Investigation of the Thermal Properties of Sayote (*Sechium edule*) Fiber Loaded Starch/PVOH Composite Blends

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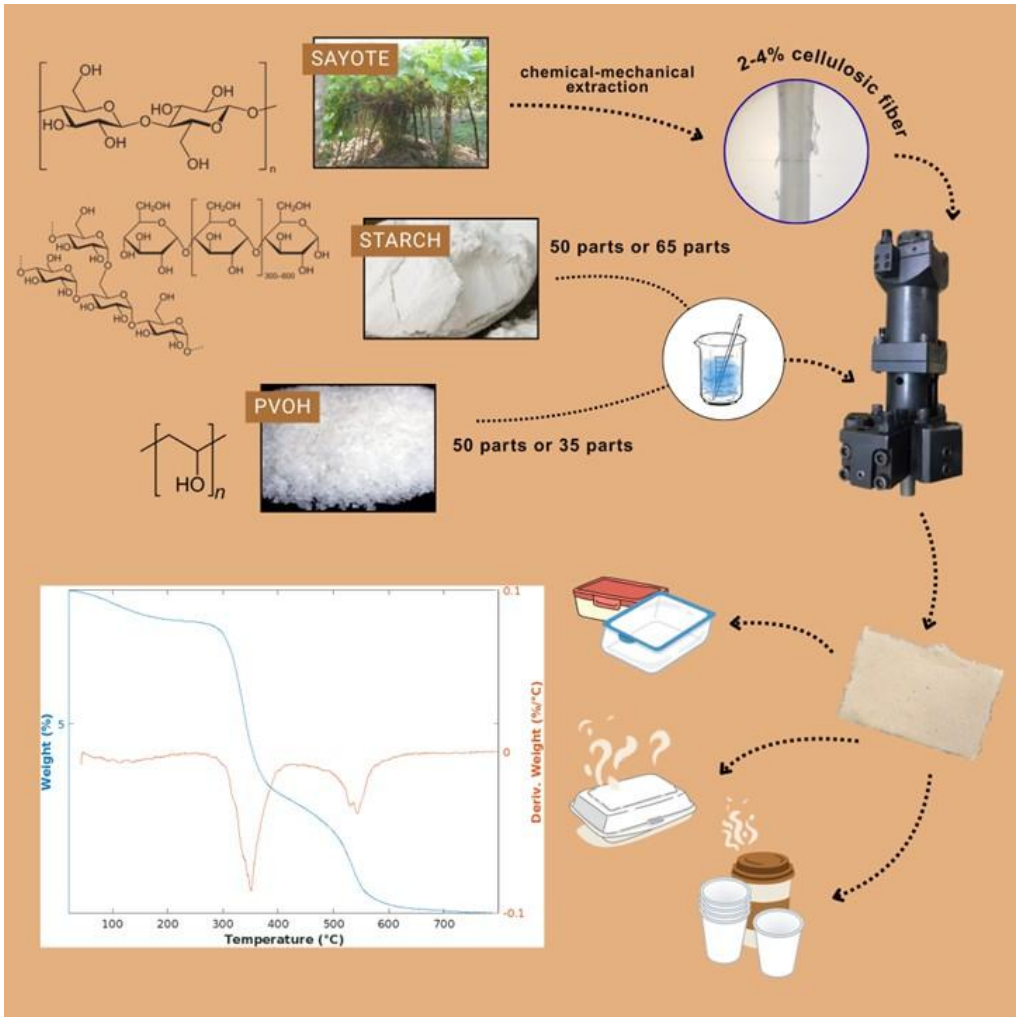
GRAPHICAL ABSTRACT



Investigation of the Thermal Properties of Sayote (*Sechium edule*) Fiber Loaded Starch/PVOH Composite Blends

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The thermal properties of starch/PVOH formulations gelatinized with glycerol, cross-linked with boric acid, incorporated with clay and loaded with 2 wt%, 4 wt%, and 7 wt% sayote fibers were investigated. The FTIR spectra, SEM micrographs, DSC, and TGA results revealed a successful blending in starch/PVOH (50/50) and starch/PVOH (65/35) fomulations with glycerol as plasticizer and boric acid as cross-linking agent. Plasticized and cross-linked starch/PVOH reinforced with clay and varying amounts of sayote fiber suggest more inter- and intra- molecular hydrogen bonding interactions, making the composite more crystalline and thermally stable. The SEM micrographs showed a smoother surface with the addition of boric acid and a more orderly woven surface with 2 wt% sayote fiber loading. DSC thermograms reveal that the formulations were compatible and had good blending interactions, since the experimental enthalpies of melting were higher than their theoretical values. The addition of sayote fiber increased the thermal stability of starch/PVOH composite blends and prevented the re-crystallization of starch. TGA curves showed that the addition of sayote fibers formed stronger blends that delayed the degradation of the composite. The starch/PVOH (50/50) and starch/PVOH (65/35) composite blends were more crystalline and thermally stable at 2 wt% to 4 wt% sayote fiber loading.

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Keywords: Starch/PVOH; Thermal stability; Sayote fiber loading; Composite blending; Delayed degradation; Crystallinity

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INTRODUCTION

Thermoplastic starches are blended with other synthetic biodegradable polymers to improve the mechanical and thermal properties of the product and to decrease the total production cost. Pure starch, when used in material processing, exhibits poor mechanical properties due to its brittle nature. Thus, studies on blending starch with other biopolymers are continuously explored. Starch composite blends find its application in food packaging, aerospace, automotive, medical, and dental industries due to better mechanical, thermal, and chemical properties as well as reduced cost of fabrication. In addition, the move towards sustainable development in industry is already receiving more attention around the world. Thus, the use of synthetic polymers in materials production is being continuously reduced due to their non-biodegradability and the emergence of micro/nano plastics in water, food, and soil. Examples of biodegradable polymers that are commonly blended

with starch are polyvinyl acetate (PVAc), benzoxazine resin, poly(ester-urethane-acrylate) (PEUA), polylactic acid (PLA), polyamide, polycaprolactone (PCL), and polyvinyl alcohol (PVOH). Cassava starch/cassava bagasse hybrid composite loaded with sugar palm fiber with fructose as plasticizer has increased relative crystallinity and decreased degradation temperature with increased fiber loading, which is attributed to low degradation temperature of natural fibers (Edhirej *et al.* 2017). In a study by Zegaoui *et al.* (2018), cyanate ester/benzoxazine resin composite reinforced by silane-treated natural hemp fibers was found to be thermally stable at 20 wt% fiber loading. The incorporation of fibers increases the glass transition temperature (T_g) and decreased the decomposition temperature, which means that the thermal stability of the composite was enhanced as the microhardness and flexural strength became higher. Petrenko *et al.* (2022) studied the natural fiber-reinforced poly(ester-urethane-acrylate) PEUA and found that with jute, flax, ramie, and cotton fiber reinforcement, cotton fiber reinforcement to PEUA resulted in delayed onset of degradation as compared to unreinforced PEUA. In addition, cotton reinforcement to PEUA resulted in better tensile and flexural properties. Polyamide composite filled with flax, kenaf, and hemp fibers improved thermal stability up to 20 wt% fiber loading, but with an increase in fiber content, the thermal stability decreases. The crystallinity (Xc) was also seen to increase with lower fiber loading, which was 5 to 20 wt% for flax, kenaf, and hemp fiber mixtures as well as with individual fibers (Kiziltas *et al.* 2016). Polycaprolactone (PCL) grafted with maleic anhydride and rice straw fiber (RSF) loaded decreased in melting temperature as rice straw fiber composition was increased. The initial decomposition temperature was decreased with the increased addition of rice straw fiber from 10 wt% to 40 wt%. However, between maleic acid-grafted PCL and non-grafted PCL, PCL grafted with maleic acid loaded with RSF increased the initial degradation temperature (Wu and Liao 2012). Epoxy-based bio composites, such as bisphenol A reinforced with non-woven and powder fique fibers through resin infusion process, revealed that fiber loading resulted in a better stiffening and reinforcing effect. Moreover, thermal stability was improved with fiber addition (Centeno-Mesa *et al.* 2022). Another related study was done by Raouf (2023) on the mechanical, electrical, thermal, and structural properties of starch and polyvinyl acetate. Increasing the starch content from 40% starch to 60% starch increased the material's hardness, tensile strength, compression resistance, and impact strength, but it was the other way around for thermal property and conductivity. An increase in starch content caused a decrease in thermal property and conductivity. The use of fillers and additives such as cellulosic fiber is a potential solution to the weakness of starch/PVA composite.

