The thermal degradation effect on Thermoplastic Starch (TPS) / Montmorillonite nano-clay (MMT) / Alumina Trihydrate (ATH) nanocomposites

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Abstract

In the chase of enhance performance and characteristics of polymers in terms of thermal degradation, one of the answer is introducing nanoclay and flame-retardant component to produce nanocomposites. Although cross-linking is a common approach to enhance the properties of starch films, current starch cross-linking methods are either expensive, toxic or did not offer desired properties. In this research, TPS based nanocomposites is prepared using ATH and MMT by solution casting method with citric acid (CA) as cross-linking agent. The mechanical disadvantage of TPS can be improved by introducing MMT and ATH whereas ATH is capable to reduce thermal decomposition and acts as fire retardant in polymer. This study aims at determining the effect of thermal degradation of TPS/MMT/ATH blends. Moreover, the combined interaction between the nano-clay, ATH and CA component in weight loss of thermoplastic starch are analysed using a Design of Experiment approach. The prepared nanocomposites are characterized through Differential Scanning Calorimetry (DSC) and method of Weight Loss at Different Temperature is introduced to determine thermal properties and weight loss of blends, respectively. In addition, the formation of crosslinking networks in polymer matrix could enhance the thermal stability when CA is used. Meanwhile, high loading level of ATH will result of better thermal stability effect as the weight loss % reduces. However, MMT offer the optimum thermal stability at medium loading level given that it delays the thermal decomposition temperature and also increases formation of the char residue which is able to slow down the combustion process. Consequently, nanocomposite has result an overall improvement in terms of thermal stability thus presenting new class of biodegradable and environmental acceptable material.

Keywords: Nanoclay, Nanocomposite, Citric Acid, Thermal Degradation, Cassava Starch.

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1. Introduction

In recent years, synthetic polymers are produced from petrochemicals and are non-biodegradable. These polymers are the origin of environmental pollution, endangering human-welfare and wildlife when implemented into nature. Apart from this, plastics also play a role in waste management where the society responsible with large amount of waste discharging expenses. To overcome this drawback, by introducing biodegradable polymers would be another alternative way to overcome restriction of the petrochemical resources in the future. There are some abundant biodegrable polymers that originates from biomass, micro-organisms, biotechnology and petrochemicals such as chitin, protein, polyhydroxyalkanotes as well as poly(lactic acid)[1].

Starch is economically competitive with polymers originated from petroleum manufactured packaging materials since starch can be biodegrade in soil and water entirely and it is rather low cost. Starch is comprised of repeating α-D-glucopyranosyl units which include of a mixture of a linear polysaccharide-amylose and a highly branched polysaccharide-amylopectin. Unfortunately, starch has poor mechanical properties, brittle, sensitive to environmental humidity and difficulty in processing when compared with synthetic polymers since they have the nature of hydrophilic. Besides, starch exists in granular form where the molecular order within the granules must be destroyed to enhance its processeability [2]. Cassava starch is chosen for research since cassava starch or commonly named as tapioca starch is widely cultivated and commercialized in Malaysia due to sufficient availability and this type of starch is proven to be highly effective for TPS production [3].

Native starch can be converted into thermoplastic materials via addition of plasticisers (e.g. glycerol) under high temperature and extensive shear stress conditions, which results in the gel like material which is thermoplastic starch (TPS). Hence, plasticiser is used to modify properties of polymer matrix by heating polymer and mixed well with plasticiser in order to ensure resin is completely dispersed in plasticiser. At the meantime, it opens up free volume between molecular chains as well as molecular mobility of polymers [4]. Glycerol is the most common used plasticiser when blended with cassava starch that could increase the molecular mobility of glucan chain which indirectly enhance starch characteristics for this promising bio-polymer based film formulation [5].

The mechanical weakness of TPS can be ameliorate by introducing inorganic reinforcing material, nanoclay or more specifically known as Montmorillonite (MMT). Despite of these, MMT has nowadays arise as grand interest for science researchers due to its nature and low content could achieve favourable mechanical properties. Due to its large specific surface area, high swelling capacity, adsorption capacity, high cation exchange; hence, outstanding mechanical and its thermal resistance characters can be achieved [6]. Modification of natural clays using organic cations is taken place in order to favour dispersion of clay nanolayers within the polymer matrix to form organo-modified nanoclays. As Huang et al. [7] has been said that the mass loss of composites with 30wt% of MMT is 11.64% which is relatively lower than only glycerol plasticised TPS. Chang et al. [8] indicated that thermal stability of composite sample containing ATH and MMT performed better at higher temperature since MMT offer better barrier in EVA matrix.

The widespread synthetic polymer has raised the flammability of human's environment that accompanied by releasing of corrosive or toxic gases and smoke during combustion. Aluminum Trihydroxide (ATH) blends could improve fire retardancy of polymer. For physical action, endothermic decomposition of flame retardant additives will reduce the temperature by heat consumption. These additives is the reason to form protective solid or gaseous layer between the gaseous phases where combustion process occur [9]. Protective layer formed enable to restrict the transfer of substance such as oxygen and combustible volatile gases. Hence, the amount of decomposition gases released will reduce. ATH filler enhance the stiffness of the polymer matrix, heat resistance significantly as well as cut down the expenses of material [10]. It is also known as non-halogen flame retardants which is used to replaced halogen-flame retardants that would emit hazardous gases during combustion and reduce smoke emission [11]. Chang et al. [8] revealed that EVA/ATH/Organic MMT(OMMT) sample exhibited a two-stage weight loss. It is also realized that ATH enhances flame retardancy by delaying the oxidation of material, decomposition of material are non-combustible and eventually, EVA will be more stable.

