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Biodegradable Pineapple Leaf Fiber/Clay Reinforced Polylactic Acid Nanocomposites: Effects of Extrusion Mixing on Tensile and Thermal Properties

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Abstract

Hybrid biodegradable composites have been explored as an alternative to overcome the current problem of depletion of resources. The combination of pineapple leaf fiber and clay is studied to improve specific properties that cannot be achieved by polylactic acid only. This study explores different extrusion speeds and mixing times toward the mechanical and thermal properties of polylactic acid/clay/ pineapple leaf fiber composites. The nanocomposites were formed by melt blending using a co-rotating twin screw extruder followed by compression molding. In this study, the composition of pineapple leaf fiber at used was fixed at 10 wt%, while the clay and polylactic acid were based on the ratio of 1:99.The results indicate that mixing all of the materials in a double step extrusion PC30BP2 improved tensile strength and elongation by 13.4% and 19.0% compared to single extrusion, PC30BP1. This was supported by the intercalation structure in X-ray diffraction analysis. The microstructure of nanocomposites exhibits a good interaction between fiber, nanoclay, and matrix for PC30BP2, with a diminution of fiber pull-out compared to PC30BP1. PC30BP2 produced the highest tensile strength at 32.5 MPa and elongation at 3.917 MPa and exhibited a higher degradation temperature at 383.7°C with no significant change in melting temperature than PLA.

Keywords: Biodegradable, Clay, Hybrid, Natural fiber, Nanocomposites, Thermal

Full length article **Corresponding Author*, e-mail: afiqah@miros.gov.my

1. Introduction

The depletion of natural resources has widened the possibility of researching alternative biodegradable materials to replace synthetic fiber and polymer. Polylactic Acid (PLA) is a biodegradable polymer that is produced from renewable resources. Nevertheless, the price of PLA is still prominent compared to synthetic polymers in the industry. One of the methods to maintain the biodegradability of the material and reducing the cost is by utilizing natural fiber as a filler in the composites. The advantages include being abundantly available, low cost and density, renewability, and ease of process. Pineapple leaf fiber (PALF), a type of biodegradable fiber, is a byproduct of agriculture and possesses a high amount of cellulose (70-82%) and a low spiral angle (14%). This contributes to its good mechanical properties. The addition of PALF improves the mechanical properties and reduces the overall density and cost of composites.

The addition of 30 wt% PALF in polypropylene composites improves tensile and Young's modulus by 72%, and 115% compared to polypropylene only [1]. In a report by Rajakumaran adding 10 wt% PALF with 5 mm thickness in epoxy composites improved tensile, flexural, and impact strength by 49%, 25%, and 77% [2]. The positive increment resulted from appropriate stress distribution between matrix and fiber. However, PALF in nature is sensitive to moisture and has low thermal stability. The small addition of clays may improve the mechanical and thermal properties of the composites. The advantage of clay is accentuated by its high aspect ratio and low cost. Introducing a small amount of clay in polymer matrix composites can improve the mechanical and thermal properties [3-5]. Hybridization of clay and natural fiber shows a promising result due to biodegradability and improvement in flexibility and thermal properties without magnifying the density.

In a study conducted by Ramakrishnan et al., the addition of 5 wt% of Cloisite 20A clay in jute fiber reinforced epoxy composites improved tensile, flexural, and impact strength as the clay improved the interaction between fiber and polymer, thus reducing fiber pull-out [6]. Furthermore, water absorption was reduced by 31% compared to jute fiber/ epoxy composites due to the hydrophobicity of clay. In another study, Ramesh et al., reported that the addition of aloe vera fiber in PLA composites deeply reduced the degradation temperature compared to PLA only [7]. Increasing montmorillonite clay loading in aloe vera fiber/PLA composites improves the degradation temperature, slightly approaching the degradation temperature of PLA. However, adverse effects were reported for mechanical strength. Only 1 wt% clay loading improves the tensile, flexural, and impact strength. Higher clay loading resulted in agglomeration that reduced the proper distribution of stress. Uniform filler dispersion in the matrix plays an important role in improving composites' mechanical and thermal properties. The intercalation/exfoliation structure of polymer nanocomposites can be improved by applying appropriate shear force and mixing time [8].

Kaiser et. al., have reported that implying double extrusion on hybrid kenaf, MMT Nanomers I.31 PS reinforced PLA composites showing efficacious results in thermal and mechanical properties due to better interfacial interaction between filler and matrix [9]. In contrast, the study conducted by Meng et. Al reported PLA/Poly (butylene succinate-co-butyleneadipate) /starch composites produced in single mixing exhibit better mechanical performance than double mixing [10]. This is because increasing shear force and mixing time for double mixing resulted in polymer molecular degradation thus reducing the mechanical properties. Most studies tended to focus on the influence of fiber and/or clay loading on the nanocomposite's properties. There is a lack of studies reporting on the effect of the number of extrusion steps on the properties of hybrid composites. In this paper, the introduction of the biodegradable hybrid composite using PALF and clay in single and double step mixing is the novel finding. This paper uses two extrusion steps to examine the tensile and thermal properties of hybrid PALF and clay reinforced PLA nanocomposites. The mechanical and thermal properties of hybrid composites were then compared with PLA, and PLA/C30B nanocomposites to explore the efficacy of the different extrusion steps.

