystallites. Instead, they freeze in their high entropic state resulting in minimal crystallinity. As this PLA is intended to be extruded, lower cooling rate would be adequate for realistic study. Additionally, the sensitivity of DSC would improve at low rates. Therefore, a slow cooling rate of 2°C/min scan is performed and the thermograph is presented in figure 2.

Neat, plasticized and reinforced PLA materials showed exothermic crystallization peaks at 108°C, 109°C and 112°C respectively. The slightly higher crystallization temperature of reinforced PLA compared to other samples can be explained as heterogeneous crystallization resulting from the fiber surface which can act as nucleating agent. Since lower crystallization temperature in PLA leads to deformed crystals [57,58], neat PLA is believed to have unstable \( \alpha' \)-crystal form.

Using Equation 1, the degree of crystallinity \( (X_c) \) can be calculated from the enthalpy of fusion \( (\Delta H_m) \), the enthalpy of crystallization \( (\Delta H_c) \) and the theoretical enthalpy of fusion \( (\Delta H_m^0 = 93 \text{ J/g}) \) [59]. The results are presented in table 2.

\[
X_c = \left( \frac{\Delta H_m - \Delta H_c}{\Delta H_m^0} \right) \times 100\%
\]  

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The addition of GTA plasticizer enhanced the crystallinity through increasing the PLA chains mobility and allowing them to easily disentangle from the amorphous molten state and rearrange in an order manner to form crystallites. However, the lower crystallization temperature (109°C) did not offer enough thermal energy for these chains to diffuse toward the crystallite surface which eventually reduced the overall degree of crystallinity.

Among the three samples, reinforced PLA showed the highest crystallization temperature (112°C), it is therefore expected to possess the highest degree of crystallinity. Surprisingly, plasticized PLA showed higher level than reinforced PLA. This strange result calls for further investigation using proper technique that cannot be dependent on the heating /cooling rates assessment. X-ray diffraction technique was used for deeper insight in the structure of these materials.

3.2. Crystallinity analysis

Using the WAXD spectrum ranging from 5° to 25°, it was possible to identify the crystalline structure of neat, plasticized and reinforced PLA samples. As shown in figure 3, these materials showed typical semi-crystalline spectra containing both amorphous “halo” and crystalline peaks [60].

![Figure 3. XRD spectra of different samples with an orthorhombic cell (upper corner).](image-url)
Neat PLA showed fewer diffraction peaks compared to plasticized and reinforced PLA. Based on the diffraction patterns presented in figure 3, PLA chains in plasticized and reinforced samples are crystallized in the α-form orthorhombic crystals [11]. In addition to the absence of (103) and (015) peaks, neat PLA pattern shows a slight shift of (200/110) and (203) peaks positions toward lower angles. These observations can be attributed to low degree of order and deformation in the crystalline structure [61-64]. It is therefore clear that neat PLA crystallites adopted the distorted α'-form orthorhombic crystal.

The orthorhombic cell parameters were calculated by combining the Bragg’s law with equation (2). The geometrical characteristics of the (010), (200) and the (203) plans were used to obtain three mathematical equations with which the parameters can be obtained.

\[(d_{hkl})^2 = (h/a)^2 + (k/b)^2 + (l/c)^2\]  

(2)

The crystal parameters for plasticized and reinforced PLA were a=1.06 nm, b=0.59 nm, c=2.78 nm. Whereas those of neat PLA where found to be a'=1.08 nm, b'=0.59 nm, c'=2.87 nm. These values are in good agreement with literature [65,66]. The large cell dimensions in neat sample are due to the stiff nature of PLA chains [67,68]. The oxygen and methyl side groups in the PLA chains (figure 3) result in low degree of symmetry therefore, PLA molecules folds in large cells compared to polymers with flexible symmetrical chains.

