Mechanical Properties Investigation on Thermoplastic Starch (TPS)/ Montmorillonite Nano-clay (MMT)/ Alumina Trihydrate (ATH) Nanocomposites Film

Jun Wen Ho[1], Siew Wei Phang[1,2*], Lee Tin Sin[2], Soo Tueen Bee[2], Tiam Ting Tee[2]

[1]*School of Engineering, Taylor's University Lakeside Campus, Malaysia.*
[2]*Department of Chemical Engineering, Faculty of Engineering and Science, Universiti Tunku Abdul Rahman, Kuala Lumpur, Malaysia.*

*siewwei.phang@taylors.edu.my

Abstract
Starch has been selected to produce biodegradable polymer as it is an abundant, low cost, naturally renewable and biodegradable nature polymer. However, due to hydrophilic nature of pure TPS films, it has poor mechanical properties. Hence, fillers such as MMT, and ATH are introduced to improve the mechanical, thermal and flame retardant properties respectively. On the other hand, Citric acid (CA) is added to enhance the cross-linking effect between starch and fillers. Water is used as the main plasticiser and glycerol is used to further enhance the plasticising effect of the nanocomposites film. In this research, the main purpose is to determine the mechanical properties of the TPS/ MMT/ ATH blend. Preliminary test is carried out to determine the optimum ratio of glycerol and samples are prepared by solution casting method. The effects of each fillers are determined based on the experimental result from tensile tester machine STM-SERVO. The mechanical properties of TPS/ MMT/ATH nanocomposites film are determined by tensile strength, elongation at break and young's modulus. As a result, the nanocomposites film exhibited an improvement in tensile strength due to reinforcement of MMT and ATH. The elongation at break have reduced with introducing fillers in the nanocomposites films as intercalation of fillers into starch promotes the formation of restricted environment against the movement of polymer chains. On the contrary, the Young's modulus of the nanocomposites film shown measurable enhancement due to the polymer chains restricted.

Keywords: TPS/ MMT/ ATH nanocomposites, mechanical properties, tensile strength, cross-linking

1.0 Introduction

Plastic contributed considerable societal benefits in our daily lives. In fact, approximately 4% of the total oil production in the world is converted into plastics [1]. The usage of plastics gradually increases in the developing world due to its low unit cost and excellent performance specifications, the usage and annual production of plastics have exceed 300 million tons in the year 2010 [2]. In modern society, plastic plays an important role in the range of materials, almost every field involves plastics. For instance, plastics are utilised in packaging, public health, garment sector and also on external panel of cars. However, the current approaches in production, usage and disposal are not sustainable and created concerns for the environment, human and wildlife health. One of the major problems associated with production of plastics is the greenhouse gases (GHG) emission to atmosphere during the manufacturing of plastics. Besides, the drawbacks of utilising plastics also included the poor disposal method, which accumulated the waste in landfills. On the other hand, wildlife might be harm resulting from ingestion or entanglement in plastics. Also, during the production of plastic products, hazardous materials are released, which have the potential to endanger humans and wildlife [3]. Hence, compromise solution has to be found to overcome the current drawbacks of utilising plastics.

In order to reduce the GHG emission, one of the strategies adopted by several countries is to focus on the development of plastic that derived from biodegradable sources. On the other hand, the problems associated with handling and disposal of solid waste and interest in environmentally-friendly product has created a significant market opportunity for plant-based plastics. Currently, most of the synthetic plastics are derived from petrochemical, which are non-biodegradable, in another word; these materials are not able to be decomposed and it is difficult to recycle and reuse due to its complex composites [4]. Therefore, plant-based plastics has arisen as the alternative materials that have similar functionality to replace the conventional oil-based plastics. Plant-based plastics also known as biopolymer, which is derived from renewable sources such as starch.

Starch is an abundant, low cost, naturally renewable and biodegradable [5]. Starch is composed of repeating α-D-glucopyranosyl unit, which is the mixture of amylose, an essentially linear polysaccharide, and amylopectin, a highly branched polysaccharide as shown in Fig. 1. The properties of starch strongly depend on the ratio of amylose and amylopectin, typical cassava starch contains approximately 17% of amylose. In this research, cassava starch has been selected to produce starch-based plastics as it is renewable, low cost, and abundant in Malaysia. Cassava starch is also known as tapioca starch in Malaysia, it is obtained from the roots of the cassava plant. Compared to other types of starch, such as corn, potato and wheat starch, the characteristic of cassava starch are low level of residual materials, for instance, the amount of fat, protein and ash are relatively lesser.

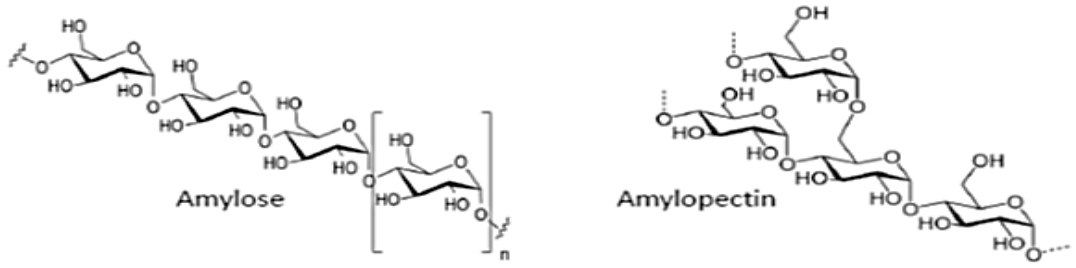

Figure 1. Structure of Amylose and Amylopectin

Few challenges existed in the starch-based plastics. For instance, due to the high hydrophilicity of starch, it has limited process ability and poor mechanical strength. Besides, starch tends to absorb the surrounding water vapour due to its characteristic in water absorption, which leads to poor long-term stability. Therefore, reinforcement of starch-based plastics is required to be carried out to eliminate the drawbacks. This research is conducted to addressed the challenges exist in the starch-based plastics, the following are the objectives that should be achieved throughout this research.