Polyvinyl alcohol, a hydrolyzed product of polyvinyl acetate, has good strength and flexibility. Like starch, PVOH is not thermoplastic, since its melting temperature exceeds its degradation temperature. It has a lower rate of biodegradation, but when plasticized and blended with other natural biopolymers, the degradation rate is increased. Sin *et al.* 2010 detected synergistic interactions of polyvinyl alcohol and cassava starch blends through differential scanning calorimetry and were able to report that PVOH and cassava starch are synergistically compatible. Adding 30 wt% or above of PVOH gave a strong physical bonding between cassava starch and PVOH. Furthermore, the incorporation of 65 to 75 wt% of PVOH in cassava starch produced a physical bonding similar to neat PVOH. Due to the limitations of starch/PVOH biopolymer blends, such as moisture absorption and retrogradation of starch with time, numerous ways to improve the characteristics of the product such as chemical and physical modification of starch or PVOH before blending, cross-linking of starch and PVOH, and incorporation of natural fibers and particulates such

as clay were suggested. Cross-linking PVOH and starch using urea formaldehyde and reinforcement with barley husk was also performed to decrease the production cost and increase biodegradability of food packaging films. Grafting of natural barley husk fiber into the cross-linked starch/PVOH blend resulted in increased tensile strength and decreased water uptake as well as increased decomposition temperature in comparison to the neat starch/PVOH films (Mittal 2016). The use of plasticizing agents such as polyethylene glycol to improve the blending interaction of starch/PVOH composite with rice straw fiber as a reinforcing agent *via* a solution casting method was investigated by Sharma *et al.* (2022). The addition of rice straw fibers improved the thermal stability of the films, and the crystallinity (X_c) was found to be highest at 30 wt.% fiber loading. Aside from fiber reinforcement to starch/PVOH composite, other additives such as glycerol, nano-clay, and boric acid can also be employed in small fraction to starch/PVOH composite blends to further improve properties. An investigation of the thermal behavior and interactions of cassava starch filled glycerol- polyvinyl alcohols resulted in a decrease in onset and endpoint melting temperature, which means that glycerol was able to promote internal lubrication and disrupted the rigidity arrangements of PVOH and starch and, in turn, improved the thermal property of the composite blend (Rahman *et al.* 2010). The addition of glycerol was also found to reduce the decomposition onset temperature and mass loss of the starch/PVA blend films. In one study, glycerol as a plasticizer increased the elongation but reduced tensile strength and modulus. But with the addition of borax as a cross-linking agent, there was an increase in the starch film's modulus and tensile strength while decreasing elongation. Blending glycerol and borax to improve the mechanical properties of starch was found to give a better mechanical property for starch at a formulation of 0.5% for borax and 10% glycerol (Frost *et al.* 2013). The incorporation of kaolin clay at 5.5 wt% to 3.5 g PVOH and 2.5 g potato starch for the production of environment friendly packaging materials was also reported to have improved the composite's mechanical properties (Tabassum *et al*. 2024). The findings both coincides with the characterization of samples and optimization using Response Surface Methodology (RSM) that was employed in the study.

Recent works on starch/PVOH composite materials reinforced with cellulosic fibers confirm the effectiveness of fibers at a specific quantity in improving the thermal properties of biopackaging materials. Cellulose nanofibers extracted from sugarcane bagasse showed an improvement on the mechanical and thermal properties of the starch/PVOH composite film at 4% fiber loading (Ali *et al.* 2022). The thermal resistance and degradation temperature of PVOH reinforced with cellulose nanofiber from pineapple leaf was also reported to have increased as compared to the neat PVOH (Mahardika *et al.* 2024). The study of the mechanical and thermal properties of polyvinyl alcohol/nanofiber cellulose/nanosilicon dioxide composite films prepared *via* solution casting reported that an increase of nanofiber cellulose and nanosilicon dioxide content by 10 wt. % resulted to a poor water vapor permeability. The researchers recommended the incorporation of 5 wt.% of both nanofiber cellulose and nanosilicon dioxide to improve mechanical property and increased thermal stability (Bay *et al.* 2021). Potdar *et al.* 2023 investigated on the properties of plasticized starch-pva-paddy straw composites and were able to observe that 2 parts of the paddy straw fiber was able to delay the degradation temperature of the composite.

In view of the literature presented, experiments were performed to explore the thermal properties of starch and PVOH as the primary matrices with the addition of sayote fibers in different weight percentages and the incorporation of glycerol, boric acid, and

clay in minimal amounts. It was the objective of this study to produce starch/PVOH composite blends for single-use food biopackaging applications. The possibility of blending starch-PVOH-glycerol-boric acid- clay- fiber to form a composite was characterized using Fourier Transform Infrared with Attenuated Total Reflection (FTIR-ATR) analysis and Scanning Electron Microscopy (SEM) to support the Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) results.

EXPERIMENTAL

Starch/PVOH/Clay/Fiber Composite Blending

The Queen brand pure corn starch sold in the Philippine market and locally sourced clay was used in the study. Reagents such as 99% hydrolyzed polyvinyl alcohol (PVOH), boric acid, and glycerol were purchased from Sigma-Aldrich Corporation. These are 99.5% ACS reagent grade.

To improve the properties of starch/PVOH composites, chemical modification of starch and PVOH was done before the blending process. Plasticization of both starch and PVOH with glycerol were done followed by cross-linking reaction with boric acid. Figure 1 shows the preparation of starch/PVOH/clay/fiber composite blends. Polyvinyl alcohol and starch were plasticized with glycerol to enhance the flexibility of the molecular chains thereby improving the processability of the matrices. Starch and PVOH were mixed together, then boric acid was added. Sayote (*Sechium edule*) fiber and unmodified clay deposit were suspended in the mixture and ultrasonicated as described previously (Bensadoun *et al.* 2011). The blended colloidal suspension was casted in petri-dishes, dried in a Gallenkamp oven, and pressed in an Elmes Chicago hydraulic press.