In order to overcome hydrophilic and hygroscopic character of thermoplastic starch, barrier properties against both water vapour and liquid water is improved by cross-linking method [12]. Citric acid is selected because it is biodegradable and renewable since it can be obtained from fruit. Cross-linking starch with citric acid could enhance tensile strength, thermal stability and reduce dissolution of starch films in water. Several researchers reported that citric acid could form ester bond with starch, it enhance thermal and water stability to hinder retrogradation to occur [13]. The thermal degradation effect of starch films can be observed using thermogravimetric analyzer (TGA) where about 20% lower weight loss than the non-cross-linked films after heating the films to 600 °C which indicate better resistance to thermal degradation when citric acid used as cross-linking agent [14]. Citric acid is more favourable for starch cross-linking as low amount (5% or less) are needed for cross-linking reaction.

In this research, TPS based nanocomposites can be prepared using two different nano fillers: ATH and MMT via solution casting method. Sample preparation might be an intricate process; the interaction of the fillers may result in complex conclusions. Hence, a design method known as full factorial design is employed to interpret the data. Characterization of TPS nanocomposite takes place to investigate the properties of thermal stability by using Differential Scanning Calorimetry (DSC) and also applying method of Weight Loss at Different Temperature to determine thermal degradation as well as weight loss effect. This research is mainly focused on the thermal degradation of TPS/ATH/MMT composite with two major objectives as shown:

- To study the thermal degradation of TPS/MMT/ATH blends.
- To analyse the combined interaction between the nano-clay, ATH and citric acid component in weight loss of thermoplastic starch using Design of Experiment approach.

2.   Materials and methods

2.1   Design of Experiments

This approach required multiple runs of experiment to investigate the complete parameter space. The experimental design approach of factorial design is implement as valid method to compare and contrast factorial experiments to randomized controlled trials and maintain quality of data collection. In the research, a 3^3 full factorial is implement and thus, 27 runs of experiment is conducted with accompany of 2 controls for better research purpose. It is essential to determine the proper selection of factors and levels. In this research, three main factors: loading levels of MMT, ATH and citric acid are experimented in three levels (eg. low, medium, high) based on literature review on similar field of publications. One of two control samples is composed with nanocomposite of TPS and citric acid with no MMT and ATH as well as nanocomposite of TPS with no addition of ATH and citric acid. The loading level of MMT varied from 1 to 3wt.% [8][15], ATH varied from 14 to 18 wt.% [8][16], glycerol loading is fixed at 27 wt% (to be further discussed in Preliminary Test) whereas citric acid varied in the range from 1 to 5wt.% [13]. In order to perform detailed data analysis, Minitab17 is utilised for visual analysis which accommodates the best way to correspond with statistical data.

2.2   Materials

Regular cassava starch containing 17% amylose is kindly supplied by SCS Food Manufacturing Sdn. Bhd., Malaysia for preparation of Thermoplastic Starch (TPS). Citric acid ($C_6H_8O_7$) with 1.665g/cm^3 density and 99% purity is used as cross-linking agent for starch based material purchased from Evergreen Engineering Resources, Malaysia. Glycerol (about 99.8% purity) is used as plasticizer for TPS are obtained from Merck Sdn. Bhd., Malaysia. Treated Montmorillonite nanoclay (Nanolin DK® nanoclay) is purchased from FCC®, Inc., China. The Alumina Trihydrate, $Al_2O_3.3H_2O$ (ATH) with purity of 90% flame retardant was also purchased from Evergreen Engineering Resources, Malaysia and used as received.

2.3   Sample Preparation

2.3.1   Preliminary Test

The samples are prepared as shown in Table 1. The objective of conducting preliminary test is to determine the optimum loading level of glycerol as plasticizers to be added into the nanocomposites of TPS, MMT and ATH. Given there are no related published results regarding to the nanocomposite of TPS, MMT and ATH, it is necessary to conduct a preliminary test to determine the optimum processing weightage of glycerol in order to formulate optimum samples. The glycerol content is yet to be determined in this preliminary test and it is estimated by selecting the rangw of glycerol based on the percentage proportion to the starch which ranged about 40, 50 and 60 wt.%. To ease formulation of nanocomposite during preparation, loading level of each additive are represent in phr which imply for parts per hundred parts of resin. Literally mean 0.32phr of MMT corresponds to put in 0.32g of MMT nanoclay into a 10g of starch based polymer or resin. The formulation corresponding with dose rate of additives is shown in Table 1. As removing the nanocomposite films from the rectangular Teflon molds, it can be noticed that the physical appearance whether it is brittle or soft. In fact, if the film appeared to be brittle indicated that addition of glycerol is too less. In a contrary, excess addition of glycerol into the suspension will turn the film appeared to be soft. As a result, nanocomposite film appeared in best physical appearance, the loading level of glycerol is chosen to be utilized in the following sample preparation.