- To produce TPS/ MMT/ ATH nanocomposites films through solution casting method
- To determine the mechanical properties of the TPS/ MMT/ ATH blend
- To investigate and illustrate the effect of CA as cross-linking agent in TPS/MMT/ATH nanocomposites

As mentioned, granular starch has limited process ability, hence, it requires plasticiser for further process. The usage of plasticisers are able to enhance the film flexibility due to their ability in reducing the internal hydrogen bonding between the polymer chains. For instance, glycerol and water are used as the plasticiser in this research. In fact, water is the main plasticiser in the gelatinisation process. However, the effect of using water alone in starch-based plastics gelatinisation is very transient. Therefore, some less volatile plasticiser such as glycerol is introduced in the gelatinisation of starch. Glycerol has been selected as the plasticiser in this research as it is hydrogen bonding polar liquid [6], which is most suitable and it able to enhance the characteristic of starch by increase the molecular mobility of glucan chain. Besides, films that plasticised by glycerol is able to adsorbed faster and more water during storage as experimented by Mali et al. [7]. Based on the gelatinisation of cassava starch studies performed by Allen, the optimum gelatinisation temperature of starch-glycerol mixture is at 64.3 ºC [8], hence, during the preparation of TPS/ MMT/ ATH nanocomposites film, the solution is required to be heated to at least 65°C in order for the solution to be plasticised.

Due to the hydrophilic nature of pure TPS films, it carries poor mechanical properties. On the other hand, based on research performed by researchers in the similar field, the mechanical strength of the polymer blends have significant increment with the addition of montmorillonite nano-clay (MMT) [7, 8]. Hence, in this research, MMT is introduced to enhance the mechanical strength of the TPS film,

the mechanical performance of the MMT in the polymer matrix is depending on the intercalation of MMT into the crystal lattice galleries. Excellent mechanical behaviour of MMT in polymer matric is able to be achieved by perfect interaction between the organic and inorganic component. The optimum loading of MMT in the TPS/ MMT/ ATH nanocomposites film is crucial to be determined, in fact, adding of MMT able to increase the tensile strength of the nanocomposites film, however, there is a limitation, as further loading of MMT might bring adverse effect.

Thermal and flame retardant properties of nanocomposites film able to be enhanced by introducing the flame retardant filler. Studies on the alumina trihydrate (ATH) shows that ATH able to improve the fire resistance by retard the combustion of polymer matrix with reducing the melt dripping [11]. Besides, ATH is one of the flame retardant filler used in the polymers industry, compared to halogenated compounds flame retardant filler, ATH is more preferable as it does not release toxic smoke during the combustion process [12]. Based on the experimental outcomes performed by Cheng et al. [13], loading of both MMT and ATH in the nanocomposites film might results in flame retardant effect declined due to MMT unable to well integrate with ATH. Therefore, the loading level of ATH must be concerned when MMT is introduced in the polymer. The total weight percentage of ATH in the polymer composites should be high enough to avoid MMT suppressed the flame retardant ability of ATH.

Furthermore, citric acid (CA) is added into the nanocomposites films as the cross-linking agent to ensure all the components in the nanocomposites film are well-intercalated. According to studies, CA molecules act as a bridge between starch and clay molecule, it enhanced the intercalation process through hydrogen bonding [14]. On the other hand, as shown in Fig. 2, CA also able to enhance the plasticising effect by promote the fragmentation and dissolution of starch granule as claimed by Wang et al. [15].

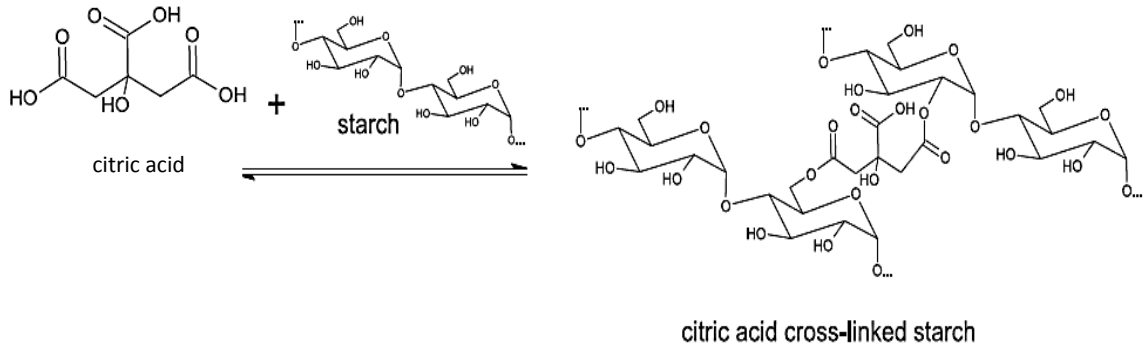

Figure 2. Cross-linking of Citric Acid with Starch

In this study, the mechanical properties such as elongation at break, young's modulus and tensile strength of the nanocomposites film are determined by Tensile Tester Machine STM-SERVO according to ASTM D882 standard.