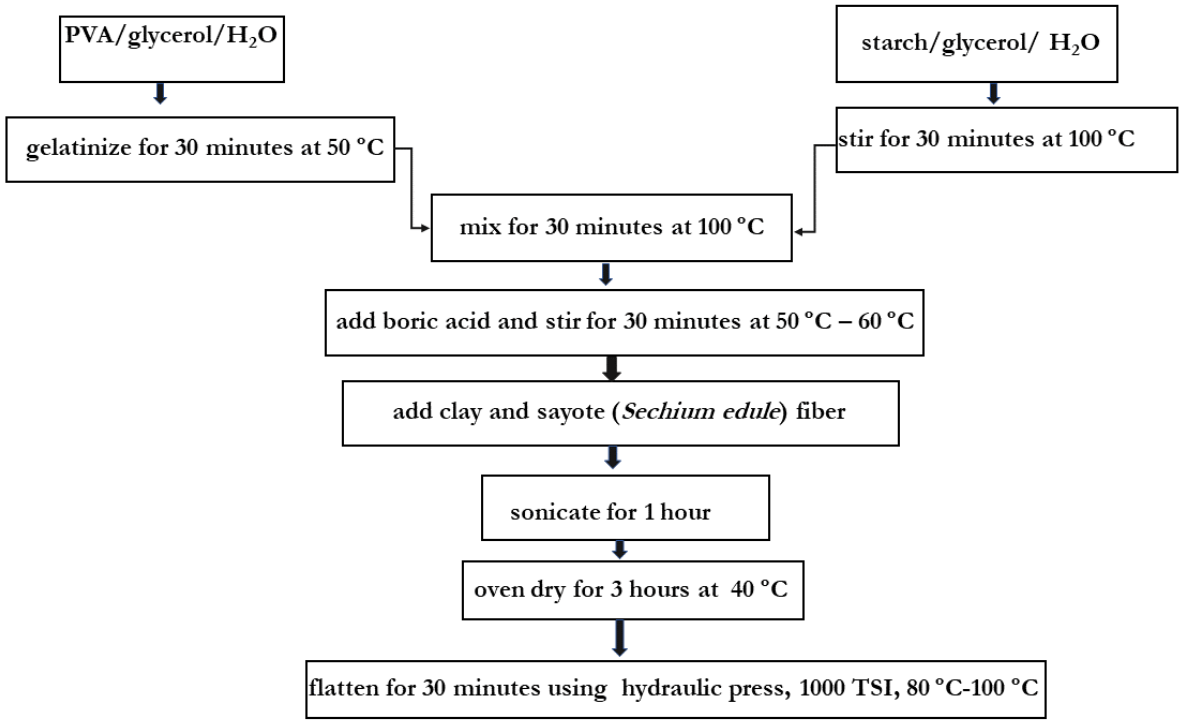

Fig. 1. Preparation of starch/PVOH/clay/sayote fiber composite blends

Table 1 presents further details on the quantity of starch, PVOH, glycerol, water, boric acid, clay, and sayote fiber used in the study. Samples of starch and PVOH blends were prepared with the following ratio in parts: 50:50 labeled as starch/PVOH (50/50) and 65:35 labeled as starch/PVOH (65/35). The amounts of sayote fiber added were 2 parts (2 wt%), 5 parts (4 wt%), and 10 parts (7 wt%) with respect to starch/PVOH. In addition, unmodified clay deposit, glycerol, and boric acid were incorporated in all samples. Samples without sayote fiber and clay reinforcing fillers were also prepared using the same procedure and ratio shown in the table.

Table 1. Quantity of Starch, PVOH, Glycerol, Boric Acid, Clay, Sayote fiber Used in Composite Fabrication

Composition	65 Parts Starch		50 Parts Starch	
	wt%	parts	wt%	parts
Starch	46.41	65	37.74	50
PVOH	24.99	35	37.74	50
Glycerol	1.46	2	1.50	2
Water	23.21	33	18.87	25
Boric Acid	1.07	2	1.14	15
Clay	1.14	2	1.21	2
A- Fiber at 2 wt.%	1.71	2	1.81	2
B- Fiber at 4 wt.%	3.78	5	3.99	5
C- Fiber at 7 wt.%	7.03	10	7.40	10

FTIR Analysis of the Composite Blends

The Fourier Transform Infrared -ATR (FTIR -ATR) spectra were obtained using an Agilent Cary 630 FTIR. The transmittance was measured at 100 scans from 400.0 to 4000.0 cm^{-1}.

SEM Analysis of the Composite Blends

The morphological characteristics were determined using Hitachi TM-1000 micrographs. The samples were Au-Pd sputtered for 1 minute and were subjected to SEM analysis for 1 hour.

Thermal Analysis of the Composite Blends

The thermal characteristics of the composite blends were identified using a Shimadzu DSC 50. The 3.00 mg sample was crimped in an aluminum cell/pan. All samples were subjected to a heating rate of 10 °C/min in a liquid nitrogen atmosphere at a flow rate of 20 mL/min. The heating temperature was set from 10 to 300 °C. The onset temperature is the lowest temperature when the material begins to undergo reaction, and in terms of starch/PVOH it is more aptly called recrystallization. The endpoint is the temperature when the material being analyzed ceases to recrystallize. Figure 2 shows the tangent line intersecting the baseline for both the onset and endpoint temperatures. The figure also shows the melting peak or (T_m). The enthalpy of melting (ΔH_m) can be taken in the extrapolated onset and endpoint are under the curve.

Roohani *et al.* (2008) used an equation for the calculation of the degree of crystallinity (X_c) from DSC data. The same equation was also used by Boroujeni *et al.* in 2024. From the enthalpy of melting (ΔH_m), the theoretical enthalpy of melting (ΔH_{m_o}) can be calculated by multiplying ΔH_m by the weight% of PVOH in the composite blend. The crystallinity was calculated by Eq. 1,

$$X_c = \frac{\Delta H_m}{\omega \, x \, \Delta H_{m0}} \quad (1)$$

where X_c is the degree of crystallinity, ω is the wt.% of PVOH in the composite, ΔH_m is the enthalpy of melting (J/g), and ΔH_{m0} is the enthalpy of melting for 100% crystalline PVOH determined at 161.6 J/g found in the ATHAS data bank.

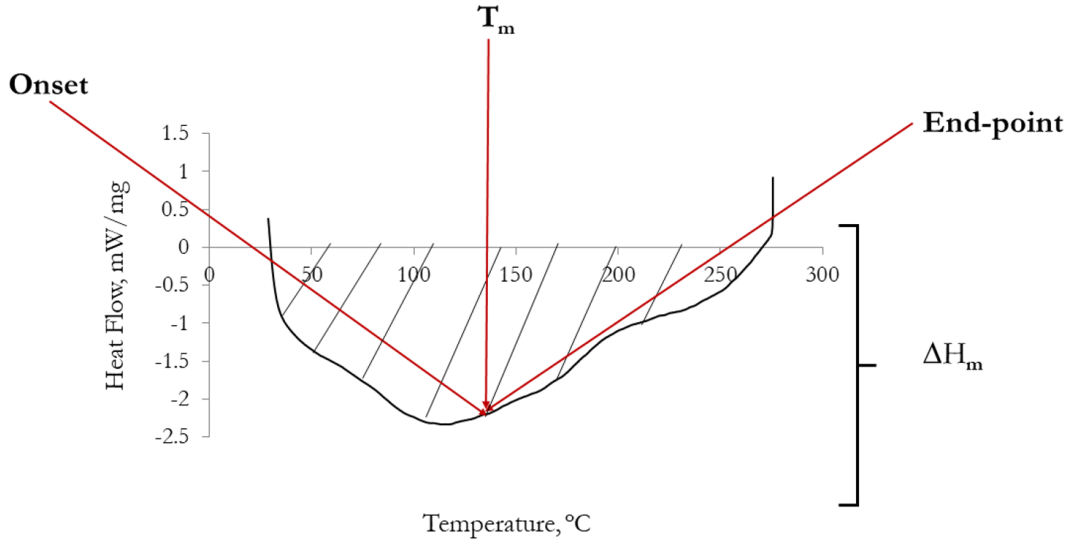

Fig. 2. Sample DSC thermogram of starch/PVOH composite blend with fiber loading

The thermogravimetry experiment was performed using a Shimadzu TA 50. The sample weight was 10 mg. Samples were heated from 20 to 800 °C at a heating rate of 10 °C/min. All experiments were carried out in a liquid nitrogen atmosphere at a flow rate of 50 mL/min. The heating temperature was set up from 20 to 800 °C.