Table 1. Formulation of Preliminary Test

Experiment	Starch	Nano-clay	Alumina Trihydrate	Citric Acid	Glycerol
	phr	phr	phr	phr	phr
1	10.00	0.32	3.00	0.48	4.00
2	10.00	0.32	3.00	0.48	5.00
3	10.00	0.32	3.00	0.48	6.00

Note: Composition as shown in table above is represent by phr, where MMT loading of 1, 2 and 3 wt.% is equivalent to 0.16, 0.32 and 0.48 phr, ATH loading of 14, 16, and 18 wt.% is equivalent to 2.5, 3.0 and 3.5 phr, CA loading of 1, 3 and 5wt.% is equivalent to 0.16, 0.48 and 0.8 phr as well as glycerol loading of 23, 27 and 31 wt.% is equivalent to 40, 50 and 60 phr respectively.

2.3.2   Preparation of TPS/ MMT/ ATH Nanocomposites Film

Cassava starch/MMT/ATH composite films are prepared by solution casting technique. It is proven that TPS nanocomposite films prepared by solution casting method where transparent and homogenous appearance are formed without breaks, fractures, insoluble particles or bubbles [17]. Optimum loading level of glycerol and starch can be determined earlier during preliminary test. Then, 10g of cassava starch, powder form of MMT (0.16, 0.32 and 0.48phr), ATH (2.5, 3.0 and 3.5phr) and citric acid (0.16, 0.48 and 0.8 phr) are added simultaneously into the suspension of glycerol for dispersion. The suspension is then dissolved and dispersed in 400ml of distilled water and stirred with a glass rod until the all the particles are not clumped together. Then, the suspension is heated to 70°C and stirred under hot plate stirrer (SMHS-3 WiseStir) with appropriate speed (600rpm) for 1 hour to gelatinize the cassava starch

granules. The hot suspension is casted pour into rectangular Teflon molds and the cast film is dried overnight at 60°C in an air-circulating oven. After water completely evaporated, nanocomposite films are removed and conditioned according to requirements the of the characterization method followed. The obtained nanocomposites films are stored tightly in a sealed polyethylene zipper bags contained silica gels to avoid moisture absorption. The formulation of nanocomposite is shown in Table 2.

Table 2. Formulation of TPS/ MMT/ ATH nanocomposites film

Experiment	Starch	Nano-clay	Alumina Trihydrate	Citric Acid	Glycerol
	phr	phr	phr	phr	phr
1	10.00	0.16	2.50	0.16	5.00
2	10.00	0.32	2.50	0.16	5.00
3	10.00	0.48	2.50	0.16	5.00
4	10.00	0.16	2.50	0.48	5.00
5	10.00	0.32	2.50	0.48	5.00
6	10.00	0.48	2.50	0.48	5.00
7	10.00	0.16	2.50	0.80	5.00
8	10.00	0.32	2.50	0.80	5.00
9	10.00	0.48	2.50	0.80	5.00
10	10.00	0.16	3.00	0.16	5.00
11	10.00	0.32	3.00	0.16	5.00
12	10.00	0.48	3.00	0.16	5.00
13	10.00	0.16	3.00	0.48	5.00
14	10.00	0.32	3.00	0.48	5.00
15	10.00	0.48	3.00	0.48	5.00
16	10.00	0.16	3.00	0.80	5.00
17	10.00	0.32	3.00	0.80	5.00
18	10.00	0.48	3.00	0.80	5.00
19	10.00	0.16	3.50	0.16	5.00
20	10.00	0.32	3.50	0.16	5.00
21	10.00	0.48	3.50	0.16	5.00
22	10.00	0.16	3.50	0.48	5.00
23	10.00	0.32	3.50	0.48	5.00
24	10.00	0.48	3.50	0.48	5.00
25	10.00	0.16	3.50	0.80	5.00
26	10.00	0.32	3.50	0.80	5.00
27	10.00	0.48	3.50	0.80	5.00

Note: Composition in the table above represent in phr, where MMT loading of 1, 2 and 3 wt.% is equivalent to 0.16, 0.32 and 0.48 phr, ATH loading of 14, 16, and 18 wt.% is equivalent to 2.5, 3.0 and 3.5 phr, CA loading of 1, 3 and 5wt.% of CA is equivalent to 0.16, 0.48 and 0.8 phr as well as glycerol loading of 27 wt.% is equivalent to 50 phr.

2.4   Sample Characterization

2.4.1   *Differential Scanning Calorimetry (DSC) and crystallinity*

Differential scanning calorimetry (DSC) was performed using a differential scanning calorimeter (DSC 8500, Perkin Elmer) to study the thermal behaviour of nanocomposite films. Around 6 to 10mg of nanocomposite films were weighed into aluminium pans, sealed and then heated from 80℃ to 220℃ at 10℃ per minute under nitrogen flow of 20mLmin^{-1} and holding at 80℃ for 1 minute to remove moisture before heated to 220℃.