2.0 Experimental Methodology

2.1 Materials

Native cassava starch powder with 17% of amylose is chosen in this research for the preparation of plant-based plastics due to its abundant availability, as cassava starch is widely cultivated and commercialised in Malaysia. For the main plasticizer – distilled water is obtained from Taylor's Engineering laboratory, and glycerol was chosen to be one of the plasticizers in the preparation of nanocomposites film and it was purchased from Merck Sdn. Bhd., Malaysia. For the different fillers, in enhancing mechanical strength of the TPS/ MMT/ ATH nanocomposites, MMT which also denotes as Nanolin DK® Nano-clay was purchased from FCC®, Inc., China. On the other hand, ATH with 90% purity that enhanced the thermal properties and cross-linking agent, anhydrous CA ($C_6H_8O_7$) with 99% purity and density of 1.665 g/cm^3 was purchased from Evergreen Engineering Resources, Malaysia.

2.2 Design of Experiment

The factors and their levels are determined in the first step in design of experiment, then the experimental design approach is selected based on the factors. In this research, full factorial design of experiment is applied to investigate the effect of incorporation of TPS, MMT and ATH. Three main factors: loading of MMT, ATH and CA were considered in three levels. The three loading levels of the fillers are selected based on the literature reviews performed on journals and publication in the similar research field. The loading of MMT was chosen in the range of 1 to 3 wt.% [10], [11], [14], where the loading for ATH is selected in the range from 14 to 18 wt.% [9], [11]. On the other hand, the loading level for CA is varied from 1 to 5 wt.% [15], [16]. With three factors and three levels full factorial design, 27 runs are required for complete analysis, the formulation is shown in Table 11. Analysis software-Minitab 17 is used to calculate the interaction of the factors, and hence, main effect plots are generated.

2.3 Sample Preparation

2.3.1 Preliminary Test

Preliminary test is performed to determine the optimum amount of glycerol in the TPS/ MMT/ ATH nanocomposites in order to reduce the number of factors. As the amount of starch is fixed throughout the research, which is 10 phr, and the other factors such as MMT is crucial in determining the mechanical strength, ATH which is important in determining the effect of flame retardant properties and CA which is decisive in the effect of intercalation of fillers in the nanocomposites film. Hence, the amount of glycerol in the nanocomposites film can be determined in the preliminary test to simplify the further work. The range of glycerol selected is based on the percentage proportion to the starch, and 40, 50 and 60 wt.% is selected based on the literature review performed. Besides, to determine the optimum amount of glycerol, the nanocomposites films produced are observed. In fact, the redundant of

glycerol will result in soft and mushy nanocomposites film where on the contrary, insufficient of glycerol will produce brittle and fragile nanocomposites film. The technique applied in the preparation of TPS/ MMT/ ATH nanocomposites is solution casting method and the formulation is shown in Table 2. Detailed explanation on sample preparation can be refer to Section 2.3.1 Preparation of TPS/ MMT/ ATH Nanocomposites Film.

Table 1. Formulation of TPS/ MMT/ ATH nanocomposites film

Experiment	Starch	Nano-clay	Alumina Trihydrate	Citric Acid	Glycerol
	PHR[1]	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: Concentration in the above table is in PHR, which is equivalent of loading 1, 2 and 3 wt.% of MMT is 0.16, 0.32 and 0.48 PHR, loading 14, 16, and 18 wt.% of ATH is 2.5, 3.0 and 3.5 PHR, loading of 1, 3 and 5wt.% of CA is 0.16, 0.48 and 0.8 PHR and loading of 27 wt.% of glycerol is 5 PHR.

[1] PHR is abbreviation for parts per hundred parts of resin, which is used in composites formulations, for instance, 10 PHR means 10 grams of an ingredient would be added to 100 grams of resin.

Table 2. 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: Concentration in the above table is in PHR, which is equivalent of loading 1, 2 and 3 wt.% of MMT is 0.16, 0.32 and 0.48 PHR, loading 14, 16, and 18 wt.% of ATH is 2.5, 3.0 and 3.5 PHR, loading of 1, 3 and 5wt.% of CA is 0.16, 0.48 and 0.8 PHR and loading of 23, 27 and 31 wt.% of glycerol is 4, 5 and 6 PHR respectively.

2.3.1 Preparation of TPS/ MMT/ ATH Nanocomposites Film

Solution casting method is utilised in this research to produce the TPS/ MMT/ ATH nanocomposites film. Solution casting method is started with measure the amount of starch, fillers and plasticizers required in the experiment, the formulation is shown in Table 11. 10 g of starch, 1, 2 and 3 wt.% of MMT, 14, 16 and 18 wt.% of ATH, and 1, 3 and 5 wt.% of CA which is in solid powder form are poured into a beaker. Fillers and cross-linking agent are mixed with starch before plasticization is to ensure the fillers and cross-linking agent able to perfectly mixed together. As reported by Tang at el., the extent of intercalation of MMT increased when composites were prepared without earlier plasticization, and it might due to plasticizers affected the attractive force between starch and MMT [17]. Hereafter, 400 ml of distilled water with 5 phr of glycerol as the plasticizers are gradually added into the beaker containing all the powder. Magnetic hot plate stirrer (SMHA-3 WiseStir) with operating speed of 600 rpm is used to mix the solution to achieve homogenous mixture, the solution are required to be heated up to 70°C due the effect of glycerol will only turn up after the specific temperature as mentioned earlier. After an hour of hot place stirring, the solution will became more viscous, which indicates the result of plasticization. Then, the solution is poured on rectangular Teflon mould and oven that operated at 70°C is used to dry the solution for 24 hours. On the next day, the sample are removed from the Teflon mould. The limitation existed in the sample produced might subject to retrograde effect before testing and characterizing, therefore samples are kept into a zipper bag with silica gels to avoid the samples from having further reaction with air.