Under appropriate crystallization conditions (T, t, P), PLA adopt the left-handed 103 helix conformation (10Å rise for every 3 monomer units) in α-form crystal [69-71], while, under abnormal conditions (low crystallization temperature, fast cooling) the chains keep the 103 helix conformation with a perturbation in the rotational and the longitudinal ordering resulting from the intermolecular dipole-dipole interaction between methyl and oxygen side groups of adjacent chains [54]. The 4% \((a'xb'xc'/axbc)\) increase in the α'-crystal volume resulted from the loosely packed chains in this crystal. Therefore the plasticizer enhances the firm packing of PLA chains in their crystals.

The peak intensities observed in reinforced and plasticized PLA patterns are higher than neat PLA which reveals the higher level of crystallinity. The areas under crystalline and amorphous peaks can be used to calculate the degree of crystallinity [72,73]. Furthermore, the lamella \(L_0\) which characterize the packing ability of polymer chains can be estimated by Scherrer equation (equation (3)). Using the main peak characteristics (peak angle (θ) and Full width at half maximum height in radians (β)) for (200) and (203) plans, the thickness \(L_0\) can be calculated using wave length \(\lambda=0.154\) nm and Scherre constant K=0.9 [70,74].

\[L_0 = (k\lambda)/(\beta \cos\theta)\]  

(3)

In order to calculate the exact value of β, an open source curve fitting software (curve expert professional 2.4.0) was used on the (200) and (203) peaks. Gaussian function was found to result in the best fitting with an error less than 9%. Table 3 summarizes the results including the inter-plannar distance d, β and \(L_0\).

| AT-1 | (200/110) plan | (203) plan | Xc (%) |
|------|----------------|------------|--------|
|      | \((10^{-3})\) | \(d_{200}\) | \(\beta_{200}\) | \(L_{200}\) | \(d_{203}\) | \(\beta_{203}\) | \(L_{203}\) |
| Neat PLA | 14.2 | 0.54 | 0.0055 | 25 | 0.47 | 0.0134 | 10 | 28 |
| Plasticized PLA | 17.2 | 0.53 | 0.0045 | 31 | 0.46 | 0.0128 | 11 | 47 |
| Reinforced PLA | 17.5 | 0.53 | 0.0043 | 32 | 0.46 | 0.0117 | 12 | 50 |
A 20% increase in crystallinity is observed upon plasticization of PLA. Similarly, additions of 1% of BNF resulted in almost double the level of crystallinity observed in neat PLA. The mechanisms by which GTA and BNF affect crystallinity are different and will be discussed later. The distortion in the unit cell of neat PLA can be clearly seen by the increase in the inter-planar distance in these two main crystalline peaks. Besides Scherrer equation, the lamellae thickness \((L_0)\) can be calculated based on Gibbs-Thomson equation using the undercooling \((\Delta T = T_m - T_c)\) and the enthalpy of fusion \((\Delta H_m)\) from the DSC thermograph [75]. This equation shows that the lamella thickness is inversely proportional to the degree of supercooling \((\Delta T)\). This relationship is fulfilled according to values presented in table 3. Thus, neat PLA has thinner lamellae compared to plasticized and reinforced samples.

In figure 1, the high melting temperature of neat PLA indicates the formation of thicker lamellae in contradiction with the results in table 3. The first peak (100°C) in figure 1 shows the formation of new crystallites \((\alpha'-\text{form})\), whereas the second peak (161°C) revealed the recrystallisation of these crystals into the stable \(\alpha\)-form. This process will result in thickening the lamellae in neat PLA [76-79]. The X-ray experiment was conducted at room temperature before these thermal transitions occur therefore, the thickening due to this process cannot be observed. Nevertheless both techniques agreed on the fact that the GTA plasticizer improved the level of crystallinity in the polylactic acid polymer.

The XRD results in table 3 showed that reinforced PLA has the highest crystallinity in contradiction to what DSC results showed in table 2. Since reinforced PLA has higher crystallization temperature than plasticized PLA, the crystallinity should be also high. Therefore, the theoretical enthalpy of fusion estimated by Fischer [59] based on Flory theory for polymers and copolymers is quite inaccurate when dealing with trans-crystallization in heterogeneous nucleation.