2.4.2   *Weight Loss at Different Temperature*

All the nanocomposite films are cut manually with a stainless steel scissor into small pieces about (1 ± 0.010g) and inserted into the universal bottles, in order to study the combined interaction between the TPS/MMT/ATH and citric acid in terms of weight loss effect. Samples that are not subjected to the procedure (drying and weighing) were store in a dessicator (silica gel). In each experiment, 87 samples (3 replicates) of nanocomposite film produce earlier during sample preparation were weighted using an electronic balance (M214Ai, BEL Engineering) with a range of 220g, linearity of ±0.003mg and readability to 0.0001g. Weighted samples are then placed into universal bottle and dried in the oven (Memmert, DO6836, Germany) for 1 week at 80°C. Then, the weight loss of samples was measured at the intervals of 2, 4, 8, 24, 72 and 168 hours treated at temperature of 80°C, 120°C and 200°C.

3.   Results and Discussion

3.1   Differential Scanning Calorimetry Test (DSC)

Fig. 1 to 4 show the DSC curves of the TPS/MMT/ATH blend nanocomposites where endothermal peaks were observed indicating melting state can be found at 170 to 190℃. However, the presence of glass transition state [1] (T_g) was not noticeable meanwhile an obvious exothermic peak indicating melting state can be found ranging from 130 to 190℃. In this paper, the extent melting state of DSC is the major factor or issue to be investigated since this will directly delivered that magnitude of intermolecular bonding in the nancomposite blend. It is also noticed that large peak area denotes more thermal energy is necessary to alter into kinetic energy to enable polymer molecules escape from the ordered crystalline structure [18]. It is expected that there is enhancement in the thermal stability by adding inorganic nanoparticles such as ATH and MMT would result to formation of barrier network and chars that inhibit transfer of volatile product and heat during degradation process [19].

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[1] Glass transition, Tg: temperature at which the transition in the amorphous regions between the glassy and rubbery state occured.
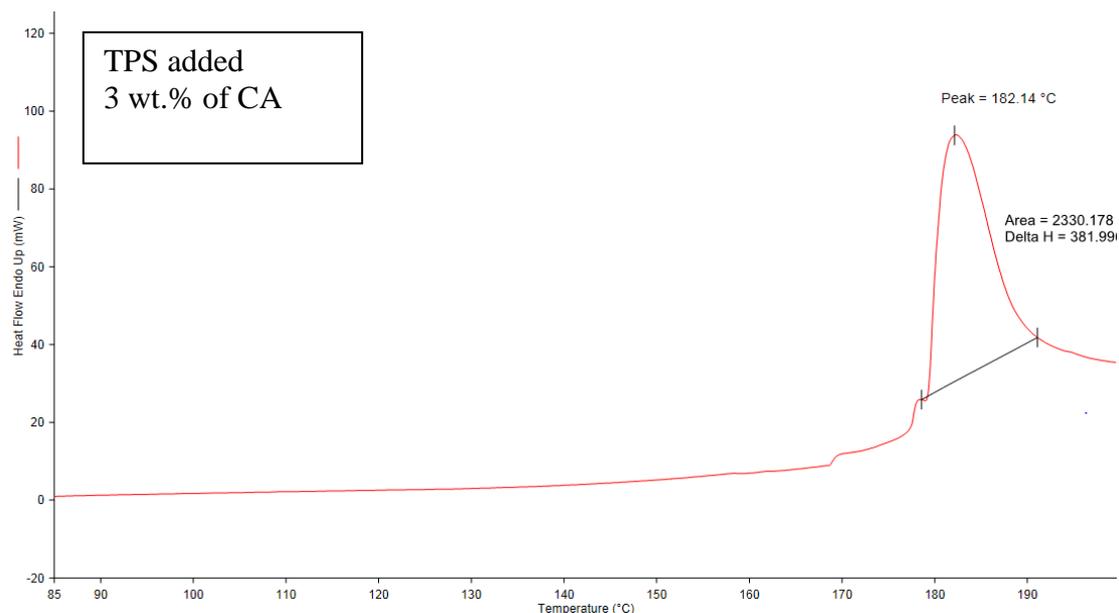
Figure 1. DSC Curve Of Cross-Linked Nanocomposite Film with 3 wt.% of
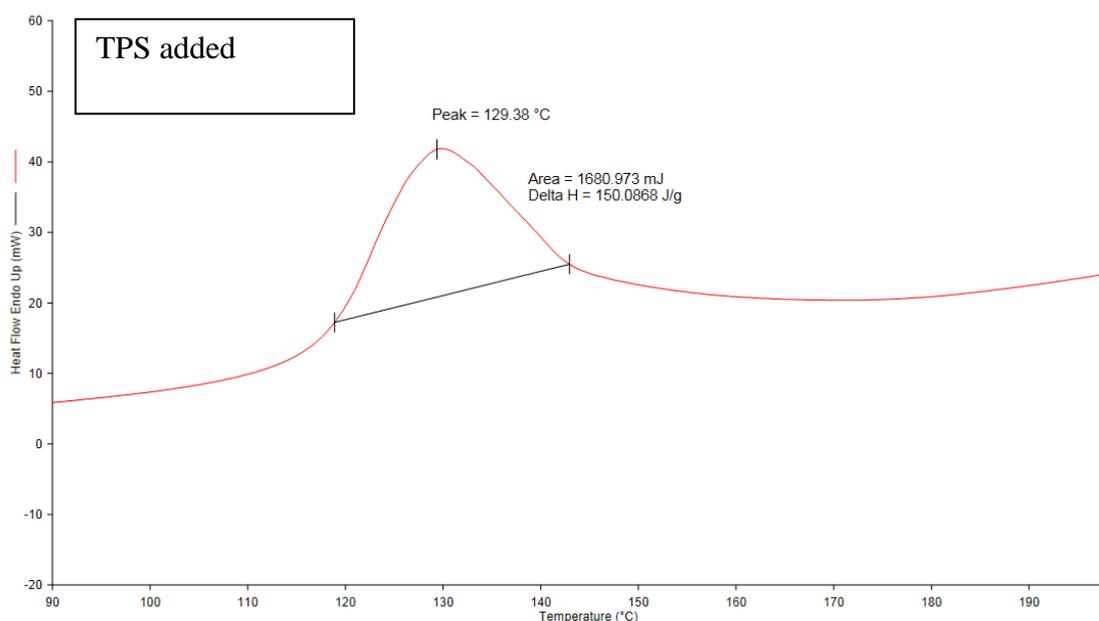Citric Acid