RESULTS AND DISCUSSION

FTIR Analysis

Table 2 is a summary of the relevant FTIR spectra peaks obtained for starch/PVOH (50/50) composite blends with different additives and different amounts of fiber. Results reveal that starch/PVOH blending was successfully achieved with the the addition of water and glycerol as plasticizers and boric acid as crosslinking agent. Peaks near 760.0 cm^{-1} are characteristic of C-O bending in starch and 1733.0 cm^{-1} for C=O stretching of acetate groups in PVOH. The neat starch/PVOH, glycerol plasticized, boric acid cross-linked, clay/fiber reinforced had characteristic peaks at wavenumbers (cm^{-1}) 756.6, 757.2, 756.9 and 756.4(A), 757.6(B), and 757.6 (C). The close values suggest the incorporation of starch in the samples. Looking at the O-H stretching at 3400.0 cm^{-1}, the shift from 3422.0 to around 3417.0 cm^{-1} in the neat starch/PVOH and across all preparations suggest more intermolecular hydrogen bonding interactions, since at higher wavelength, lesser energy is absorbed due to participation of the hydroxyl groups to hydrogen bonding interactions. The added clay and fibers disrupted the intramolecular H-bonding in starch chains, thus causing more bonding interactions between starch and PVOH. The peak at 1740.0 to 1720.0 cm^{-1} was not observed due to the absence of aldehyde groups, which means that all aldehyde groups were involved in cross-linking starch and PVOH.

Table 2. FTIR Summary of Relevant Peaks for Starch/PVOH (50/50) Composite Blends

Characteristics	Neat starch/PVOH	Starch/ PVOH/ Glycerol	Starch/ PVOH/ Glycerol/ Boric Acid	Starch/ PVOH/ Glycerol/ Boric Acid/Clay and Fiber
C-O bending(characteristic of C-O-C ring vibration in starch) ; (cm^{-1})	756.6	757.2	756.9	**A**-756.4
				B-757.6
				C-757.6
C=O stretching(Characteristic of carbonyl vibrating in the acetate residue of PVA) ; (cm^{-1})	-	-	-	**A**- -
				B- -
				C- -
O-H Stretching; (cm^{-1})	3422.0	3416.6	3416.2	**A**-3417.0
				B-3416.7
				C-3417.1

*Fiber loading at **A** – 2 wt%, **B** – 4 wt% , and **C** – 7 wt%

Table 3 shows the summary of the relevant FTIR spectra obtained for starch/PVOH 65/35 composite blends. The characteristic C-O-C ring vibration in starch at around 760.0 cm^{-1} suggests a shift in lower wavenumber from the neat starch/PVOH to the fiber loaded samples. This is correlated to aborbance at higher wavelength requiring lower energy. This means that starch was incorporated in the samples.

Table 3. FTIR Summary of Relevant Peaks for Starch/PVOH (65/35) Composite Blend

Characteristics	Starch/ PVOH	Starch/ PVOH/ Glycerol	Starch/PVOH/ Glycerol/Boric Acid	Starch/PVOH/Glycerol/Boric Acid/Clay and Fiber
C-O bending(characteristic of C-O-C ring vibration in starch); (cm^{-1})	763.5	750.8	764.7	**A**-761.6
				B-754.6
				C-758.4
C=O stretching (Characteristic of carbonyl vibrating in the acetate residue of PVA); (cm^{-1})	1730.6	1727.8	1731.3	**A**-1724.9
				B-1733.4
				C-1737.1
O-H Stretching; (cm^{-1})	3417.1	3417.0	3417.9	**A**-3416.6
				B-3415.7
				C-3420.5

*Fiber loading at **A** – 2 wt%, **B** – 4 wt% , and **C** – 7 wt%

At around 1740.0 to 1720.0 cm^{-1}, characteristic for carbonyl vibration in the acetate residue of PVOH, it can be seen that the decrease in the wavenumber or increase in wavelength from neat starch/PVOH to the plasticized and 2 wt% fiber loaded composites means a stronger bonding interaction between starch and PVOH as compared to the other samples. The characteristic O-H stretching at around 3400.0 cm^{-1} reveals a shift from 3417.1 to around 3420.5 in the 7 wt% fiber loaded blend, implying that the added fibers

caused lesser bonding interactions between starch and PVOH in the composite blend. Too much fiber might have caused more agglomeration, which disrupted the three dimensional bonding network in the blends.

SEM Analysis

The SEM micrographs of the blends at 1000X show that neat starch/PVOH composites had rough and granulated surfaces. The crystalline starch granules were still exposed on the surface. The same was observed with the composite with glycerol, which means that glycerol as plasticizing agent is not enough in improving the properties of the starch/PVOH formulation.

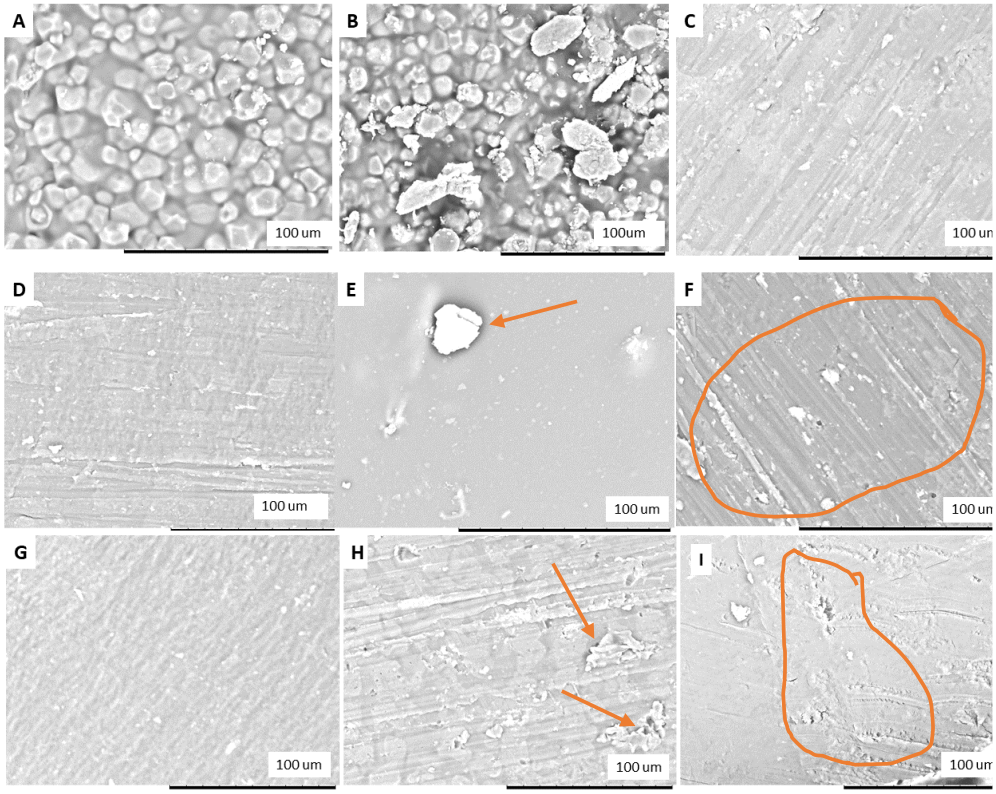

Fig. 3. SEM Micrographs of composite blends at 1000 X magnification: **A)** neat starch/PVOH; **B)** starch/PVOH with glycerol; **C)** plasticized starch/PVOH with boric acid; **D)** starch/PVOH (50/50) 2wt.% fiber loading; **E)** starch/PVOH (50/50) 4 wt.% fiber loading; **F)** starch/PVOH (50/50) with 7 wt.% fiber loading; **G)** starch/PVOH (65/35) with 2 wt.% fiber loading; **H)** starch/PVOH (65/35) with 4 wt.% fiber loading and I) starch/PVOH (65/35) with 7 wt.% fiber loading

