



## Thermal Stability of PALF-PP and PALF-PLA for Natural Fiber Honeycomb Core Materials

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### ABSTRACT

This paper studied the thermal behaviour of pineapple leaf fiber (PALF) reinforced with polypropylene (PP) and polylactic acid (PLA) composite, used for natural fiber honeycomb core. Thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) analysis were used to measure the thermal characteristic of PALF-PP/PLA composites. In particular, the TGA analysis was utilized to measure the degradation and decomposition of materials in different composition (NF-PP/PLA (0%, 15%, 30% and 50%). The measurements were carried out in the temperature of 0°C-900°C, at a heating rate of 10°Cmin<sup>-1</sup> and under an inert atmosphere (nitrogen gas). The temperature of DSC analysis was programmed to between 25°C- 500°C. The result shows the thermal stability of PALF-PP/PLA decreased as the PALF filler-loading increased. While from the DSC analysis this study clearly shows in the graph plot, the sample have glass transition temperature, crystallization and melting temperature. So that means the sample in this study is crystalline and amorphous domains.

## 1. Introduction

Thermal stability provides the ability of material to endure machining temperatures and preserve the chemical composition of the process fluid components [1]. Thermal stability sets an upper limit to the working temperature in cases where the suitability of a polymer is governed by chemical resistance to reactions that leading to the degradation of polymers in inert or oxidizing media [2]. Numerous scientific and industrial laboratories are regularly used thermal analysis techniques for learning the thermal decomposition of polymeric materials. Among them, the most popular techniques are thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis since the mass sample is easy and simple to measure accurately. Meaningful information relating to the nature of the process can be extracted from a mass loss against time or temperature plot [3].

Particularly TGA can be used to investigate the thermal stability for example strength of the material at given temperature, oxidative stabilities like oxygen absorption rate on the material and as well as the compositional properties as example like fillers, polymer resin, solvents of the samples.

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Generally, weight gain is attributed to the adsorption or oxidation, whereas weight loss is assigned to decomposition, desorption, dehydration, desolation or volatilization. The applications that use polymeric materials such as injection moulding, coating material for electrical and electronic components, paints, adhesive and many mores usually used TGA analysis [4].

Other type of thermal analysis is DSC analysis. Measure the energy absorbed or released by a material as a function of temperature when the material is heated or cooled is the responsibility of the DSC analysis. Quantitative and qualitative data on endothermic and exothermic processes could be produce in this analysis. From DSC analysis, the properties such as melting temperature, glass transition temperature, crystalline phase transition temperature, and specific heat or heat capacity could be acquired [5].

Since many volatiles are usually evolved and may influence the evolution of the reaction, the testing is very helpful in thermal degradation of polymers. Additionally, if experimental conditions are not cautiously controlled polymers usually have low thermal conductivity and heat transfer phenomena can play a significant role in thermal degradation [6].

In some previous studies, the degradation of natural fibre with TGA analysis has been research. The decomposition of natural fibres take place in two or three stages of material's loss weight under controlled temperature between 25°C to 800 °C [7-9]. It is important to notice that the different loss weight processes are dependent on the types and sources of natural fibres. The article from Aji *et al.*, [10] presents the thermal degradation behavior of hybridized kenaf (bast)/pineapple leaf fibre (PALF) reinforced high density polyethylene (HDPE) composites. The reduction in thermal stability of the hybrid with increase in fiber loading become obvious after dehydration process. So, it concludes that decomposition of hybrid composite is directly proportional to increase in fiber loading. Adli *et al.*, [11] studied the biopolymer which is polylactic acid (PLA) as a substitution conventional plastic into the biodegradable polymer in the packaging industry. PLA already known as slow degradation rate and brittleness limit its application. Therefore, the research aims to overcome the limitation of PLA by using algae as a filler to lower the cost and increase degradation rate also epoxidase palm oil (EPO) as plasticizer to increase the flexibility. Mat-Shayuti *et al.*, [12] reported in their studied thermogravimetric analysis (TGA) showed improved thermal degradation temperature of Polypropylene/Polycarbonate/Polypropylene-Graft-Maleic anhydride blends compared to pure PP.