Figure 2. DSC Curve of Non-Cross-Linked Nannocomposite Film

The DSC curves of cross-linked and non-cross-linked film with 3wt.% of citric acid are shown in Fig. 1 and 2. The curve of the non-cross-linked film as shown in Fig. 2 show endothermic event that peaks at about 130℃ whereas the cross-linked film show 50℃ later than non-cross-linked film. This is due to citric acid formed ester bond with starch that able offer thermal stability enhancement [20]. Besides, the hydrophilic and hydroscopic characteristic of TPS also improved by cross-linking method that is done by citric acid. In spite of that, cross-linked film exhibit a broader peak area and fairly higher thermal stability (lower weight loss) compared to non-cross-linked film. Therefore, citric acid is more favourable for starch cross-linking as only low amount (5% or less) are needed for cross-linking reaction.
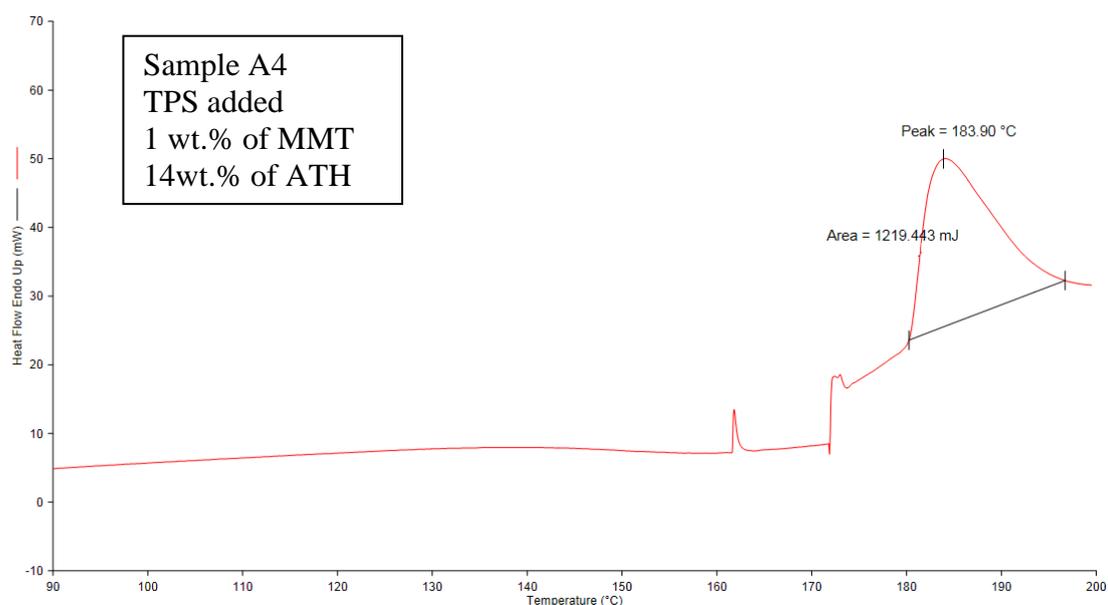
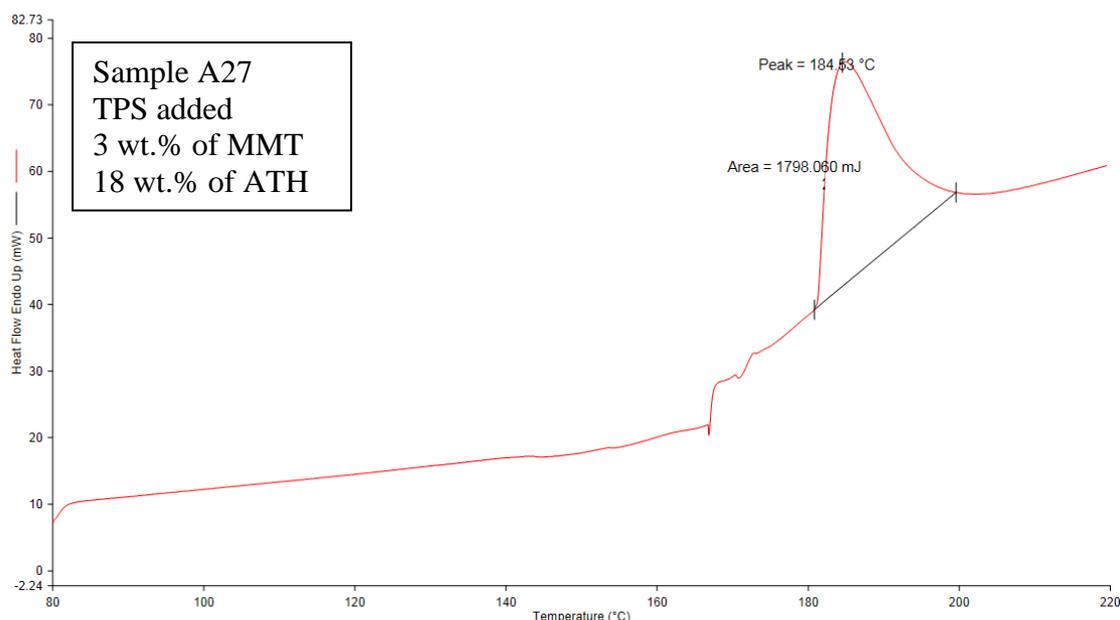Figure 3. DSC Curve of Nanocomposite Film of Sample A4.