2. Materials and methods

PLA 3251D was purchased from Natureworks Ingeo (USA). Cloisite 30B (C30B) clay, was obtained from Southern Clay Products, China. PALF were acquired from India and cut to a length of 6 mm for this study, based on findings by George et.al. [11]. The weight loading for polymer and clay is set at a ratio of 99:1, as analyzed by [12]. All the materials were dried in the oven for 24 hours at 80°C before mixing. The mixing was completed using twin screw co-rotating extruder (Thermo Prism TSE 16PC). Illustrations of the overall process were highlighted in **Figure 1.** There are two methods used to prepare the hybrid nanocomposites i.e., single step and double step mixing. The single step mixed sample labelled as PC30BP1 refers to 89.1 wt. % PLA, 1 wt. % C30B and 10 wt. % PALF that simultaneously extruded at 60 rpm screw speed. In the double step mixed sample label as PC30BP2, 89.1 wt. % PLA and 0.9 wt. % C30B was first extruded at a screw speed of 100 rpm, then placed in the oven for 8 h at 60°C to eliminate moisture content. The second mixing was done by extruding the previously extruded PLA/C30B together with 10 wt. % PALF at a screw speed of 60 rpm. The nanocomposites were then undergoing compression moulding for 13 minutes at 180°C. The reference sample, PC30B was produced using the same parameter of PC30BP1. Table 1 summarises the nanocomposite composition and the screw speed parameter for the single, double step mixing and the reference sample. Tensile test was conducted on dumbell shape size according to ASTM D638-03. Testometric M350-10CT model set at 5 kN and 5 mm/min speed were used and tested on at least 6 samples for each composition. Xray-Diffraction (XRD) testing were conducted using XRD model D8 Advance, and a sample between 10-15 mg were prepared. The samples undergo heating at a rate of 10°C/min from 30°C to 250°C, followed by cooling to room temperature and second heating until 250°C under a nitrogen atmosphere. Morphological analysis were conducted with ZEISS machine model Merlin Compact. The sample at the tensile fracture were coated with gold before observation. FTIR was prepared using FT-IR Perkin Elmer Spectrum model BX at a wavenumber of 650-4000 cm^{-1}. Metler Toledo model DSC 882^e were used to conduct phase transition temperature. Sample with weight of 10-15 mg were prepared. First heating were conducted at the rate of 10°C/min from 30°C to 250°C, cooled to room temperature and proceeded with second heating up to 250°C in nitrogem atmosphere. Crystallinity, χ_c is calculated as follows:

$$\boldsymbol{\chi_c}\,(\%) = \frac{\Delta \boldsymbol{H_e}}{\Delta \boldsymbol{H_m} \times \boldsymbol{W_f}} \times \mathbf{100}$$

Where ΔH_e is enthalpy of fusion obtained from the experiment, ΔH_m represents the melting heat of PLA at 100% crystalline, 93.0 J/g and W_f is the weight of PLA in the composites [13]. Thermogravimetric testing were conducted using Mettler Toledo $TGA/SDTA851^e$ in nitrogen atmosphere. Sample weighing between 10-15 mg were heated from 30 to 600°C at the rate of 10°C/min. The mass of the remaining sample was taken after 600°C.

3. Results and Discussions

Figures 2 and 3 exhibit the tensile strength, elongation, and modulus Young of PLA, nanocomposites PC30B, PC30BP1, and PC30BP2. Both tensile strength and elongation show a similar pattern, while modulus Young shows an opposite trend. The addition of 1% C30B in PLA improves the tensile strength and elongation by 25.4% and 10.0% respectively, compared to PLA alone. The improvement may explain the relatively good interaction between the OH group in C30B and with carbonyl group in PLA. XRD analysis in Figure 4 (b) shows that the addition of C30B in PLA does not produce any interlayer spacing, *d*. This non-detection may be due to the large gap between silicate caused by intercalation or possibly due to the small amount of clay (1 wt%) used in the composites. The interaction between PLA and C30B is further confirmed in the FTIR analysis as shown in Figure 5.