The addition of boric acid as a cross-linking agent produced a smoother surface, which signifies a stronger intermolecular bonding between starch and PVOH. The addition of particles such as clay and 2 wt% fiber produced a woven and orderly surface. Intercalation of clay was seen on the surface. This produced more surface area for the occurrence of more intermolecular bonding interactions between starch/PVOH/ and fiber. The addition of 4 wt% fiber produced a less regular surface where clay particles were not fully intercalated on the exterior of the blends. The blends reinforced with 7 wt% fiber show cracks on the surface. The cracks may be due to irregular distribution of fibers since 7 wt% may be too much for the starch/PVOH (50/50) and starch/PVOH (65/35) proportions. The clay particles are also seen not to be fully intercalated in the fiber surface.

This may mean that poor interactions occurred at 7 wt% fiber loaded starch/PVOH at 50/50 and 65/35 proportions.

DSC Analysis

Tables 4 and 5 generally provide information on the physical bonding of the blends. From the extrapolation and calculations done, the enthalpy of melting (ΔH_m) and the theoretical enthalpy of melting (ΔH_{mi}) provide an idea of the interactions occurring among the components of the composite blends. These are as follows (Yee *et al.* 2011):

a) When the enthalpy of melting (ΔH_m) is larger than the theoretical enthalpy of melting (ΔH_{mi}), there is extra physical bonding between PVOH and starch. The blending interaction is strong and preferable.

b) When ΔH_m is lower than ΔH_{mi}, the interaction of PVOH with starch is limited. The blending interaction is considered weak.

All of the sample preparations, starch/PVOH (50/50) and starch/PVOH (65/35) formulations were compatible. There was a good blending between starch and PVOH, since the enthalpies of melting (ΔH_m) were higher than the theoretical enthalpies of melting (ΔH_{mi}).

Starch/PVOH (50/50)

Table 4 reveals the onset temperature when the composite begins to melt or recrystallize and the endpoint when the melting stage or recrystallization is complete. Due to the presence of more crystallites from the neat starch/PVOH to fiber-loaded starch/PVOH, the melting enthalpy (ΔH_m) was seen to increase with degree of crystallinity (X_c).

Table 4. DSC Summary From Thermogram of Starch/PVOH (50/50) Composite Blends

Composite Blends	Onset (ºC)	End - point (ºC)	ΔH_m (J/g)	ΔH_{mi} (J/g)	T_m (˚C)	X_c (%)
Starch/PVOH	29.99	182.40	105.58	39.85	95.64	1.73
Starch/PVOH with glycerol	44.22	254.70	196.97	74.34	143.20	3.23
Gelatinized starch/PVOH with boric acid	39.01	276.50	566.97	213.97	155.30	9.29
Composite blend loaded with 2 wt% fiber	42.38	276.00	466.39	176.01	156.50	7.64
Composite blend loaded with 4 wt% fiber	29.83	270.30	350.30	132.20	145.50	5.74
Composite blend loaded with 7 wt% fiber	38.02	270.30	344.41	129.90	153.20	5.65

It can be noticed that the neat starch/PVOH easily reached its melting peak (T_m) at 95.64 °C. This shows that additives such as glycerol, boric acid, clay, and fiber delayed the melting of the composite. Looking at the degree of crystallinity (X_c), neat and plasticized starch/PVOH had low values at 1.73% and 3.23%, which suggests amorphous and weaker composites. The boric acid cross-linked starch/PVOH and 2 wt% fiber-loaded

starch/PVOH samples had higher degree of crystallinity at 9.29 and 7.64, suggesting crystalline and stronger composites.

Starch/PVOH (65/35)

Table 5 reveals the onset temperature when each composite began to melt or recrystallize and the endpoint when the melting stage or recrystallization was complete. Due to the presence of more crystallites from the neat starch/PVOH to fiber-loaded starch/PVOH, the melting enthalpy (ΔH_m) was seen to increase with degree of crystallinity (X_c). It can be noticed that neat starch/PVOH had higher melting peak (T_m) at 143.1 for the starch/PVOH(65/35) proportion compared to starch/PVOH (50/50) proportion with a melting peak (T_m) at 95.6 °C.

This might be due to the increased amount of starch, where there were more crystalline portions that needed further heating before they melt. However, it can be seen that the neat starch/PVOH composite had the lowest degree of crystallinity (X_c) among all of the preparations. Peeking at the degree of crystallinity (X_c), the increase in the values from neat starch/PVOH, plasticized starch/PVOH, cross-linked starch/PVOH, and sayote fiber reinforced blends revealed that the additives caused a stronger bonding interaction betweed starch and PVOH. However, in the fiber-loaded samples, there was a decrease in the degree of crystallinity (X_c) for 4 wt% and 7 wt% loaded samples. Perhaps sayote fiber caused agglomeration due to poor dispersion in the matrix. The sayote fiber loading at 2 wt% had good dispersion in between polymer chains, which might have also prevented the re-crystallization or retrogradation of starch.

Table 5. DSC Summary from Thermogram of Starch/PVOH (65/35) Composite Blends

Composite Blends	Onset (°C)	End -point (°C)	ΔH_m (J/g)	ΔH_{mi} (J/g)	T_m (°C)	X_c (%)
Starch/PVOH	23.06	269.00	333.73	83.40	143.10	8.26
Starch/PVOH with glycerol	20.80	243.10	534.16	133.49	130.20	13.22
Gelatinized starch/PVOH with boric acid	23.83	243.60	980.39	245.00	132.30	24.28
Composite blend loaded with 2 wt% fiber	21.69	244.60	1309.21	327.17	131.50	32.42
Composite blend loaded with 4 wt% fiber	27.54	243.40	994.43	248.51	135.70	24.62
Composite blend loaded with 7 wt% fiber	20.34	243.30	759.12	189.70	132.20	18.79

It can also be noted in the DSC results that cross-linking had been effective with the addition of glycerol, boric acid, clay, and sayote fiber with the general increase in the T_m and X_c values from the neat starch/PVOH preparation. The addition of small amounts of particles created a three dimensional network of interconnected chains through hydrogen bonding interactions with the -OH groups in starch, PVOH, boric acid, clay, and fiber. The composite material, as evidenced by the X_c values are harder, rigid, and more crystalline, thus needing higher temperature to melt or broadening the endothermic peaks. Segmental mobility is restricted with the addition of components to PVOH, resulting in an increase in T_m (Ramaraj 2007). Looking at the X_c values, it can be seen that fiber loading at 2 wt% in all formulations resulted to higher values as compared to the neat starch/PVOH formulation. For the starch/PVOH (50/50) formulation, there was an increase in the values from 1.73 for to 7.64 and for the starch/PVOH (65/35) formulation, an increase from 8.26 to 32.4 was revealed. Thus, 2 wt% fiber loading resulted to a more thermally stable composite. The thermal stability of natural fiber reinforced biocomposites is directly related to the crystallinity of the matrix and reinforcements, because high crystallinity can improve the heat resistance (Nurazzi *et al.* 2021) .