Figure 4. DSC Curve of Nanocomposite Film of Sample A27.

From the Fig. 3 and 4, it is noted that most of the melting peak as well as melting peak are sharp and broad. Given the process of melting nanocomposite film did absorbed heat, hence melting is recognized as endothermic transition. As the melting temperature reached, the nanocomposte's temperature would not rise until all the crystals have completely melted. However, it is clearly observed from Fig. 4 that the temperature continue to rise after the melting temperature, T_m due to presence of MMT since the expected melting point of MMT is 1450℃ [21]. Hence, it could be further researched with the aid of Thermogravimetric Analysis (TGA) due to temperature limitation of DSC. Nevertheless, there is appearance of a small peak at 161℃ as shown in Fig. 3. This is might be due to imperfect blending of citric acid into the nanocomposite film given that the melting point of citric acid is about 160℃ [21].

Therefore, small peak appear indicated presence of small amount of citric acid in the film.

From Fig. 3 and 4, it could be observed that the T_m of nanocomposite peak rise from 183.90℃ to 184.53℃ when the ATH loading increased from low to high loading level (14 to 18 wt.%) as well as MMT loading increased from low to high loading level (1 to 3wt.%) too. The peak position changed mainly due to the endothermic decomposition of ATH that normally occurs between 180 to 200℃ and at the same time, it released water and ended up by formation of alumina as shown in equation below:

$$2Al(OH)_3(s) \rightarrow Al_2O_3(s) + 3H_2O(g) \quad \Delta H = +1.3kJg^{-1} \quad\quad\quad (eq\ 1)$$

During this endothermic decomposition, Boehmite, "ALOOH" is formed as intermediate product that mainly corresponding to the rather low endothermic energy [9]. This endothermic decomposition of ATH process is able to reduce the temperature by heat consumption. Hence, a protective layer formed that inhibited transfer of oxygen and combustible volatile gases which lead to reduction of corrosive or toxicity decomposition gases released. Similarly, the change of peak position also indicated that the MMT contents favour the formation of larger crystal domains and lowers down the mobility of polymer chains [22].

Besides, the melting area was comparatively larger at higher amount of MMT where it increase from 1219.443 to 1798.060mJ when the MMT loading level increase from 1 to 3wt.%. This exhibited that MMT actually cause effect on the formation of secondary bonding where two or more composite parts joined together during chemical or thermal reaction. Such phenomenon also observed by Tee et al.[18]. This deduce that there is increment of 19% of thermal energy that correspond to 1 to 3wt% of MMT loading level in order to transform into kinetic energy to enable polymer molecules escaped from the crystalline structure. This investigation inferred that introduction of MMT and ATH enhanced the thermal stability due to the presence of inorganic particles.