2.4 Characterisation of TPS/ MMT/ ATH nanocomposites film

2.4.1 Mechanical Strength

The mechanical strength – tensile strength, Young's modulus and elongation at break of the TPS/ MMT/ ATH nanocomposites is determined by tensile tester machine STM-SERVO according to the ASTM D882 standard (Standard Test Method for Tensile Properties of Thin Plastic Sheeting). During tensile testing, the specimen was gripped at both ends of the tensile testing machine, elongation rate at 50 mm/min is subjected to the specimen until it break. Before testing, the specimens were cut into thin strip with dimension of 6 cm (L) × 5 mm (W),

and the thickness of the film is measured by digital micrometer. The cross-sectional area of the specimens is calculated by considered the length, width and thickness of the specimens.

3.0 Results and Discussions

3.1 Tensile Strength

The mechanical properties of TPS/ MMT/ATH nanocomposites film are determined by tensile strength, elongation at break and Young's modulus. The mechanical strength of the nanocomposites film is determined by tensile tester machine STM-SERVO according to ASTM D882 – "Standard Test Method for Tensile Properties of Thin Plastic Sheeting" [18]. The shape and dimension of the sample, specimen grip type, grip pressure and elongation rate for tensile testing is covered under this standard. The working mechanism of the machine is to pull both ends of the nanocomposites strip until it break. The tensile strength is determined based on the stress required to break the samples. On the other hand, the results obtained from tensile test are rather accurate due to it considered the cross sectional area of each sample, as the thickness of samples might vary from each and other. As the TPS/ MMT/ ATH nanocomposites film contains fillers and cross-linking agent, hence the effect of each filler and cross-linking on the tensile strength will be clearly discussed.

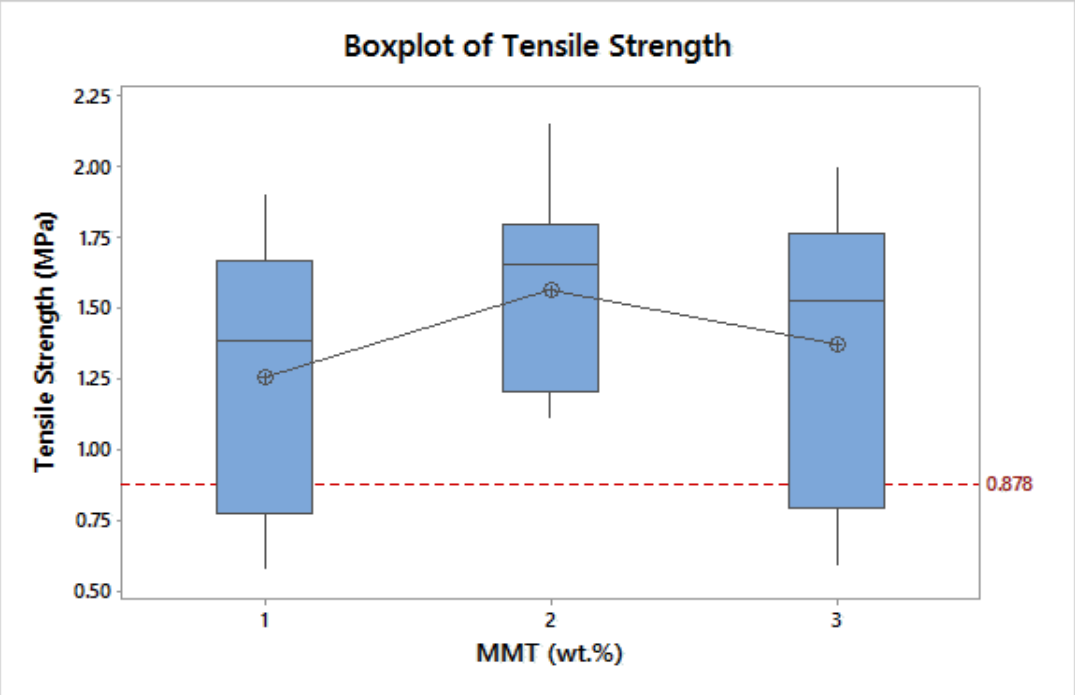

Figure 3. Boxplot of Tensile Strength against Loading of MMT

Based on the boxplot generated by Minitab 17 as shown in Fig. 3, it shown the mean tensile strength at various loading of MMT. The mean tensile strength of MMT loading level at 1, 2 and 3 wt.% are 1.252, 1.564 and 1.369 MPa respectively. The dotted line indicated the

tensile strength of control sample which only contains starch and glycerol, and it has tensile strength of 0.878 MPa. The effect of MMT in the nanocomposites film is significant as the tensile strength have gradually increased with the loading of MMT. With loading of 1 wt.% of MMT, the mean tensile strength of the nanocomposites film increased 0.374 MPa, which is equivalent to 42.6% enhancement. As the loading level of MMT increases, the tensile strength increases, it is because present of MMT in the nanocomposites increased the stiffness, hence, more stress is required to break the samples.