The missing peak in PC30B at 2920 and 2850 cm^{-1} refers to the CH_2 stretch in PLA, and CH_2 is sensitive to the packing density of the methylene group [14]. The reduction in the CH_2 peak is related to the decrease of hydrogen bonding between polymer chains, due to the formation of hydrogen bonding between C30B and PLA. The intensity of the C=O group in PC30B at 1740 cm^{-1} was also reduced and slightly moved to a higher frequency. This also proved that the reduction of hydrogen bonding between the polymer chain resulted from a developed interaction between the C=O group in PLA and the hydroxyl group in C30B. When PALF was introduced in the hybrid nanocomposites, mixing in one step reduced the tensile strength and elongation by 7% and 15% respectively compared to PC30B nanocomposites. The reason for this reduction might be due to the increases in the coalescence of C30B around PALF surface, thus reducing the interaction between PLA and PALF. By comparing PC30BP1 in Figure 6 with PC30BP2 in Figure 7, there is more fiber pull out in Figure 6 as shown in the red circle. Short mixing time in PC30BP1 may probably result in improper blending between the fillers and the matrix. The stress was not distributed properly while the fiber became the weak point. Nevertheless, the strength is still higher compared to PLA only. On the other hand, mixing in two steps improved tensile strength and elongation by 5.7% and 3% than PC30B, respectively. Double extrusion was found to improve the interfacial interaction between clay, PALF, and polymer matrix. This can be supported by a slightly higher *d* spacing (3.044 nm) exhibited by a wider peak in Figure 4(d) compared to *d* spacing of PC30BP1 at 2.933 nm. Our experiments are consistent with previous results [9] suggesting that increased shear stress improves intercalation. The improvement of *d* spacing in hybrid nanocomposites compared to *d* spacing produced by C30B only at 1.805 nm confirmed the formation of an intercalated structure. Furthermore, SEM observations in Figures 6 and 7 show less fiber pull-out in PC30BP2 than in PC30BP1. These results justify good distribution between fillers and matrix for PC30P2 thus producing higher tensile strength. The good interaction between C30B, PLA, and PALF helps to improve the tensile strength and increase elongation. However, the existence of micro cracks in the matrix as shown by the arrow may be introduced by the repeating extrusion process. All the nanocomposites produced a higher modulus Young than PLA. PC30B improves the modulus Young by 16.5% than PLA. The highest young Modulus produced by hybrid nanocomposites PC30BP1, followed by PC30BP2 with improvements of 37.7% and 15% respectively compared to PC30B. The increment of modulus Young happens due to the different size of filler between PALF and C30B. The incompatible particle sizes limited the chain movement of the polymer matrix thus resulting in high rigidity of the composites. Results of TGA and DTG for PLA, nanocomposites PC30B, PC30BP1 and PC30BP2 were shown in Figure 8 and simplified in Table 2. T_{10} refers to the temperature during 10% of the sample weight loss. T_{peak} represents the temperature where the maximum rate of change in weight loss occurred and is referred to as an inflection point. T_{90} is the temperature during 90% of weight loss. Residual mass denotes the remaining mass taken at a temperature of 600°C. The reference sample, PC30B produced higher T_{10}, T_{peak} and T_{90} than PLA. The addition of C30B fills in the micro voids in the composites and acts as heat barrier thus increasing the degradation temperature of PLA, as agreed in findings by George et al. [15]. However, both hybrid PC30BP1 and PC30BP2 nanocomposites produced lower T_{10} than PLA. This result may be explained by the fact that water and moisture were released from PALF, at the earlier temperature of 230°C [16]. Interestingly, the value of T_{peak} (Figure 8 (b)) and T_{90} is slightly higher for PC30BP2, followed by PC30BP1 compared to PLA, showing that the combination of PALF and C30B slightly improve thermal degradation of composites at higher temperature. C30B limits the movement of the matrix polymer chain, thus reducing the degradation of the composites. As discussed in SEM and XRD analysis before, PC30BP2 has better interaction between clay, fiber and matrix than PC30BP1, producing better T_{peak} and T_{90}. Both PC30BP1 and PC30BP2 produce similar amounts of residual mass, representing the lignin in the PALF that is slowly carbonized, as reported by [17]. This finding highlights the positive effects of adding C30B. The usage of untreated natural fiber was reported to reduce the degradation temperature of composites [18]. DSC analysis is shown in Figure 9 and the results are summarized in Table 3. All the nanocomposites produced less T_g than PLA, with the highest reduction on PC30BP2, followed by PC30B and PC30BP1. A wider peak was formed especially on PC30BP2 sample. This is because C30B in PC30BP2 acts as a better nucleus agent, producing interfacial adhesion with polymer thus producing a shorter molecular chain of matrix and increasing the free volume in the composites. By producing more nucleus sites, the crystallization of the composites occurred at the value of T_c lower than PLA and increased the percentage of crystallinity (χ_c). On the other hand, the T_c and T_m value of PC30B is higher than PLA and hybrid nanocomposites. This is due to the absence of PALF, where C30B promotes a higher order of crystalline zones in PLA. For hybrid nanocomposites of PC30BP1 and PC30BP2, no significant changes were found for T_m after the addition of natural fiber.

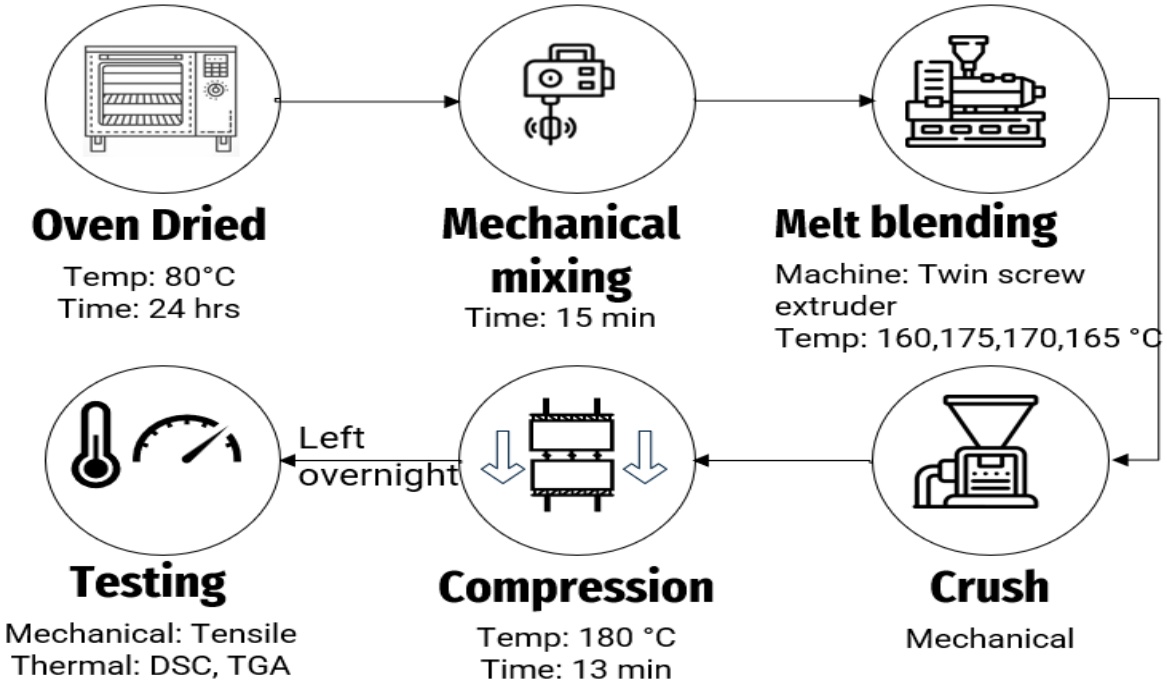

Figure 1: Processing flow of nanocomposite production.