For such instance, Threepopnatkul *et al.*, [13] presented TG curves (no conditions given) for pineapple leaf fibre (PALF) as well as polycarbonate (PC) and related composites reinforced with up to 20 wt% of both alkali and saline treated PALF. It was remarked, without quantitative parameters, that the PALF has the lowest, while the PC the highest thermal stability with all composites lying in between. The authors specified that the PALF composites pointed the onset for thermal degradation at lower temperature, approximately 270°C. It was then explained that composites have lower stability than the neat PC because of the low thermal stability of the PALF. Besides, the thermal behavior of pineapple leaf fibre (PALF) reinforced high impact polystyrene (HIPS) composite has been studied by Siregar *et al.*, [14]. From their study, the results from TGA analysis show that the addition of pineapple leaf fibre has improved the thermal stability of the composited as compared to neat HIPS. In other hand, Mothe *et al.*, [15] do the thermal properties of recycled polypropylene composites with vegetal leaves contents. They used 1%, 5%, 10% and 15% of vegetal leaves. The results revealed that the viscoelastic properties were influenced by fiber content. However, the glass transition ( $T_g$ ) of the composite did not show significant changes to the fiber content.

Therefore, this study will further evaluate the thermal stability of PALF-PP and PALF-PLA with different composition NF-PP/PLA (0%, 15%, 30% and 50%) and to determine the thermal stability of the PALF itself, which was used to fabricate the honeycomb core structure. The thermal evaluation was carried out through TGA under an inert atmosphere (nitrogen gas). As no similar study has been

conducted involving PALF-PP/PLA with different composition on the thermogravimetric behavior, the article presents the recent update on the thermal properties of PALF-PP and PALF-PLA composites under TGA and DSC analysis.

## 2. Materials and Methods

The extracted pineapple leaf fibers (PALF) from the leaves of *Ananas comosus* was used in the study (Figure 1). Prior to the mixing of PALF natural fiber with polypropylene and polylactic acid polymer, the material was crushed into powder. The mixing was conducted using a single screw extruder machine, Stand-alone extruder KE 19/25D Brabender GmbH & Co. KG.

The mixing of material was left overnight in an oven at 55°C, before undergoing compounding process. For the extrusion compounding process, the screw speed was set at 40 rpm. Table 1 shows the experimental conditions of compounding process.



**Fig. 1.** Extract of pineapple leaf fibers (PALF)

**Table 1**

Process parameters of compounding		
Material	PALF-PP	PALF-PLA
Mixing ratio (%)	15/30/50	
Screw speed (rpm)	40 rpm	
Temperature (°C)		
Feed zone	175	170
Melting zone	195	190
Metering zone	195	190
Die	190	185

Eight samples were prepared at 0%, 15%, 30% and 50% wt. fiber loadings mixing of PALF-PP and PLAF-PLA accordingly, weighted between 10 mg and 15 mg. Thermal evaluation was conducted through TGA under an inert atmosphere of nitrogen gas at heating rate of 10°C/min from 0°C to 800°C. TGA analysis was conducted on an instrument referred to as a thermogravimetric analyzer, with the mass is continuously measured as the temperature of a sample is progressively changed over time.