3.2   Weight Loss at Different Temperature

The combined interaction between the TPS/MMT/ATH nanocomposite in terms of weight loss effect were investigated by plotting out the weight loss % at different temperature with respect to loading level of ATH and MMT. When the samples exhibit low weight loss % literally means that the sample did not easily lose its weight corresponding to different thermal degradation temperature. In another word, this sample has better thermal stability effect given that the clay and flame retardant material acts as heat barrier that able to enhances the overall thermal stability of the nanocomposite. Besides, it was also noted that the samples ceased to be yellowish in colour after treated at high temperature or long periods of time that indicated changes in chemical composition and morphology. Fig. 5 and 6 show the weight loss % at different temperature corresponding to loading level of ATH and MMT.
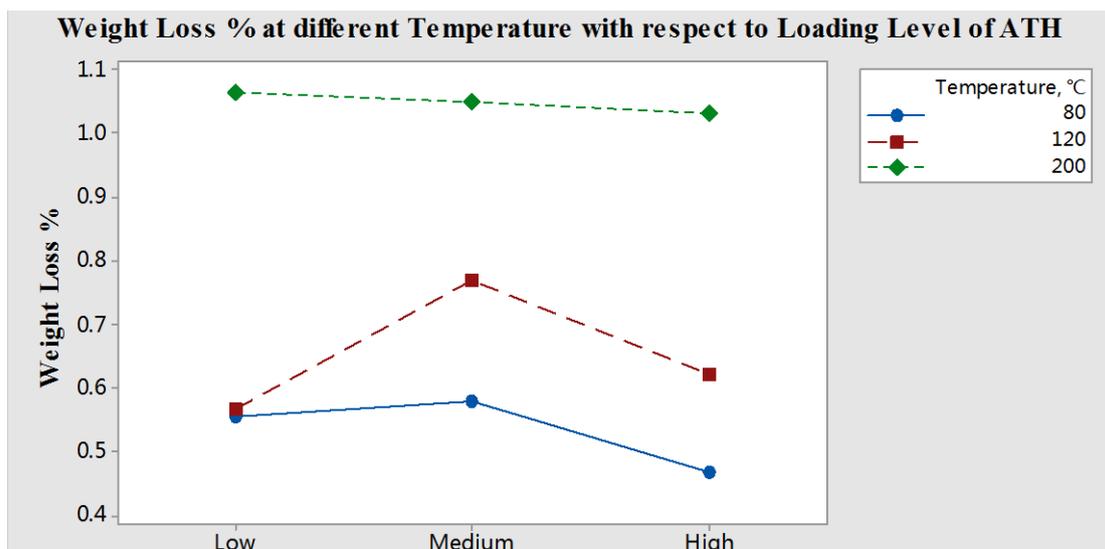
Figure 5. Weight Loss % at different Temperature with respect to Loading Level
of ATH

The weight loss effect of samples at different temperature corresponding to loading level of ATH is shown in Fig. 5. From the observation, this satisfy the hypothesis where high loading level of ATH will give better thermal stability effect or in another word, the weight loss effect decrease when the loading level of ATH is at high level which is approximately 18 wt.%. Furthermore, the weight loss % that corresponds to different loading level of ATH is rather low which only range about 1.065% to 0.468% weight loss %. However, the weight loss % between 80℃ and 120℃ is almost similar; this possibly due to water inside the sample started to evaporate out at 120℃ since water's boiling point at 100℃. At 200℃, weight loss % decrease when loading level of ATH increases which exhibit an inversely proportional relationship. ATH as flame retardant element could lead formation of carbonized or vitreous layer at the surface of polymer by chemical transformation of polymer chain degradation which indicates by the colour change of sample as mentioned earlier.

It exhibits a relatively high weight loss % which is approximately 0.578 weight loss % at medium loading level at 16 wt.% during thermal degradation temperature at 80℃. This is due to presence of MMT where it takes the major role at that moment. It is considered that burning nanocomposite with low content of ATH, the nanoclay in the nanocomposite would not be able to integrate perfectly with ATH to constitute a rigid insulation layer on the ablating surface and might shed away the melting element. In a contrary, MMT is able to blend with high loading of ATH in order to produce solid insulation barrier when exhibited at high temperature [23]. This in turn created a synergistic effect with flame retardants material and nancoclay in the nanocomposite blend.

Figure 6. Scatter Plot of Weight Loss % with respect to Starch Weight %.

Fig. 6 is plotted in order to determine the effect of starch weight % in the specific temperature at 80℃ and 120℃, given there is almost similar effect of weight loss as shown in Fig. 5. Moreover, it is shown that the weight loss % at 120℃ scatter around and the two main variables (starch weight % and weight loss %) did not have correlation where no apparent relationship shown between this two main variables. Therefore, starch did not make a major role for the effect of weight loss at this temperature. As mentioned earlier, it might be due to water evaporated out at 120℃ given water's boiling point occur at 100℃. However, weight loss % of 80℃ shows an increasing effect when the starch weight % increases due to the loss of moisture content as proposed by other authors who also able to demonstrate mass loss of cassava bagasse occurred at 30°C [26].
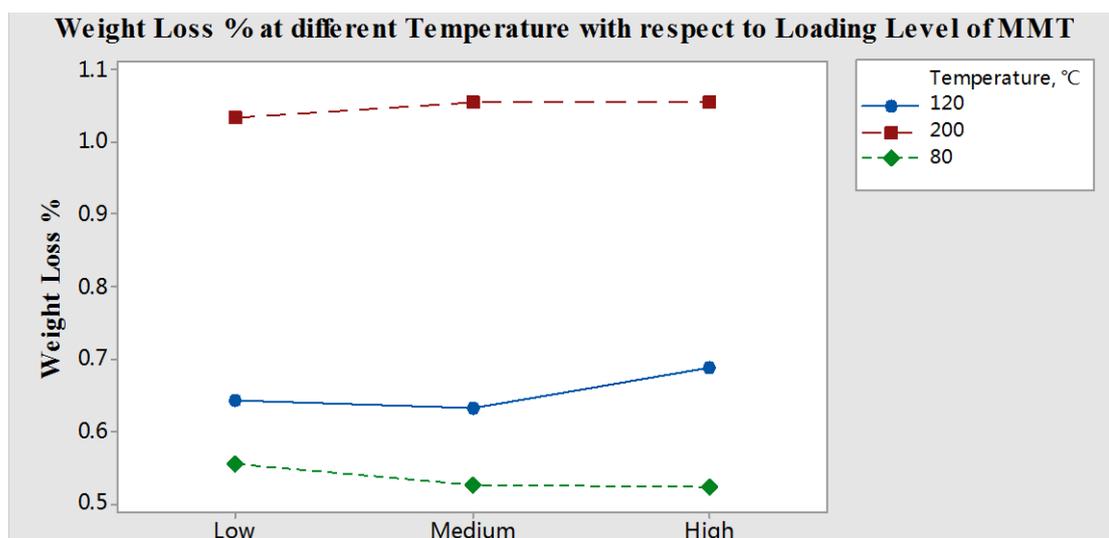