Table 1: Material composition and processing parameters of the produced nanocomposites.

Nanocomposites	Materials	Weight loading (wt%)	Screw speed	
			1st mix	2nd mix
PC30B	PLA	99.0	100	-
	C30B	1.0		
PC30BP1 (single step)	PLA	89.1	60	-
	C30B	0.9		
	PALF	10		
PC30BP2 (double step)	PLA	89.1	100	60
	C30B	0.9		
	PALF	10	-	

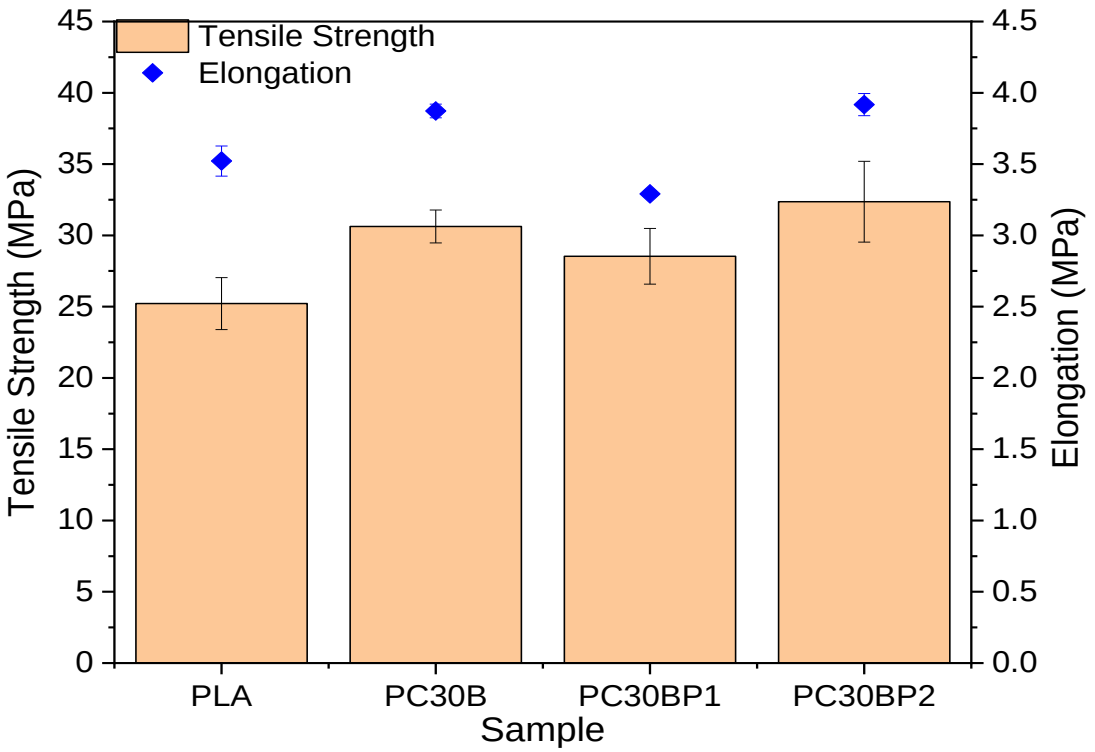

Figure 2: Tensile strength and elongation of PLA, nanocomposites PC30B, PC30BP1 and PC30BP2.