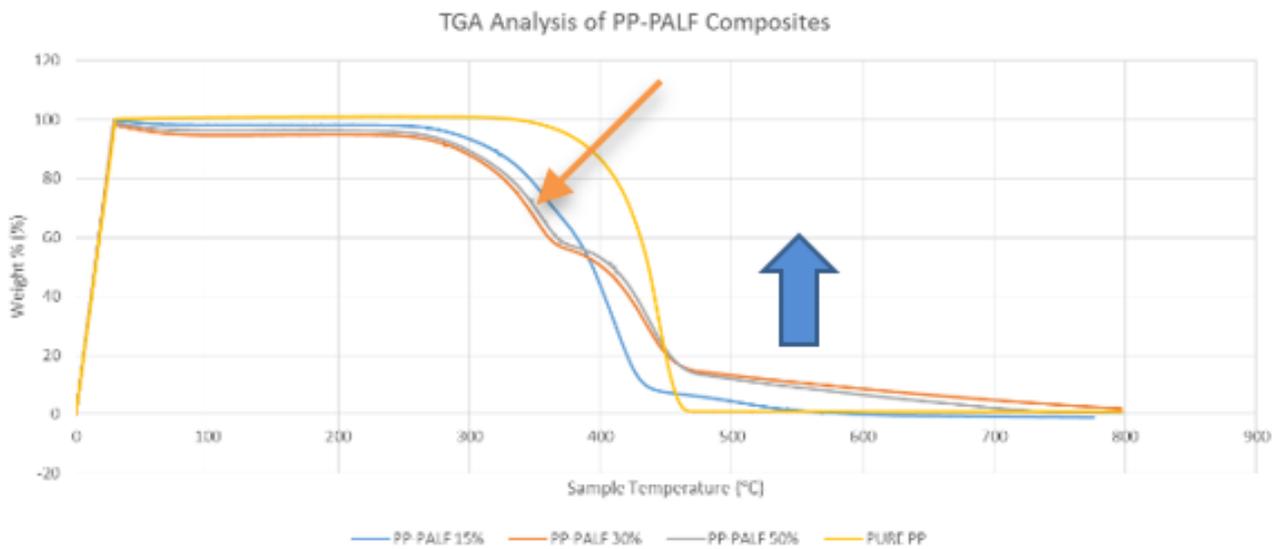
While in DSC analysis, the heating range was set from 20°C to 800°C at heating rate of 10°C/min. DSC analysis was conducted using differential scanning calorimeter. A small amount of samples (1-

15mg) was held within a closed crucible and set into a temperature-controlled DSC cell. A second crucible without samples was used as a reference. A normal DSC run require heating/cooling the sample at a controlled steady rate. The heat flow was continuously monitored to characterize the phase transitions and also cure reactions as a function of temperature.