TGA Analysis

The thermal degradation of the starch/PVOH samples is affected by the incorporation of plasticizing agents such as glycerol, cross-linking agents such as boric acid, and reinforcing fillers such as clay and sayote fibers. The first stage of thermal degradation is attributed to the loss of volatiles, H_2O, and glycerol in the range 75 to 200 °C. The second stage is due to the main degradation zone of starch and PVOH, which is due to the dehydration of hydroxyl groups and formation of low molecular weight unsaturated and aliphatic carbon species. The third stage is attributed to carbonization at 500 °C (Salgado *et al.* 2008).

Starch/PVOH (50/50)

Table 6 shows that neat starch/PVOH at 50:50 formulation, plasticized with glycerol, boric acid cross-linked, clay and sayote fiber loaded composite blends exhibited increasing value of the starting degradation temperature. This means that the addition of glycerol, boric acid, clay and sayote fiber to starch/PVOH caused the formation of stronger blends that delayed the degradation of the composite. The end of degradation attributed to carbonization shows that the degradation peak temperature was lowest for the neat starch/PVOH sample at 504.0 °C and highest for the glycerol plasticized sample. In the sayote fiber reinforced sample, 4 wt% fiber loading resulted to the highest degradation peak relative to the neat starch/PVOH. It can also be seen that the % weight loss for 2wt% and 4 wt% sayote fiber loading to starch/PVOH are very low at around 76 to 78%, which means that the carbonization of blends were delayed by fiber addition due to its reinforcing effect to starch/PVOH. In the same way, an increase in the end degradation peaks relative to neat starch/PVOH indicated thermal stability, since it would take higher temperature for the fiber reinforced composites to be carbonized. Thus, low % weight loss and higher degradation peaks is indicative of thermal stability. Looking at the Derivative Thermogravimetry (DTG) heating curves in Fig. 4, it can be noted that fiber loading shifted the end degradation peaks to the right, suggesting that the fiber-loaded composites were thermally stable.

Table 6. TGA Summary From Heating Curves of starch/PVOH (50/50) Composite Blends

Composition	Degradation Peaks (ºC)			% Weight Loss at End Degradation Peak
	Start	*Mid Point*	*End*	
Starch/PVOH	286.9	364.7	504.0	85.12
Starch/PVOH with glycerol	291.7	363.1	595.5	91.15
Gelatinized starch/PVOH with boric acid	292.4	359.6	503.3	84.64
Composite blend loaded with 2 wt% fiber	299.2	354.2	515.5	**76.35**
Composite blend loaded with 4 wt% fiber	304.4	366.4	520.6	**77.83**
Composite blend loaded with 7 wt% fiber	300.5	356.2	580.2	94.08

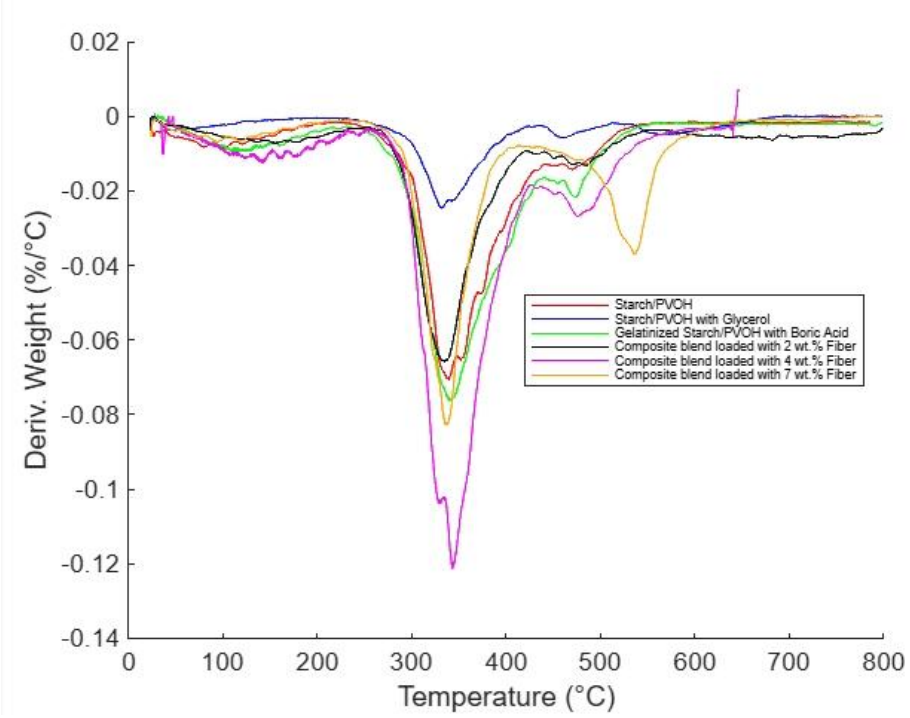

Fig. 4. DTG Heating Curves for starch/PVOH (50/50)

Starch/PVOH (65/35)

Table 7 shows that neat starch/PVOH, starch/PVOH plasticized with glycerol, and boric acid cross-linked, clay, and fiber loaded showed an increasing value of the starting degradation temperature. This means that the addition of glycerol, boric acid, clay, and sayote fiber to starch/PVOH caused the formation of stronger blends due to an increased hydrogen bonding interactions in starch/PVOH blends, resulting in delayed degradation of the composite. This is consistent with the result for starch/PVOH (50/50) formulation. The end of degradation attributed to carbonization shows that the degradation peak temperature was highest for 4 wt% sayote fiber-loaded starch/PVOH sample at 591.6 °C and lowest for the glycerol-plasticized sample. This means that 4 wt.% sayote fiber loading to

starch/PVOH resulted in better blending interaction and successful reinforcement of sayote fiber in the formulation. The % weight loss for 2 wt% to 4 wt% sayote fiber loaded composite blends were low at 90 to 91%. DTG curves in Fig. 5 show the end degradation peaks shifted to the right for 2 wt.% and 4 wt% sayote fiber loaded composite blends as compared to the neat starch/PVOH. Low % weight loss and increased degradation peaks is indicative of a thermally stable biocomposite attributed to the reinforcing effect of sayote fibers. Fiber loading might have provided more hydroxyl (-OH) groups, increasing the hydrogen bonding interactions between starch and PVOH thus needing an increased temperature to degrade.

Table 7. TGA Summary From Heating Curves of starch/PVOH (65/35) Composite Blends

Composition	Degradation Peaks (°C)			% Weight Loss at End Degradation Peak
	Start	*Mid Point*	*End*	
starch/PVOH	306.2	353.3	543.2	96.83
starch/PVOH with glycerol	309.9	354.0	504.3	90.29
Gelatinized starch/PVOH with boric acid	313.7	353.7	595.3	93.86
Composite blend loaded with 2 wt% fiber	302.6	356.3	590.6	**90.80**
Composite blend loaded with 4 wt% fiber	303.0	349.1	591.6	**90.59**
Composite blend loaded with 7 wt% fiber	303.8	356.3	504.2	94.63