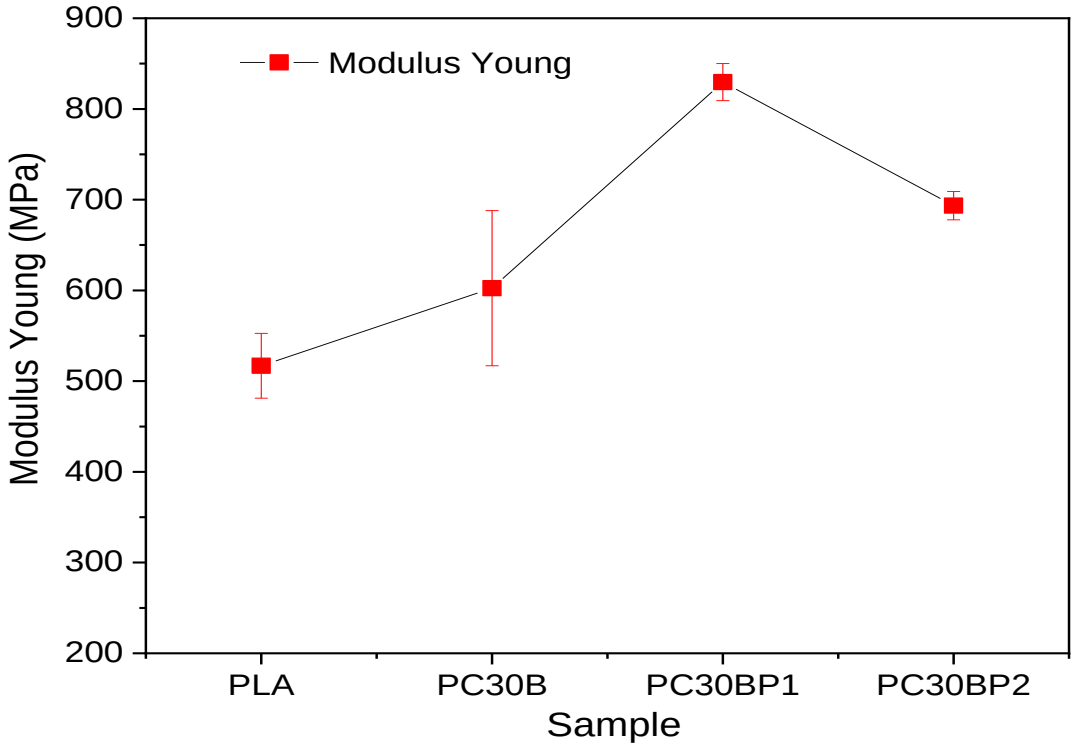

Figure 3: Modulus Young of PLA, nanocomposites PC30B, PC30BP1 and PC30BP2.

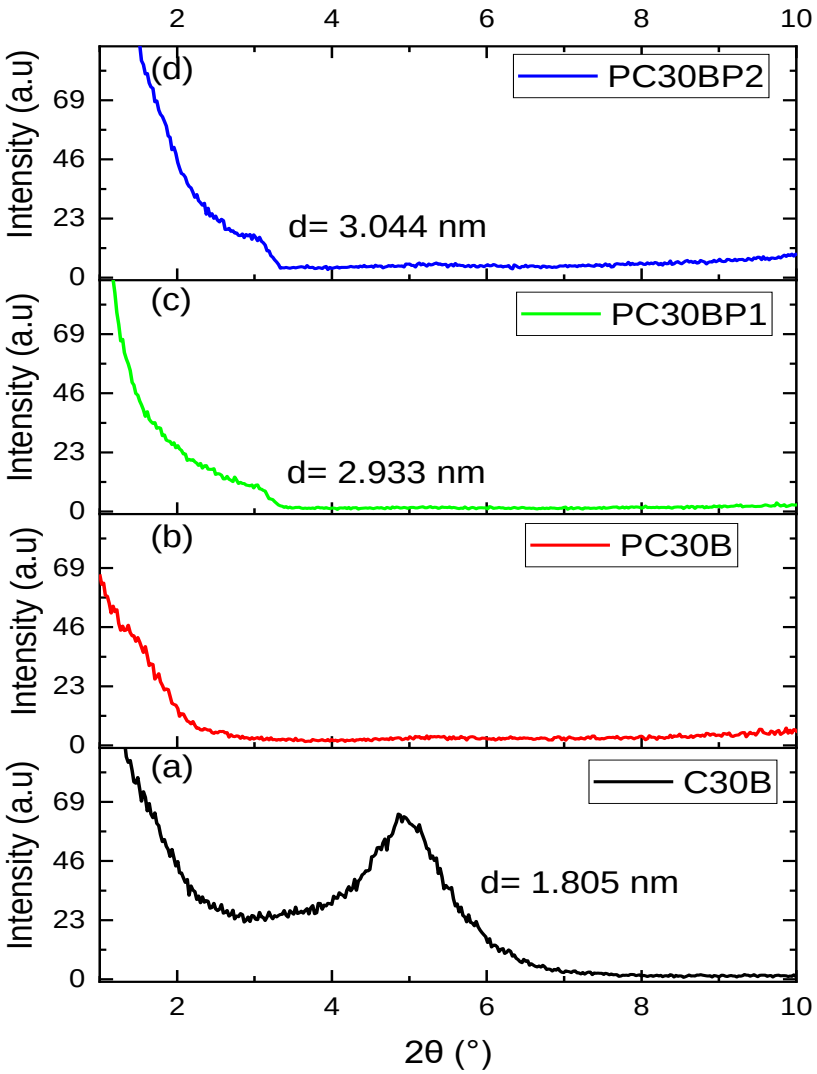

Figure 4: X-Ray Diffraction peak of (a) C30B; (b) PC30B; (c) PC30BP1 and (d)PC30BP2 nanocomposites.