### 3.3. Thermomechanical analysis

GTA plasticizer and BNF reinforcement do clearly affect Thermomechanical properties of PLA as shown in figure 4. The modulus of neat PLA (~3 GPa) is higher than plasticized and reinforced samples. Around Tg (64°C), the modulus falls sharply below the moduli of other samples. This can be attributed to the fast rearrangement in the amorphous region resulted in large internal macromolecular motion suggesting that neat PLA molecules were frozen in stressful conformation during cooling stage. Around 100°C ±10, neat PLA gained certain elasticity resulting in a slight increase in the modulus. This is clearly due to cold crystallization as showed in the DSC thermograph.

![Figure 4](image-url)

Figure 4. Storage modulus and loss factor of different samples.
Plasticized PLA sample showed a 50% reduction in elasticity compared to neat sample. This is expected since GTA plasticizer allows for higher elongations at low level of applied stress. However, the transition from glassy to rubber was smoother compared to that of neat PLA as it occurred along large temperature range (50°C to 80°C). Therefore, plasticizer induced high thermal stability and negligible level of residual stress. The enhanced chain mobility in plasticized PLA is clearly manifested by the low elasticity at the rubbery state. Loss factor peaks (dashed lines in figure 4) for plasticized and reinforced PLA samples are broader and shorter compared to neat PLA which is believed to be due to high level of crystallinity [80].

Adding 1% BNF to plasticized PLA resulted in 10% increase in the glassy state modulus. The introduction of stiffer phase within the viscoelastic soft matrix will increase the elasticity. At the rubbery plateau, certain molecular motion is observed in the material which can be attributed to weak interfacial interaction between the plasticized matrix and BNF surface. The general trends shows that GTA improves the thermal stability but it deteriorate the PLA elasticity. The addition of 1% BNF showed negligible impact on the modulus.

Figure 5. Crystalline morphology of neat (A), plasticized (B) and reinforced PLA (C) using AFM (1), Polarized (2) and dark field (3) imaging.

3.4. Microscopy analysis
Atomic force microscopy and optical microscopes are used to investigate the crystalline morphology of PLA samples. Images in figure 5 show the spherulitic microstructure of neat, plasticized and reinforced PLA. In (A1) image, neat PLA showed isolated cauliflower-like spherulites [81], whereas
plasticized and reinforced PLA showed a coalescent spherulitic structure (B1, C1). The average size of PLA spherulites measured using AFM was 22 µm ± 7. This large size is expected to result in a brittle behavior [68,82]. The few scattered spherulites in neat PLA (A2) revealed the formation of few nucleation sites during crystallization. Furthermore, the isolated spherulites is a clear indication of low crystallization rates since at high rate they would grow to form a spherulitic polyhedral structure [83]. In the dark field image (A3) few lamellae bundles are present indicating an early stage of spherulites formation [84].

In plasticized PLA, high nuclei density is observed (B1, B2, B3) as expected [85]. Using AFM, the average spherulites size was 9 µm ± 3, which would show enhancement in the plasticized PLA toughness. In reinforced PLA, the nucleation occurs at two different locations (C2); the plasticized matrix and on the fiber surface which is suitable location for Tran-scrystallization [86,87]. The spherulites average size (11 µm ± 5) is smaller than neat PLA which is due to the enhancement in nucleation process.

In the literature a 30°C increase in the crystallization temperature (Tc) were obtained when 1% Poly-D-lactic acid was added to PLLA sample as heterogeneous crystallization agent [88]. Whereas, adding 1% of BNF resulted in 4°C increase in Tc (figure 2). The spherulites average size in reinforced PLA was higher than that of plasticized PLA. These results highlight the poor nucleation efficiency of BNF. This poor nucleation efficiency may result from surface contaminations occurred during pretreatment process prior to extrusion. The fiber was first subjected to solvent exchange (water/aceton) after fibrillation, then dispersed in GTA plasticizer before mixing it with molten PLA matrix. Therefore, the true contact between the real BNF surface and PLA matrix is minor. Nevertheless, the enhancement in the degree of crystallinity at 1% BNF shows its potential as a heterogeneous nucleating agent.