The peak of tensile strength is obtained at loading of 2 wt.% of MMT, which is 2.15 MPa, compared to control sample, the enhancement is about 144.9%. As mentioned, pure starch-based plastics have poor mechanical strength, therefore, with loading of MMT, the tensile strength is greatly enhanced, which overcome the drawback of pure starch-based plastics. However, further increment of MMT to 3 wt.%, it shown adverse effect, where the mean tensile strength have decreased from 1.564 to 1.369 MPa. The adverse effect found in further increment of MMT might due to large amount of MMT particles tend to agglomerated into larger particles, which affect the intercalation effect of MMT particles in the polymer matrix. This phenomena also reported by other researchers in the similar field, Bee et al. found the LDPE/ EVA/ MMT blend has lower tensile strength with further increment of MMT to certain limit [11]. On the other hand, the TPS/ MMT nanocomposites research done by Majdzadeh-Ardakani et al. have the similar result, further increment of MMT brought deterioration effect on the samples [14]. Based on the results from tensile test, the loading of MMT is crucial in determining the tensile strength of the nanocomposites film, optimum loading of MMT is required to be found out in order to produce nanocomposites film with good tensile strength.

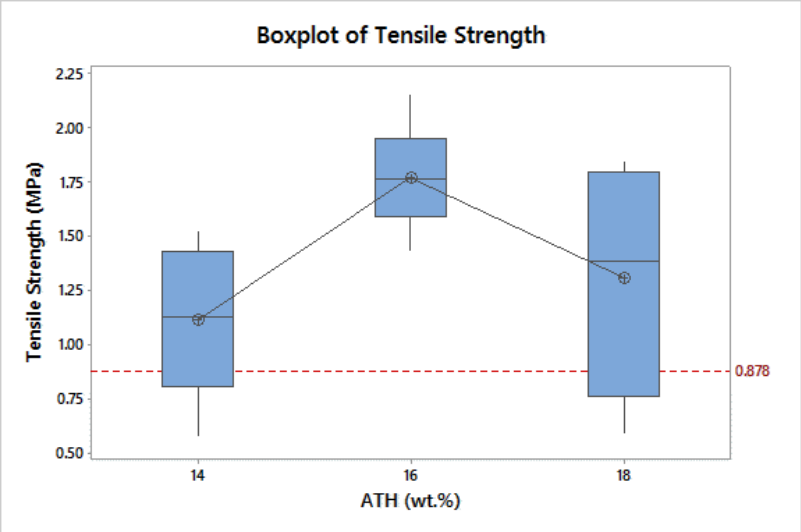

Figure 4. Boxplot of Tensile Strength against Loading of ATH

As compared to loading amount of MMT and CA, large amount of ATH loading is required in the nanocomposites to observe the effect of ATH. The mean tensile strength of nanocomposites film with various loading of ATH is shown in Fig. 16, the mean tensile

strength of loading of ATH at 14, 16 and 18 wt.% are 1.109, 1.769, and 1.305 MPa respectively. As compared the control samples and loading level of ATH at 14 wt.%, the mean tensile strength of the nanocomposites film has increased 0.66 MPa which is equivalent to 59.5%. Somehow, the results obtained in this research are accordance to previously published work, as reported by Beyer and Kilialis [12], [19], loading of ATH enhanced the mechanical strength of the nanocomposites, and sometimes, high loading of ATH deteriorated the mechanical strength. Likewise, loading of ATH in this research shown contribution to tensile strength of the nanocomposites film although the main function of ATH is to enhance the flame retardant properties. Similar concept to loading of MMT, the particles size of ATH is larger than MMT, however, with the cross-linking agent, ATH is well-intercalated into the nanocomposites film, which increased the strength of the sample, indirectly, more stress is required to break the nanocomposites strip during the tensile test. In spite of that, the tensile strength of nanocomposites film is decreased at loading of ATH at 18 wt.%, this is due redundant amount of ATH suppressed the effect of cross-linking agent in the nanocomposites film, consequently, it lead to poor intercalation of fillers in the nanocomposites, with poor intercalation, the nanocomposites film is structurally weak, and hence, the tensile strength decreased.

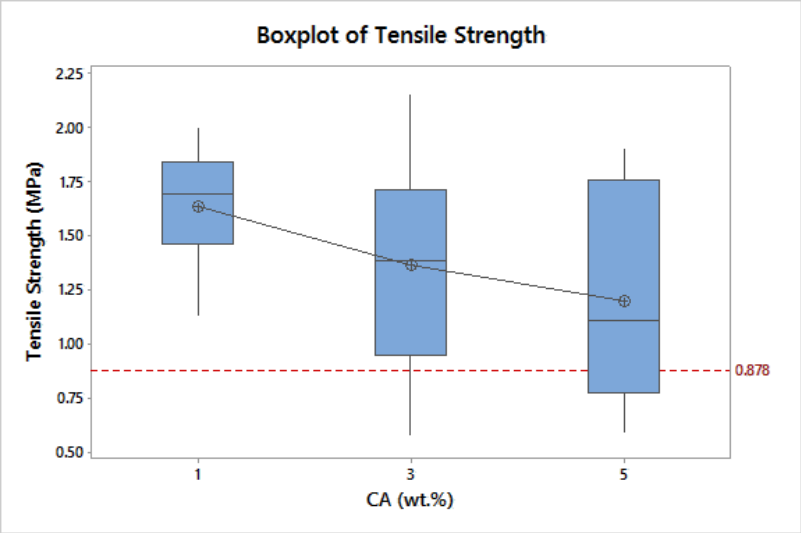

Figure 5. Boxplot of Tensile Strength against Loading of CA

Blending of CA as cross-linking agent into TPS/ MMT/ ATH nanocomposites film is novel and no similar research have been done. The effect of loading CA into the nanocomposites film with respect to tensile strength in shown in Fig. 5, the mean tensile strength of loading of CA at 1, 3 and 5 wt.% are 1.631, 1.361, and 1.139 MPa respectively. The cross-linking effect of CA in the nanocomposites film is shown in every loading of CA from 1 to 5 wt.%. Based on the result, it is believed that the d-spacing of MMT is enlarged with the present of CA, larger the d-spacing of MMT, the better effect of intercalation as other components able to bind into MMT easily. Moreover, due to acidic nature of CA promote the fragmentation and dissolution of starch granule, the smaller pieces of starch granule are easily permeated by plasticers and fillers, thus, better intercalation and better mechanical strength. Based on the result obtained in individual effect plot, loading of CA at 1