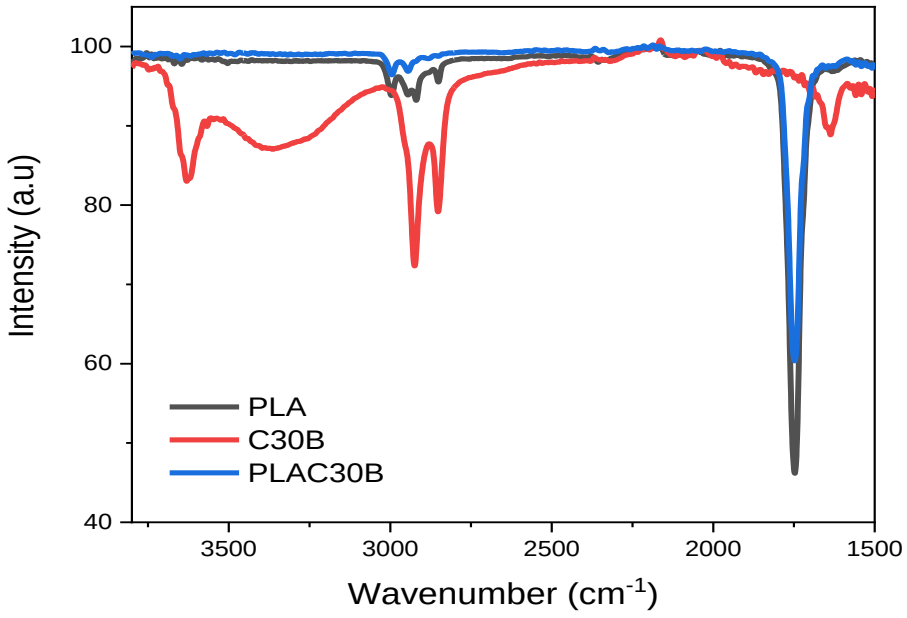

Figure 5: FTIR analysis for PLA, C30B and PC30B nanocomposites

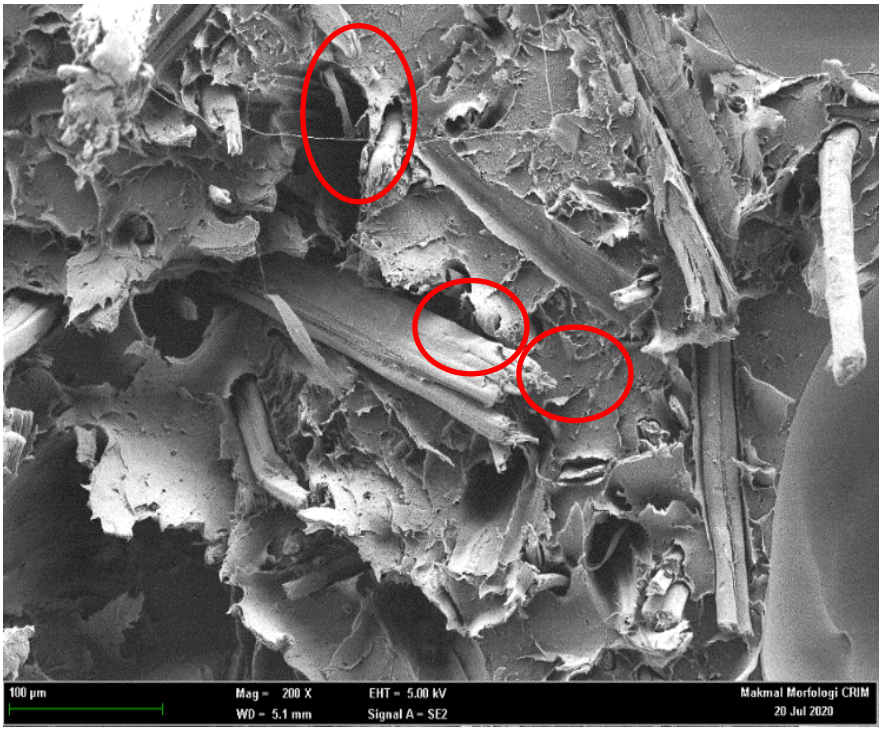

Figure 6: SEM analysis of PC30BP1 at magnification of 200x.