Figure 7. Weight Loss % at different Temperature with respect to Loading Level
of MMT

The weight loss effect of samples at different temperature corresponding to loading level of MMT is shown in Fig. 7. It could be observed from the line plots where the weight loss effect decrease when the loading level of MMT under medium

level which is approximately 2wt.%. In another word, it offers the optimum thermal stability at the medium level of MMT loading. Incorporation of MMT delays the thermal decomposition temperature, at the same time increases formation of the char residue that could delay the combustion process as well as improvement of mechanical properties [24]. An almost constant effect of weight loss % is shown at 200℃ which only offer difference of 0.02% of weight loss since MMT is expected to be decomposing at high temperature. However, a high loading of MMT (3%) offer a deterioration effect or literally means that effect of thermal stability is lower which brought about 0.685% weight loss that could be clearly demonstrated at 120℃. This can be attribute by the fact of increasing clay content up to a percent at which the silicate layers cannot be exfoliated anymore [25]. Hence, addition of more amount of nanoclay into matrix leads to appearance of clay stacks and even aggregates that deteriorate the thermal properties.
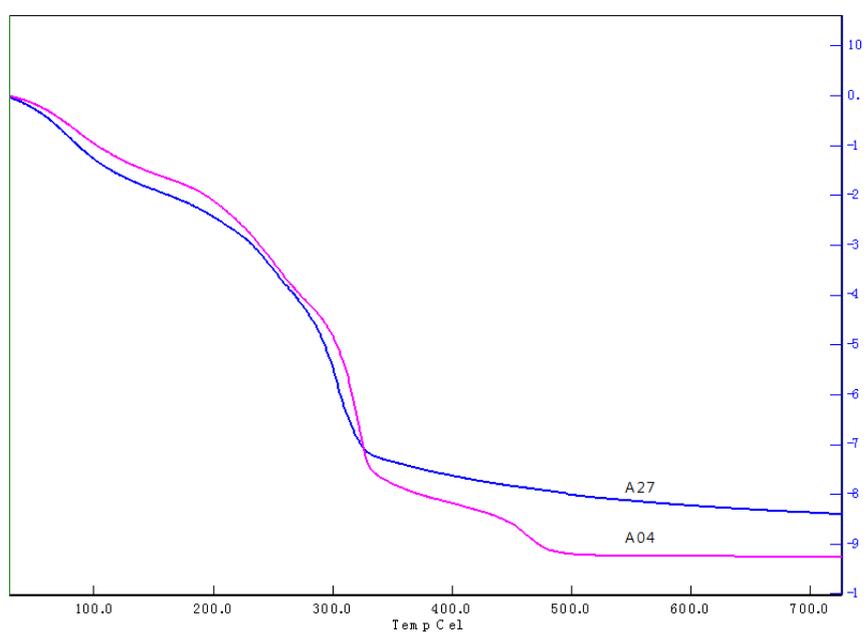
4.0   Conclusion

Nanocomposite films were prepared using the method of solution casting using thermoplastic starch, montmorillonite (MMT) and alumina trihydrate (ATH) with existence of citric acid as cross linking agent. DSC showed that cross-linked nanocomposite film larger area and fairly high thermal stability compared to non-cross-linked nanocomposite film from 182.14℃ to 129.38℃. Besides, it was also possible to conclude that T_m of nanocomposite peak rise from 183.90℃ to 184.53℃ when the ATH and MMT loading increased. This indicated that endothermic decomposition of ATH taken place and MMT content favour formation of large crystal and reduced the mobility of the polymer chains. Meanwhile, the melting area offered increment of 19% when the MMT loading level increase from 1 to 3wt.% where MMT cause an effect on the formation of secondary bonding. It also can be deduced that high loading level of ATH will give better thermal stability effect as weight loss % decrease. However, MMT offer the optimum thermal stability at medium level of MMT loading at 2wt.% given that incorporation of MMT delays the thermal decomposition temperature and also increases formation of the char residue which is able to slow down the combustion process. Therefore, elaboration of TPS/MMT/ATH nanocomposite film with citric acid as cross linking agent arise as an uprising alternative with its excellent thermal properties for application as fire-retardant coating materials in the future.

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