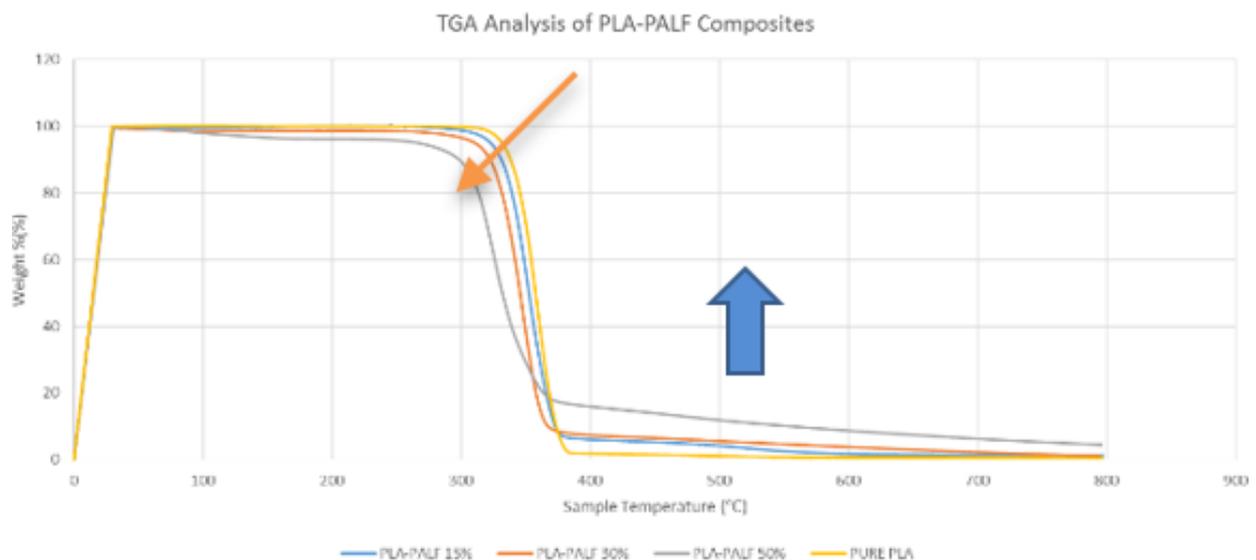
### 3. Result and Discussion

#### 3.1 Thermal degradation by Thermogravimetric Analysis (TGA)

Figure 2 and Figure 3 shows the TGA profiles of PALF-PP and PALF-PLA, respectively at 0%, 15%, 30% and 50% wt. loadings. All composites displayed corresponding pattern even with different percentages of filler loading in the thermal degradation profile.



**Fig. 2.** TGA analysis of PALF-PP



**Fig. 3.** TGA analysis of PALF-PLA

It was observed that the composite has burned faster as the percentage of PALF filler loading increased. The blue arrow indicates the increasing ash content and the orange arrow shows higher loading burns at lower temperature. There was noticeable difference between the PP-PALF (Figure 2) composites; 0% PALF-PP has started to drop at 350°C, 15% PALF-PP has started to drop weight at 280°C while the composites at the highest 50% PALF loading began to lose weight at lower temperature of 250°C. The mass loss step for all the loading break off at temperature 440°C and the composites started to burn and turn into ash.

On the other hand, in Figure 3, weight drop of 0% PALF-PLA started at 320°C, 15% PALF-PLA started at 310°C while the 50% PALF-PLA composite has started to reduce weight at 280°C. The mass loss step for all the material percentage ended at 360°C with the composites started to burn and turn into ash.

The blue arrow in the figures indicated the temperature range after the mass loss step, with higher PALF loadings produced higher ash contents. These results verified as the PALF filler loading increased, the thermal stability of the composites reduced.

### 3.2 Differential Scanning Calorimetry (DSC) Analysis

Compared to TGA analysis, DSC analysis was a bit different. DSC analysis measures the exothermic and endothermic responses of the polymer as it is heated/cooled through thermal transitions. Exothermic reaction occurred when heat was dissipated from the samples during the analysis. On the other hand, the endothermic reaction ensued when heat was absorbed by the sample (e.g. melting) [16].

#### 3.2.1 Glass transition temperature

When the sample is heated, a sudden temperature shift is observed in the plot as shown in Figure 4. It indicates that the sample is getting more heat flow over the time.

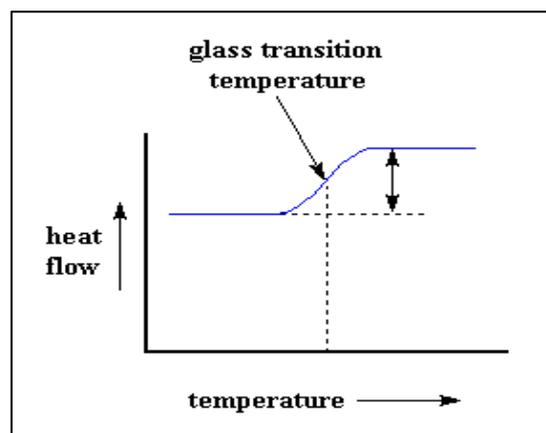


Fig. 4. Glass transition temperature ( $T_g$ ) [11]

This come up because the sample has experienced the glass transition ( $T_g$ ) phase. A glass transition ( $T_g$ ) is the temperature at which a sample turns from a ductile material to a hard, brittle material. This phenomenon has been observed in the DCS results for the tested samples, as indicated by red arrow in Figure 5 and Figure 6. In addition, Table 2 summarizes the  $T_g$  of the PALF-PP and PALF-PLA composites.