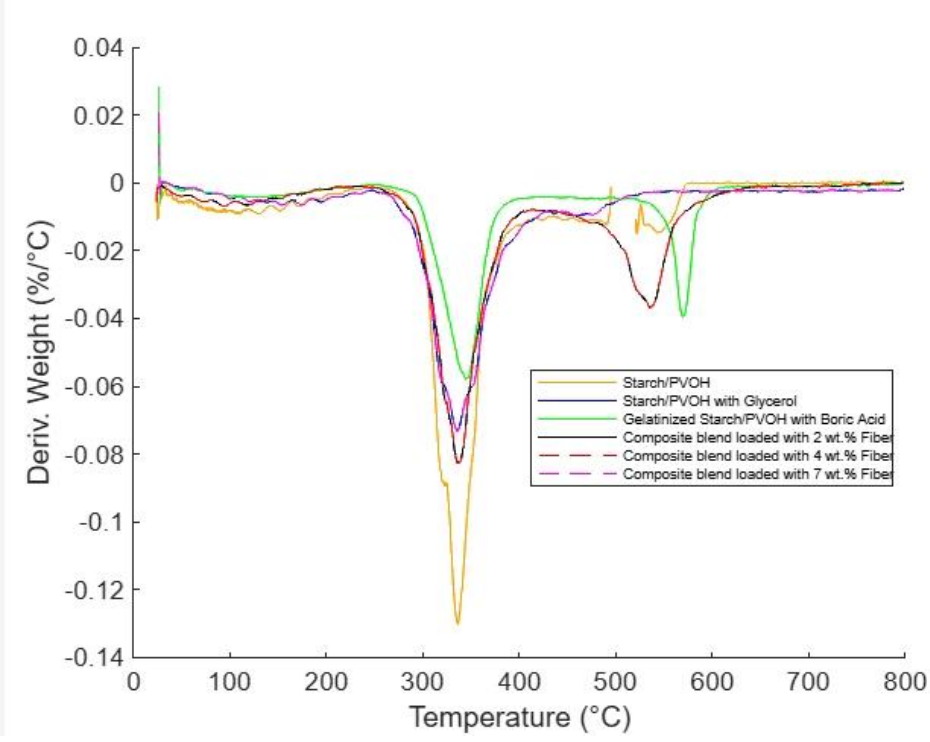

Fig. 5. DTG heating curves for starch/PVOH (65/35)

CONCLUSIONS

1. Fourier transform infrared (FTIR) analysis revealed that the addition of additives such as glycerol, boric acid, clay, and sayote fibers was effective in increasing the bonding interactions of starch/PVOH (50/50) composite blends. For starch/PVOH (65/35) composite blends, there was a weaker interaction between starch and PVOH but the addition of glycerol and 2 wt% sayote fiber reinforced the bonding interaction between starch and PVOH. However, at 7 wt% fiber loading, starch and PVOH interaction were weakened which may be due to higher bonding interactions among cellulosic fibers at higher wt%.
2. Scanning electron microscopy (SEM) revealed a smoother surface with the addition of boric acid as cross-linking agent in all samples. The addition of 2 wt% sayote fiber produced a more orderly, woven surface in both starch/PVOH (50/50) and starch/PVOH (65/35).

2. Differential scanning calorimetry (DSC) analysis showed that all sample preparations, including starch/PVOH (50/50) and starch/PVOH (65/35), were compatible and had a good blending interaction based on the melting enthalpy (ΔH_m), which was higher than their theoretical enthalpies of melting (ΔH_{mi}). However, comparing the formulations based on melting peak (T_m) and crystallinity (X_c), the incorporation of glycerol, boric acid, clay, and 2 wt.% to 4 wt% sayote fiber produced a stronger starch/PVOH (50/50) composite blend. The same observation was true for starch/PVOH (65/35) formulation at 2 wt% fiber loading, whereas fiber loading at 4 wt% and 7 wt% produced somewhat weaker blends. Generally, DSC results revealed better thermal stability of starch/PVOH loaded with 2 wt% to 4 wt% sayote fiber, as evidenced by an increased X_c when compared to neat starch/PVOH in all formulations.
3. Thermogravimetric analysis (TGA) revealed that the addition of glycerol as plasticizer, boric acid as cross-linking agent, clay and sayote fibers improved the thermal stability of the starch/PVOH composite blends by delaying the degradation of the composite in all formulations. For starch/PVOH (50/50) and starch PVOH (65/35), 2 wt% to 4 wt% fiber loading is recommended due to a general increase in the end degradation peaks and lower % weight loss as compared to that of the neat starch/PVOH composite blends. Derivative thermogravimetry (DTG) curves also show that sayote fiber loading shifted the degradation peaks to a higher temperature.

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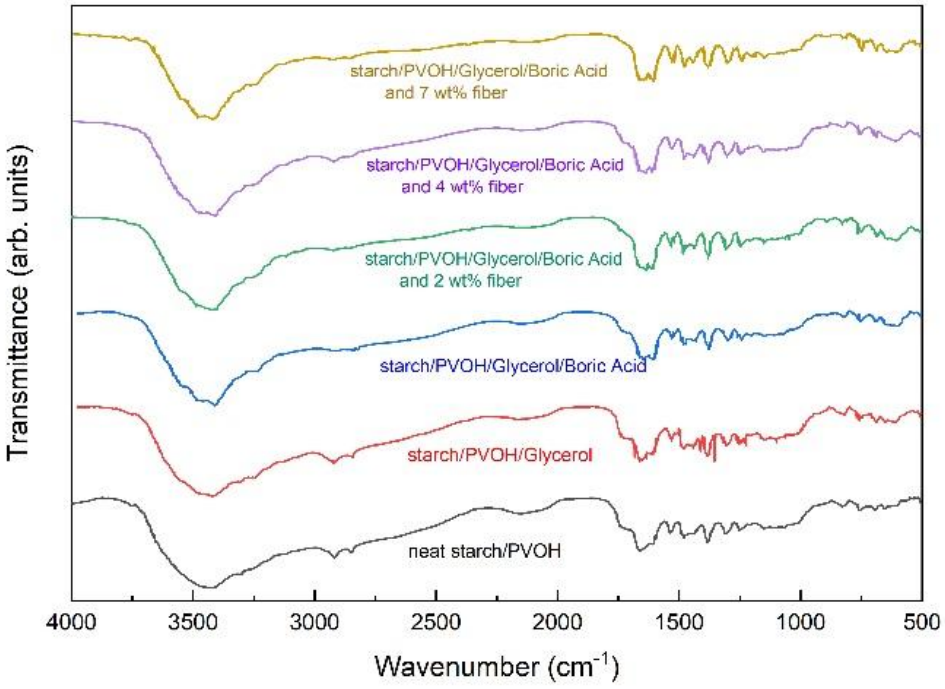
DOI: 10.15376/biores.20.2.4096-4114