wt.% exhibited highest mean tensile strength, and the mean tensile strength gradually decreased with further increment of CA. Thus, it can be said that the high loading level of CA might cause the starch badly acidolysis, which deteriorated the rigid structure of starch. Therefore, it is suggested that the loading of CA can be reduces accordingly in further studies, and the effect of lower loading of CA should be observed.

3.2 Elongation

Elongation at break is one of the mechanical properties, sometimes, it is also known as fracture strain, which is the ratio between initial length and changed length after the test sample breakage. Elongation at break expresses the capability of a material to withstand changes of shape without crack formation.

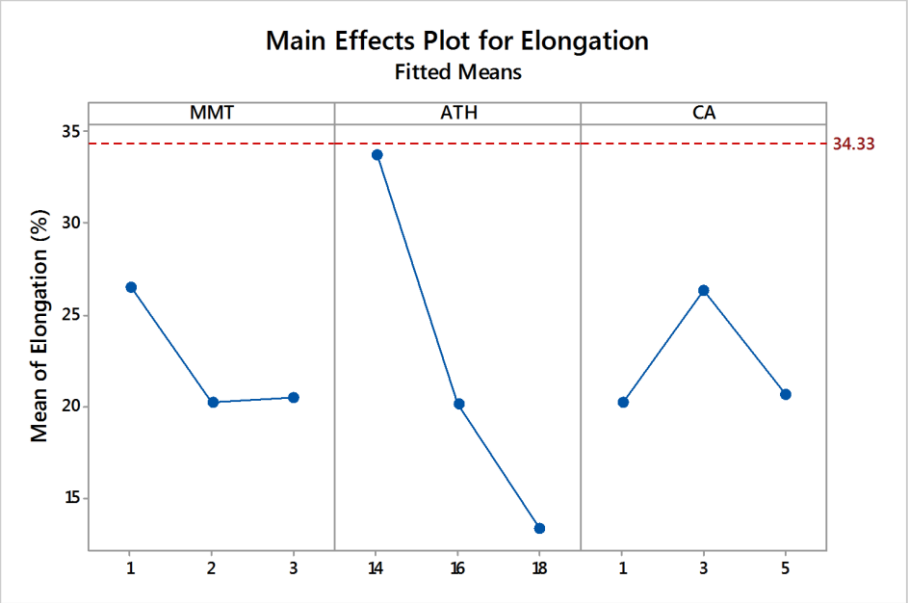

Figure 6. Main Effect Plots of Fillers with Respect to Elongation

The mean elongation with respected to loading of MMT, ATH and CA is shown in Fig. 6. The dotted line indicates the control sample without fillers and cross-linking agent, the elongation at break of the control sample is obtained as 34.44%, and it shown the highest percentage of elongation at break. The intercalation of MMT and ATH into starch promoted the formation of restricted environment against the movement of polymer chains as reported by Bee et al. [11], and hence, as the polymer chains are restricted and not able to move freely, the elongation ability of the polymer reduced.

Similar trend is obtained for both loading of MMT and ATH, the mean elongation at break of the samples are significantly decreased with higher loading of fillers. At low loading level of both MMT and ATH, the mean elongation are 26.54 % and 33.80% respectively. Compared low loading of MMT and ATH, the mean elongation of MMT is lower than ATH, this is due to the particles size of MMT are way smaller than ATH, hence, the ability of

intercalated of MMT into starch is much greater than ATH, consequently, the elongation at break of samples reduces. Moreover, at high loading level of MMT and ATH, the mean elongation are reduced to 20.54 and 13.37% respectively. At higher loading, MMT and ATH particles tend to agglomerated and formed larger particles, in this case, poor intercalation existed between starch and fillers, which lead to the stress acting on the sample is not even and weak point present in the particular area where the starch and fillers are not binded.

For loading of CA, as the main function of CA is to enhance the intercalation between the starch and fillers, as the intercalation effect is better, the weak point will be eliminated. Based on Figure 6, it shows that the mean elongation is enhanced from loading of CA at 1 to 3 wt.%, which is 20.24 to 26.35%, thus, the effect of introducing CA in the nanocomposites film is again shown. However, at further loading of CA to 5 wt.%, the mean elongation is reduced to 20.70%. As mentioned, introduced of MMT and ATH into starch restricted the movement of the polymer chains, hence, even the components in the nanocomposites film are well intercalated, it is believed that the elongation ability of the nanocomposites film will still be affected.

3.3 Young's Modulus

Young's modulus or elastic modulus is the fundamental measure of the film stiffness, in other words, it measures the material resists to elastics deformation under load. As higher Young's modulus, higher the stiffness of the mate1rial, with high stiffness material, it only slightly changes its shape under elastic loads. Hence, the relationship between elongation at break and Young's modulus is some kind of inversely proportional relation, when the material able to undergo high elongation before crack formation, the percentage of elongation of the sample is high, where the Young's modulus of the sample will be low.