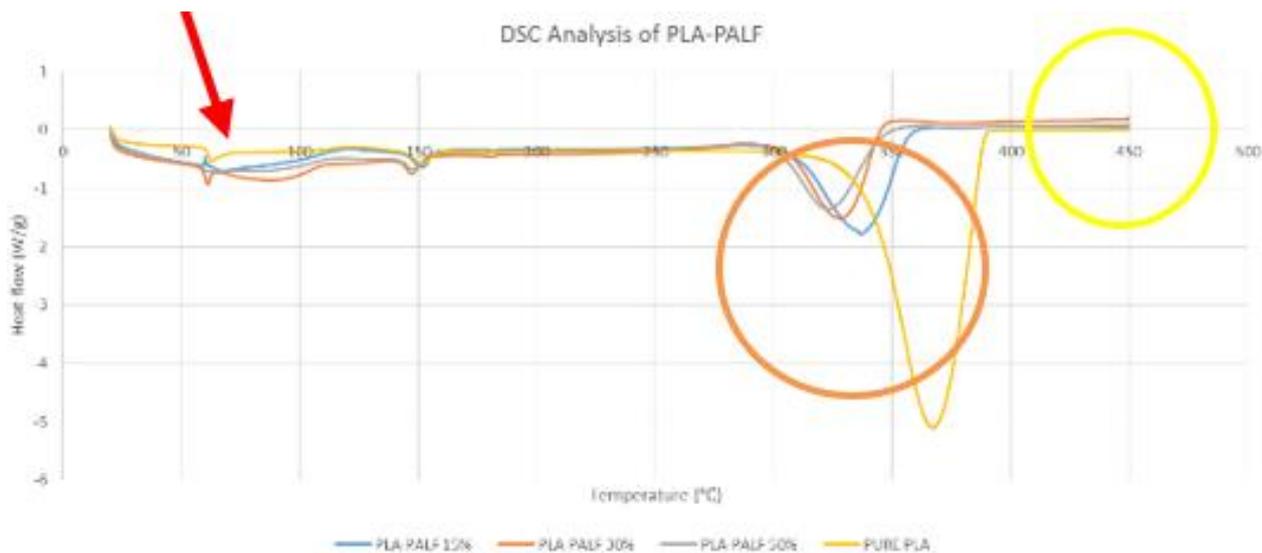


Fig. 5. DSC analysis of PALF-PLA

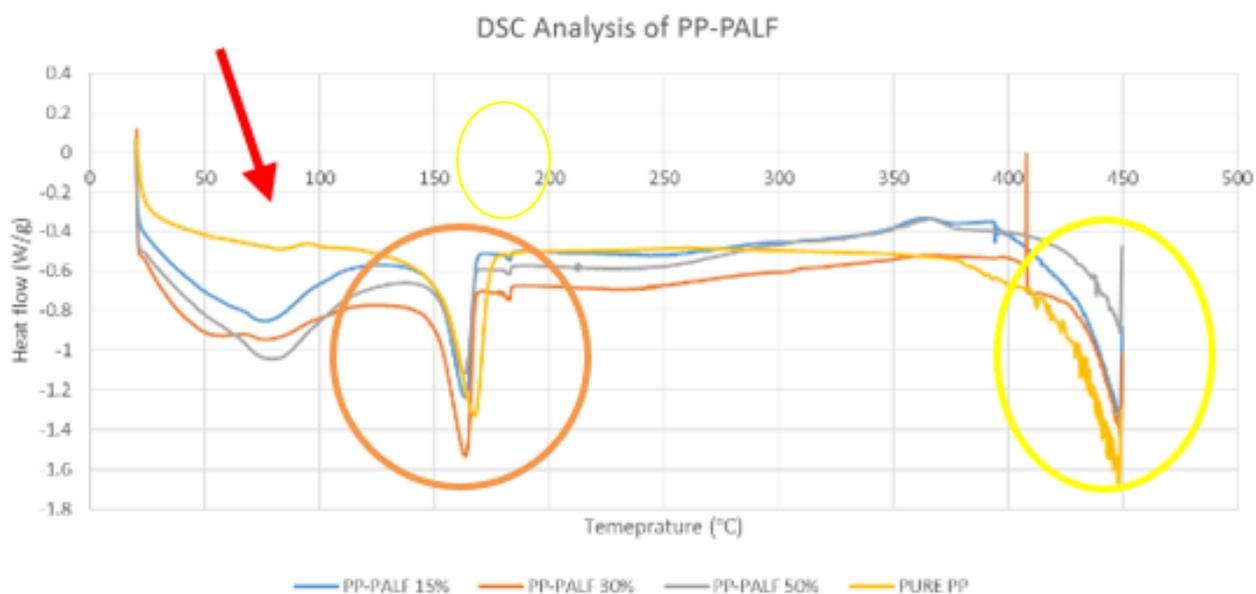


Fig. 6. DSC analysis of PALF-PP

**Table 2**

$T_g$  of the PALF-PP and PALF-PLA composites

Material	Filler %	$T_g$ °C
PALF-PLA	0%	130
	15%	120
	30%	110
	50%	100
PALF-PP	0%	95
	15%	90
	30%	85
	50%	80

### 3.2.2 Crystallization

Crystallization occurs when the materials reach a certain temperature, as enough energy is gained to change into very ordered arrangements. The heat off when polymers drop into these crystalline arrangements. This reflects in the drop of heat flow as a big dip in the plot, indicated by the orange circle in Figure 5 and Figure 6. The material doesn't have to set out much