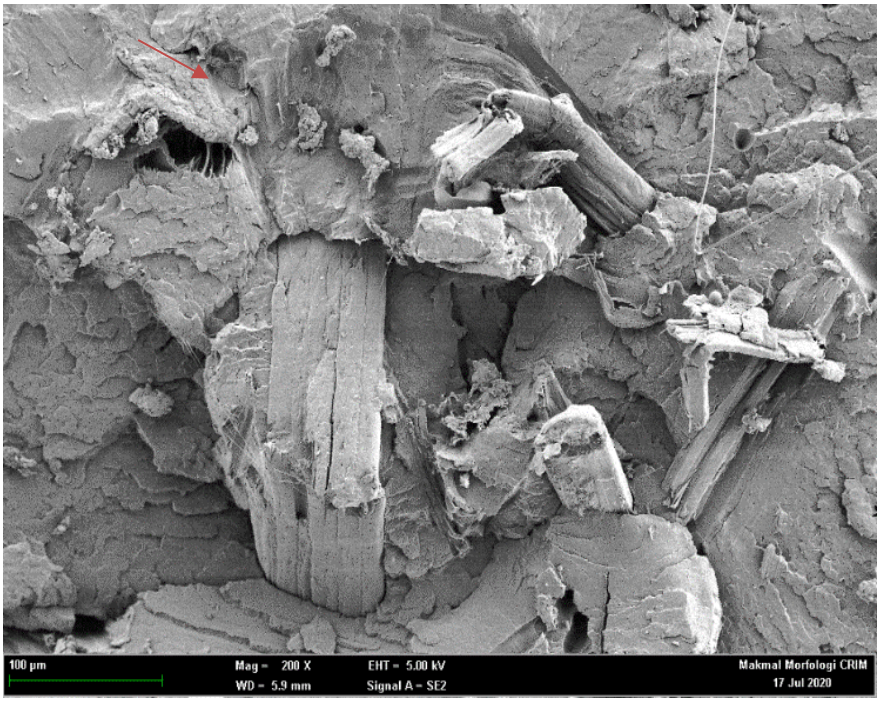

Figure 7: SEM analysis of PC30BP2 at magnification of 200x

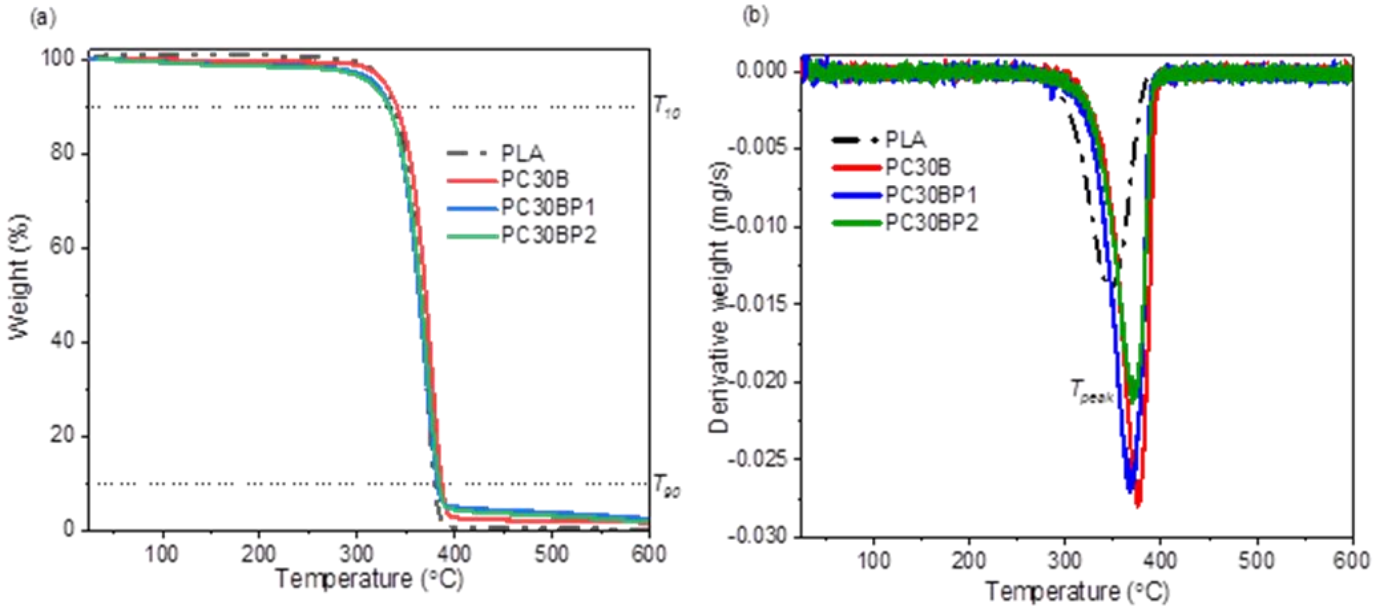

Figure 8: Thermal analysis (a)TGA;(b) DTG graph of PLA, PC30B, PC30P1 and PC30BP2 nanocomposites.

Table 2: TGA and DTG analysis of PLA, PC30B, PC30P1 and PC30BP2 nanocomposites.

Sample	T_{10} (°C)	T_{peak} (°C)	T_{90} (°C)	Residual Mass (%)
PLA	336.9	363.3	380.8	0.4
PC30B	340.2	375.9	388.4	0.6
PC30BP1	332.5	368.0	381.9	2.5
PC30BP2	331.6	369.4	383.7	2.4

Table 3: DSC analysis of PLA, nanocomposites PC30B, PC30BP1 and PC30BP2.

Sample	T_g (°C)	T_c (°C)	T_m (°C)	χ_c (%)
PLA	58.4	95.9	169.8	26.3
PC30B	56.4	97.0	171.3	29.9
PC30BP1	57.3	91.3	169.4	33.3
PC30BP2	53.7	91.1	169.1	30.6

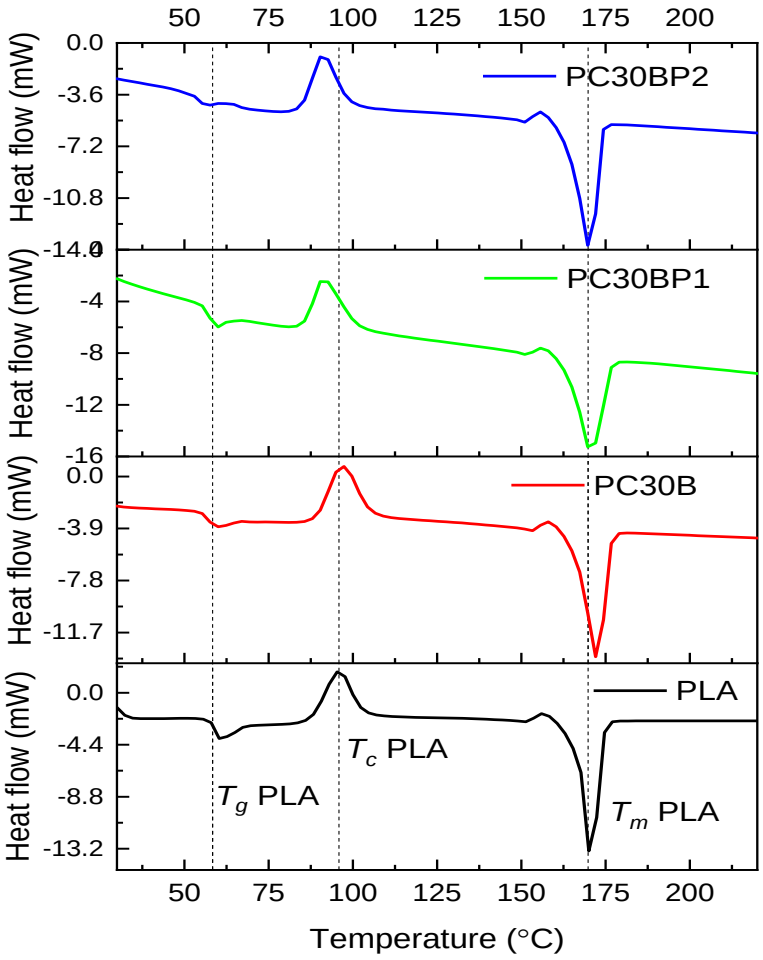

Figure 9*:* DSC graph of PLA, nanocomposites PC30B, PC30BP1 and PC30BP2.