3.5. The mechanism by which GTA enhanced crystallinity

In theory, the enhancement in chain mobility is suggested to improve polymer crystallinity. The depression of glass transition temperature will expand the temperature range where macromolecules are able to crystallize in optimum conformation. This logic idea does not explain why in many studies GTA plasticizer decreased Tg but it did not enhance crystallinity [89,90]. According to literature, the plasticizer has also a thermodynamic impact since it increases the lamellae lateral surface energy at the growing front of spherulites [91]. It is therefore clear that the plasticizer impact is beyond a simple depression of Tg, and a new mechanism should be proposed taking into account the literature and the current results.

The GTA plasticizer has similar chemical nature as PLA polymer since they both possess methyl and carbonyl groups and develops similar intermolecular forces. This explains why they both have high degree of miscibility (similar solubility parameter (δ=20.1 MPa⁻¹/²) and compatibility (interaction factor=0.34) [89]. As a consequence, the plasticizer’s small molecules can easily mixed and diffuse through PLA chains. When PLA and GTA are mixed together in melt, GTA molecules will easily diffuse into PLA chains to lubricate them and diminish the internal friction. Consequently, the entanglements density within this plasticized melt is expected to be far below that of neat PLA resulting in reduction in the entropic barrier for nuclei formation. This can explains the large number of spherulites in plasticized and reinforced PLA (figure 5). Meanwhile, the PLA macromolecules have the opportunity to adopt easily the optimum crystallographic conformation (α-form) and form many stable nuclei (figure 3).

After the formation of stable nuclei, more macromolecular segments are packed together forming lamellae as the early stage of spherulites formation (image B3 in figure 5). The GTA molecules are excluded from the crystals as proven by XRD Spectrum (figure 3). These small impurities gather at the growing lamellae interface (front) with the super-cooled melt [83]. Upon cooling, the crystal growth is directly dependent on the chains diffusion ability through the melt into the lamellae at the growing spherulites front as shown in figure 6. The continuously accumulating GTA molecules will decrease the local melt viscosity at the vicinity of the growing lamellae front (figure 6). Additionally,
they increase the lamellae lateral surface energy leading to faster growth which explains the fully developed polyhedral spherulitic morphology in figure 5 (images B1, B2, C1, C2). As temperature drops, the diffusion activation energy decreases and the structure freezes. Finally, the morphology will show crystalline regions where PLA chains are concentrated in the spherulites and an amorphous region at the spherulites edges (figure 6) mostly rich of GTA molecules.

![Figure 6. Illustration of the plasticization enhanced crystallinity mechanism.](image)

The dilution mechanism proposed here agrees with the work of Tsuji and his co-workers when they found that dilution effect assists the nucleation and increases the nuclei density [92]. In order to efficiently enhance crystallinity, the optimum GTA plasticizer concentration has to be reached to trigger the dilution effect. This concentration is believed to dependent on many factors such as the polymer molecular weight, cooling rate and chemical interactions and compatibility.

The GTA concentration should take into account the thermomechanical properties; the loss of 50\% of storage modulus (figure 4) must be addressed when looking for suitable formulation. Therefore, the optimum GTA content should assure the maximum crystallinity with the lowest possible loss in elastic modulus.

4. Conclusions
This study shows that at a cooling rate of around 2°C/min, extruded neat PLA samples showed lower degree of crystallinity and thermal stability. This material shows cold crystallization upon heating with a recrystallization before melting. These indications of instability in the crystalline state are confirmed by the crystallographic (XRD) and microscopic studies (AFM and optical microscopy).

The addition of 20 wt\% of glycerol triacetate (GTA) with 1wt\% of banana nanofibers (BNF) almost doubled the crystallinity. This modification believed to act through a dilution mechanism in order to increase crystallization rate yielding a more stable crystalline structure. However, 30\% to 50\% reduction in the room temperature storage modulus (stiffness) is observed. Thus further optimization studies of PLA/GTA formulation is needed. This is believed to result in a new material with the ability to replace commodity plastics.

5. Outlook
Future contribution to this work can be summarized in two objectives:
- Find the minimum GTA concentration to enhance crystallinity.
- Find the best GTA content for concentrated BNF suspension (3-5% BNF).
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