heat to make the sample temperature remain rising. The polymer's crystallization temperature ( $T_c$ ) usually indicates the lowest point of the dip. This is shown in Figure 7. Most importantly, this dip explains that the polymer can in fact undergoing crystallization. In addition, as the tested polymers release heat at this phase, the exothermic transition has been observed. Table 3 summarizes the  $T_c$  of the PALF-PP and PALF-PLA composites.

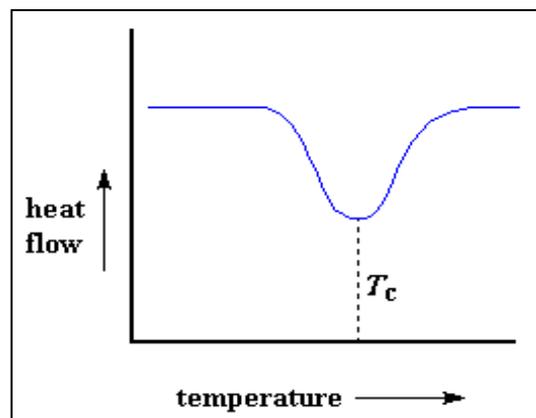


Fig. 7. Crystallization temperature ( $T_c$ ) [11]

**Table 3**

$T_c$  of the PALF-PP and PALF-PLA composites

Material	Filler %	$T_c$ °C
PALF-PLA	0%	370
	15%	340
	30%	330
	50%	320
	0%	170
PALF-PP	15%	160
	30%	158
	50%	157