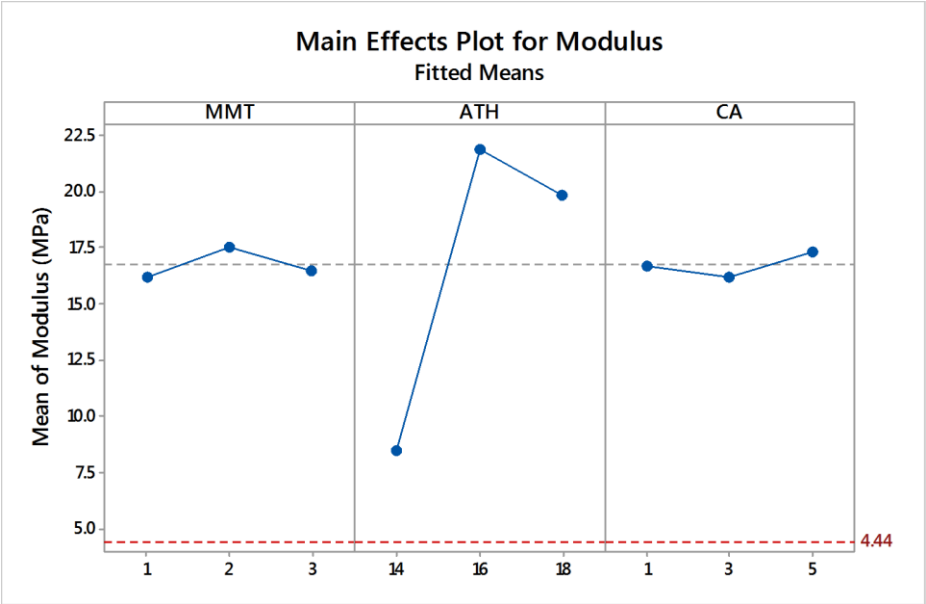

Figure 7. Main Effect Plots of Fillers with Respect to Young's Modulus

Mean of Young's modulus of loading of MMT, ATH and CA are shown in Fig. 7. The Young's modulus is the measure of stiffness of the materials, hence, higher the Young's modulus, the stiffness of the material increased. The dotted line in Fig. 7 shown the Young's modulus of the control sample which do not contain fillers and cross-linking agent, the Young's modulus for control sample is comparably low, which is only 4.44 MPa. As refer to Fig. 7, as the loading of MMT increased from 1 to 2 wt.%, the mean Young's modulus increased from 16.23 to 17.56 MPa. On top of that, compared the control sample with loading of MMT at 1 wt.%, the Young's modulus have increased from 4.44 to 16.23 MPa, which is about 265.5%. The Young's Modulus value is increased when introduced and increased the loading level of MMT into the nanocomposites film, and this is due to strong interaction present between the polymer matrix and the MMT silicate layer via formation of hydrogen bond as well as strong hydrophilicity of the clay edges [20]. In spite of that, at further loading of MMT from 2 to 3 wt.%, adverse effect of MMT is found, the mean Young's modulus have dropped from 17.56 to 16.50 MPa. Although the variation is small, however, the adverse effect of MMT found in the experiment might due to at high loading of MMT into the nanocomposites film, the MMT particles tend to agglomerated, which causes the present of weak point.

Noticeable effect of ATH is found on the mean Young's modulus, from loading of 14 to 16 wt.% of ATH, the mean Young's modulus increased from 8.47 to 21.95 MPa. Besides, at further loading of ATH to 18 wt.%, the mean Young's modulus is 19.90 MPa. As compared to mean Young's modulus of MMT and CA, the variation of ATH is much higher, it might due to the loading of ATH into the nanocomposites film is much greater than both MMT and CA, thus, ATH possess significant effect on the Young's modulus. Similar theory with MMT, with loading of ATH, the linear polymer chains are disrupted. Moreover, the increment in Young's modulus also indicated CA enhanced the intercalation between the fillers and starch, as such MMT particles able to effectively fit and intercalate into the interfacial between ATH and starch matrix, therefore, the mobility of polymer chains have been restricted. Nevertheless, the retrograde of mean of Young's modulus is found at further loading of ATH, which again shown the effect of cross-linking is unable to improve the intercalation effects at high loading of MMT and ATH, where the particles of MMT and ATH are agglomerated into larger particles. On the other hand, the mean Young's modulus for loading level of CA at 1, 3 and 5 wt.% are 16.69, 16.23 and 17.38 MPa respectively. The individual effect of CA is not significant as compared to ATH, it is believed no matter how well intercalate existed between the fillers and starch, the linear polymer matrix is still disrupted, hence, the effect of cross-linking do not have great effect on the Young's modulus.

4.0 Conclusion

In a nutshell, this study has illustrated the investigation on the mechanical properties such as tensile strength, elongation at break and Young's modulus of the TPS/ MMT/ ATH nanocomposites films. It is found that both MMT and ATH able to contribute to the tensile strength of the nanocomposites films. Besides, at high loading of MMT and ATH, the particles tend to agglomerated into larger particles, which deteriorated the mechanical strength of the nanocomposites films, hence, the loading levels of fillers are crucial in determining the mechanical strength of the nanocomposites films. In addition, the effect of CA as cross-linking agent is significant in this study, better intercalation effect is found with introducing CA into the nanocomposites films. Moreover, the elongation at break have reduced with introducing fillers in the nanocomposites films as intercalation of MMT and ATH into starch promotes the formation of restricted environment against the movement of polymer chains. On the contrary, with the polymer chains restricted, the Young's modulus of the nanocomposites film shown measurable enhancement. Last but not least, with introduced fillers and cross-linking agent into starch-based plastics, the drawbacks are eliminated, thus, the applications of this plastic are opened to wider areas.