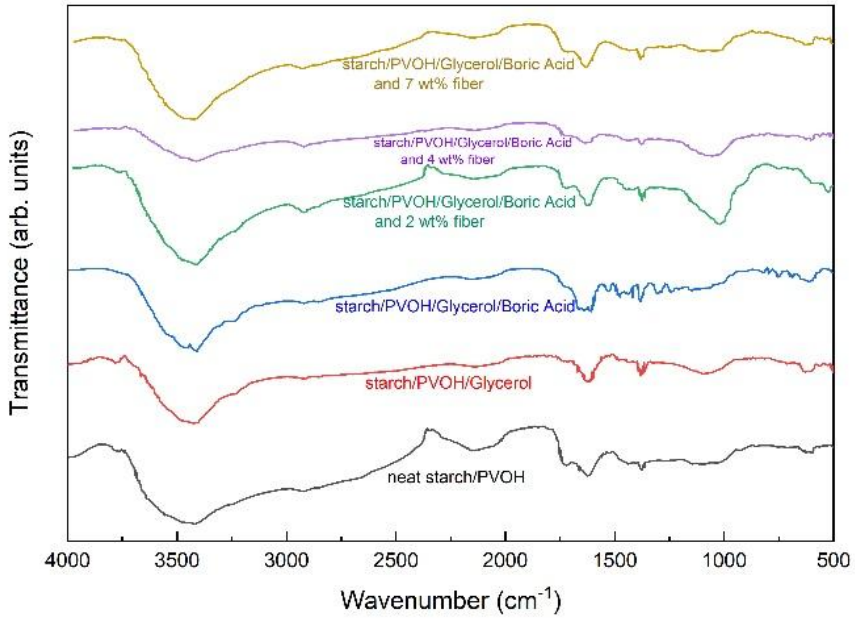
APPENDIX

FTIR Spectra for Composite Blends

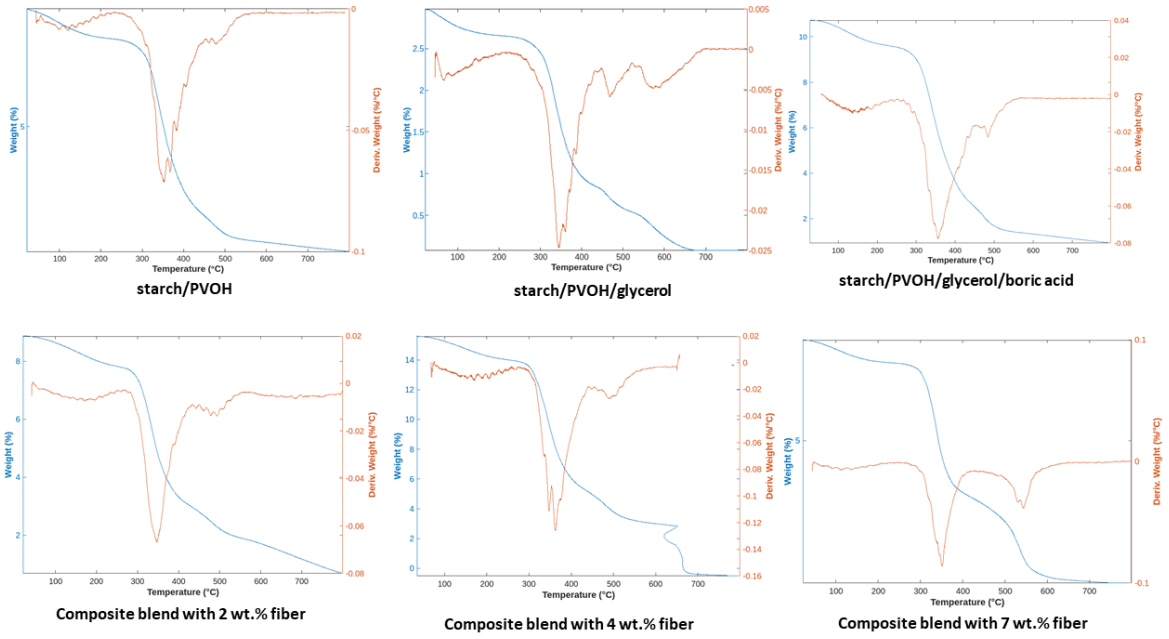
starch/PVOH (50/50)



Starch/PVOH (65/35)



TGA and DTGA Heating Curves for starch/PVOH (50/50)



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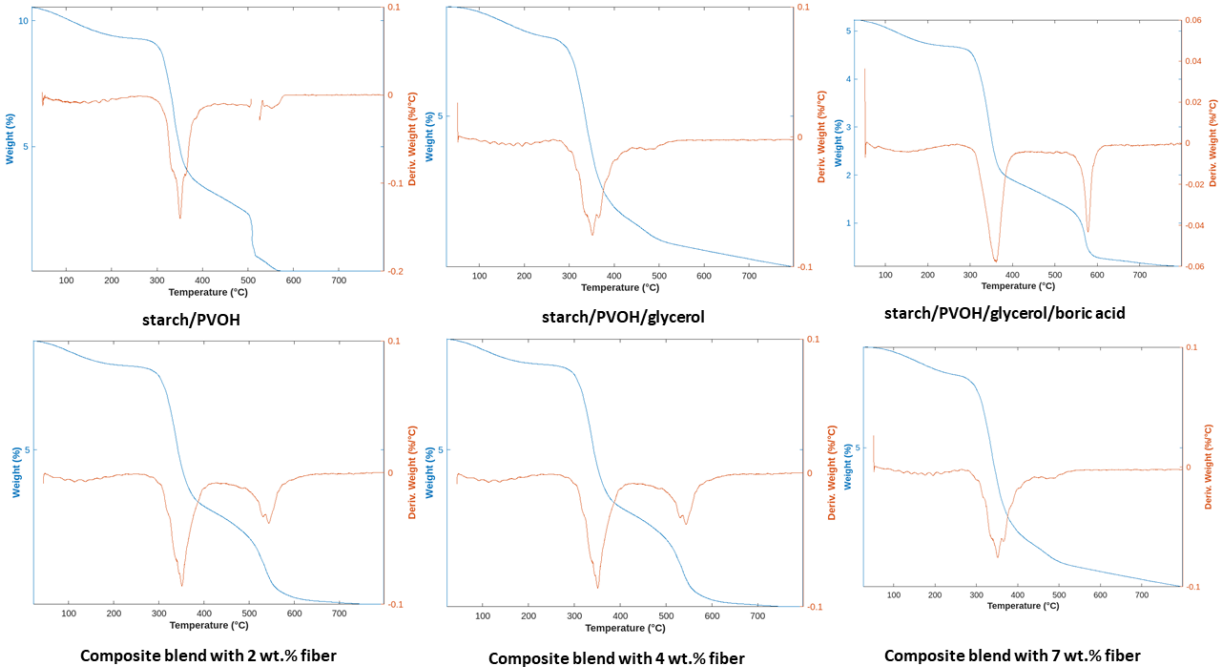
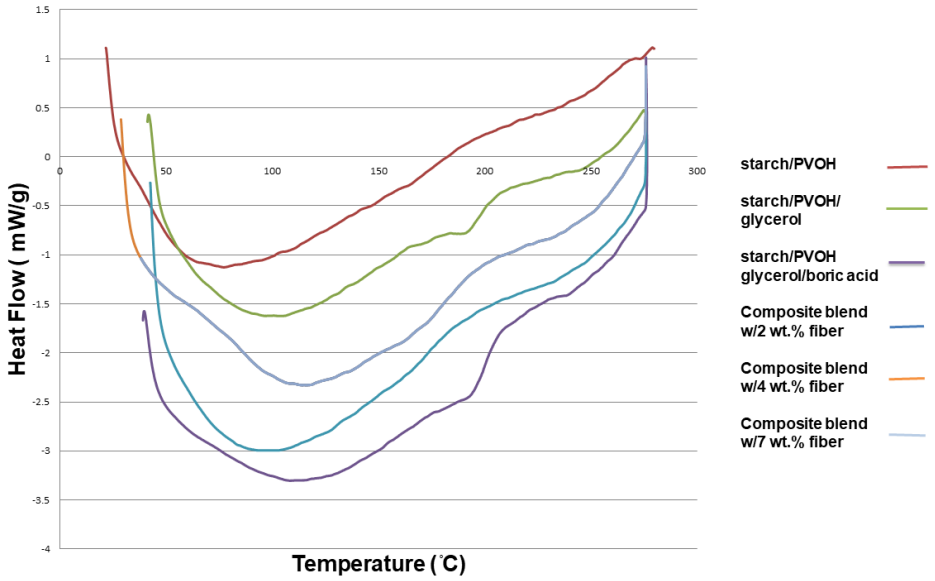


DSC Thermograms for starch/PVOH (50/50)



DSC Thermograms for starch/PVOH (65/35)