4. Conclusions

This paper has investigated the effect of the number of extrusion steps on the mechanical and thermal properties of hybrid nanocomposites consisting of filler C30B, PALF and PLA. The evidence from this study suggests that increasing appropriate shear mixing stress and time leads to higher tensile strength and better thermal stability of the produced composites. In the one step extrusion, lower tensile strength was produced as PALF may obstruct the interfacial adhesion between C30B and the molecular chain of PLA. By ascribing two step extrusion, C30B has already established a good interfacial interaction with PLA, thus further enhancing interaction with PALF in the second mixing. Future work will focus on increasing the filler loading to reduce the overall cost of production. The presented findings are promising for integrating biodegradable materials in producing competitive properties of nanocomposite for future advanced materials development.

References

[1] F. Berzin, T. Amornsakchai, A. Lemaitre, R. Castellani, and B. Vergnes, (2019). Influence of fiber content on rheological and mechanical properties of pineapple leaf fibers-polypropylene composites prepared by twin-screw extrusion. Polymer Composites. 40 (12): 4519-4529.

[2] M. Rajakumaran and A. Ray. (2020). Investigation on mechanical properties of pineapple leaf – based short fiber – reinforced polymer composite from selected Indian (northeastern part) cultivars. Journals of Thermoplastic Composite Materials. 33 (3): 324-342.

[3] D. Diniz, C. Bruno, B. Luna, E. Maria, and E. Antônio. (2019). Biodegradable Compounds of Poly (Ɛ-Caprolactone)/ Montmorillonite Clays. Materials Research. 22: 1–10.

[4] A. Bacigalupe, M. Fernández, P. Eisenberg, and M. M. Escobar. (2020). Greener adhesives based on UF/soy protein reinforced with montmorillonite clay for wood particleboard. Journal of Applied Polymer Science. 137 (37): 49086.

[5] A. Bacigalupe, M. Fernández, P. Eisenberg, & M. M. Escobar. (2020). Greener adhesives based on UF/soy protein reinforced with montmorillonite clay for wood particleboard. Journal of Applied Polymer Science. 137 (37): 49086.

[6] P. Ramesh, B. D. Prasad, and K. L. Narayana. (2020). Effect of MMT Clay on Mechanical,

Thermal and Barrier Properties of Treated Aloevera Fiber / PLA-Hybrid Biocomposites. Silicon. 12 (7): 1751-1760.

[7] G. Sui, D. Liu, Y. Liu, W. Ji, Q. Zhang, and Q. Fu. (2019). The dispersion of CNT in TPU matrix with different preparation methods: solution mixing vs melt mixing. Polymer. 182: 121838.

[8] M. R. Kaiser, H. B. Anuar, N. B. Samat, and S. B. A. Razak. (2013). Effect of processing routes on the mechanical, thermal and morphological properties of PLA-based hybrid biocomposite. Iranian Polymer Journal. 22: 123-131.

[9] L. Meng, L. Yu, S. Khalid, H. Liu, S. Zhang, Q. Duan & L. Chen (2019). Preparation, microstructure and performance of poly (lactic acid)-Poly (butylene succinate-co-butyleneadipate)-starch hybrid composites. Composites Part B: Engineering. 177: 107384.

[10] J. George and S. Thomas. (1995). Short Pineapple-Leaf-Fiber-Reinforced Low-Density Polyethylene Composites. Journal of Applied Polymer Science. 57: 843–854.

[11] A. Omar, R. S. Chen, D. Shahdan, and S. Ahmad (2022). Thermal, water absorption, and mechanical characterizations of polylactide based nanocomposites: Comparison between sodium and modified montmorillonite as reinforcement materials. Journal of Applied Polymer Science. 139 (12): 51836.

[12] E. W. Fischer, H. J. Sterzel, and G. Wegner. (1973). Investigation of the structure of solution grown crystals of lactide copolymers by means of chemical Kolloid-Zeitschrift und Zeitschrift für Polymere. 251: 980-990.

[13] N. Kishore Pradhan, M. Das, and P. L. Nayak (2020). Biodegradation study of soya protein concentrate blended with poly (lactic acid) and cloisite 30b nanocomposites, *Environmental biotechnology*. 22 (4): 604–613.

[14] M. George, G. E. Kochimoolayil, and H. Jayadas Narakathra. (2016). Mechanical and thermal properties of modified kaolin clay/unsaturated polyester nanocomposites. Journal of Applied Polymer Science. 133 (13).

[15] J. Chaishome and S. Supapvanich. (2018). Polylactic acid (PLA) based green composites reinforced pineapple leaf fibres: evaluation of processing and tensile performance. In MATEC Web of Conferences (Vol. 192, p. 03002). EDP Sciences.

[16] J. Jain and S. Sinha. (2022). Potential of Pineapple Leaf Fibers and Their Modifications for Development of Tile Composites. Journal of Natural Fibers. 19 (13): 4822-4834.

[17] R. Siakeng, M. Jawaid, M. Asim, N. Saba, M. Sajay, S. Siengchin & H. Fouad. (2020). Alkali treated coir / pineapple leaf fibres reinforced PLA hybrid composites: Evaluation of mechanical, morphological, thermal and physical properties. eXPRESS Polymer Letters. 14 (8): 717-730.