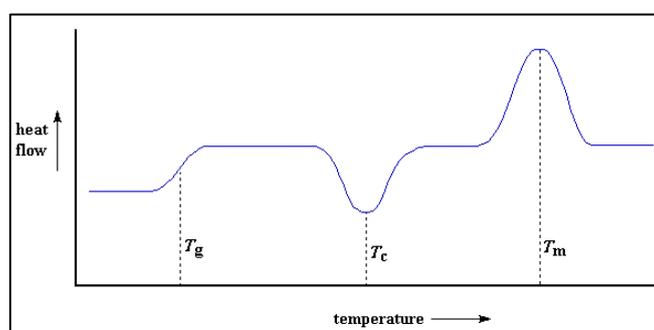
### 3.2.3 Melting

Heat may grant crystals to form in a polymer, but too much of it may nullify the properties. If heating is progressively applied to the polymer past its  $T_c$ , at some point we will achieve another thermal transition, known as melting. As the material reaches the melting temperature ( $T_m$ ), those polymer crystals will begin to fall apart, as melting takes place. The chains come out of their ordered arrangements, and start to move around freely as you can see in Figure 5 and Figure 6 (yellow circle). Furthermore, Table 4 summarizes the  $T_m$  of the PALF-PP and PALF-PL3A composites.

**Table 4**  
 $T_m$  of the PALF-PP and PALF-PLA composites

Material	Filler %	$T_m$ °C
PALF-PLA	0%	450
	15%	450
	30%	450
	50%	450
	0%	450
PALF-PP	15%	450
	30%	450
	50%	450

Putting together all steps in a plot we will see a super dip when the polymer reached its crystallization temperature as the polymer was heated past its glass transition temperature. Subsequently, apparent peak was observed when the polymer reached its melting temperature. Figure 8 summarizes the main occurrences during the DCS analysis of polymer composites.



**Fig. 8.** The entire DSC plot [11]

If we look at the DSC plot, a huge contrast was observed between the glass transition and the other two thermal transitions; crystallization and melting. At the glass transition phase, there was neither temperature dip nor temperature peak observed. This was attributed to the absence of latent heat release/absorbed by the polymer during the phase. But both crystallization and melting phases involve releasing or absorbing the heat during the processes. So, the only thing we do see at the glass transition stage is a change in the heat capacity of the polymer. From the data analysis of DSC in this study (Figure 5 and Figure 6), the testing graphs matched with the theoretical DSC plot, as in Figure 8. Therefore, the tested samples of PLAF-PP and PLAF-PLA polymer composites exhibit crystalline and amorphous domains. This is because a complete amorphous polymer would not demonstrate any crystallization or melting process either.

#### 4. Conclusions

The thermal stability of polymer composites of PLAF-PP and PLAF-PLA at different filler loading percentages has been characterized using TGA and DCS testing. From the analysis data of TGA and DSC, it can conclude that the thermal stability of PALF-PP/PLA polymer composites decreased as the PALF filler-loading was increased.

The TGA analysis indicated that 15% PALF-PP composite started to lose weight at 280°C while the 50% PALF filled composites showed mass reduction at a lower temperature of 250°C. The mass loss step for all the loading ended at temperature 440°C with the composites began to burn and turn into ash. On the other hand, the mass of 15% PALF-PLA started to degrade at 310°C and while the

composites filled with the highest percentage of 50% PALF started to lose weight at a lower temperature of 280°C. The mass loss step for all PALF-PLA ended at temperature 360°C and subsequently the materials were burnt and turned into ash.

The DCS data analysis presented the graph plot that matched with the theoretical DSC plot. The results indicated that the tested samples of PLAF-PP and PLAF-PLA polymer composites exhibit crystalline and amorphous domains.

Conclusion, TGA analysis is one of the thermal stability and decomposition of polymeric materials play a reliable technique that can be applied to study. It determines whereas the material is being heated or cooled at a controlled temperature, the rate weight of the material will change. By mixing with other techniques such as DSC analysis, the instruments manufactures have improved the fundamental design of TGA instruments. The combination of these techniques can shorten the experiment duration as it utilizes different analysis principle during a single measurement.

In the future, this study will analyse polymer composites of PLAF-PP and PLAF-PLA at different filler loading percentages and adding some additive in improving the mechanical properties and also thermal stability.

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