References

[1] Y. J. Chen, "Journal of Chemical and Pharmaceutical Research , 2014 , 6 (1): 226-231 Bioplastics and their role in achieving global sustainability," vol. 6, no. 1, pp. 226–231, 2014.

[2] R. C. Thompson, C. J. Moore, F. S. vom Saal, and S. H. Swan, "Plastics, the environment and human health: current consensus and future trends.," *Philos. Trans. R. Soc. Lond. B. Biol. Sci.*, vol. 364, no. 1526, pp. 2153–66, Jul. 2009.

[3] H. H. Impacts, "Plastic Waste : Ecological and Human Health Impacts," no. November, 2011.

[4] J. H. Song, R. J. Murphy, R. Narayan, and G. B. H. Davies, "Biodegradable and compostable alternatives to conventional plastics.," *Philos. Trans. R. Soc. Lond. B. Biol. Sci.*, vol. 364, no. 1526, pp. 2127–39, Jul. 2009.

[5] L. Ren, M. Jiang, L. Wang, J. Zhou, and J. Tong, "A method for improving dispersion of starch nanocrystals in water through crosslinking modification with sodium hexametaphosphate," *Carbohydr. Polym.*, vol. 87, no. 2, pp. 1874–1876, Jan. 2012.

[6] R. Shanks and I. Kong, "Thermoplastic Starch," 2011.

[7] S. Mali, L. S. Sakanaka, F. Yamashita, and M. V. E. Grossmann, "Water sorption and mechanical properties of cassava starch films and their relation to plasticizing effect," *Carbohydr. Polym.*, vol. 60, no. 3, pp. 283–289, May 2005.

[8] J.F. Chabot, "Effect of chemical modification on the ultrastructure of corn, waxy maiza and tapoica starches.pdf." .

[9] X. Zhang, F. Guo, J. Chen, G. Wang, and H. Liu, "Investigation of interfacial modification for flame retardant ethylene vinyl acetate copolymer/alumina trihydrate nanocomposites," *Polym. Degrad. Stab.*, vol. 87, no. 3, pp. 411–418, Mar. 2005.

[10] F. a. Aouada, L. H. C. Mattoso, and E. Longo, "New strategies in the preparation of exfoliated thermoplastic starch–montmorillonite nanocomposites," *Ind. Crops Prod.*, vol. 34, no. 3, pp. 1502–1508, Nov. 2011.

[11] S.-T. Bee, A. Hassan, C. T. Ratnam, T.-T. Tee, L. T. Sin, and D. Hui, "Dispersion and roles of montmorillonite on structural, flammability, thermal and mechanical behaviours of electron beam irradiated flame retarded nanocomposite," *Compos. Part B Eng.*, vol. 61, pp. 41–48, May 2014.

[12] G. Beyer, "Flame retardant properties of EVA-nanocomposites and improvements by combination of nanofillers with aluminium trihydrate," *Fire Mater.*, vol. 25, no. 5, pp. 193–197, 2001.

[13] K. Cheng, C. Yu, W. Guo, S. Wang, T. Chuang, and Y. Lin, "Thermal properties and flammability of polylactide nanocomposites with aluminum trihydrate and organoclay," *Carbohydr. Polym.*, vol. 87, no. 2, pp. 1119–1123, 2012.

[14] K. Majdzadeh-Ardakani, A. H. Navarchian, and F. Sadeghi, "Optimization of mechanical properties of thermoplastic starch/clay nanocomposites," *Carbohydr. Polym.*, vol. 79, no. 3, pp. 547–554, Feb. 2010.

[15] N. Wang, X. Zhang, N. Han, and S. Bai, "Effect of citric acid and processing on the performance of thermoplastic starch/montmorillonite nanocomposites," *Carbohydr. Polym.*, vol. 76, no. 1, pp. 68–73, Mar. 2009.

[16] E. Olsson, M. S. Hedenqvist, C. Johansson, and L. Järnström, "Influence of citric acid and curing on moisture sorption, diffusion and permeability of starch films.," *Carbohydr. Polym.*, vol. 94, no. 2, pp. 765–72, May 2013.

[17] X. Tang, S. Alavi, and T. J. Herald, "Effects of plasticizers on the structure and properties of starch–clay nanocomposite films," *Carbohydr. Polym.*, vol. 74, no. 3, pp. 552–558, Nov. 2008.

[18] ASTM, "ASTM D882: Standard Test Method for Tensile Properties of Thin Plastic Sheeting," *ASTM Stand.*, p. 12, 2012.

[19] P. Kiliaris and C. D. Papaspyrides, "Polymer/layered silicate (clay) nanocomposites: An overview of flame retardancy," *Prog. Polym. Sci.*, vol. 35, no. 7, pp. 902–958, Jul. 2010.

[20] S.-T. Bee, A. Hassan, C. T. Ratnam, T.-T. Tee, and L. T. Sin, "Investigation of nano-size montmorillonite on electron beam irradiated flame retardant polyethylene and ethylene vinyl acetate blends," *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms*, vol. 299, pp. 42–50, Mar. 2013.