Preliminary Study of Mechanical Properties in Thermoplastic Starch (TPS) / Coffee-Waste-Derived Fillers Composites

Y.M. CHAN[1*], S.W. PHANG[1], T.T. TEE[2], T.S. LEE[2], T.B. SOO[2]
[1]*Environmental Research Group, Department of Chemical Engineering, Taylor's University Lakeside Campus, Malaysia.*
[2]*Department of Chemical Engineering, Faculty of Engineering and Sxience, University Tunku Abdul Rahman, Jalan Genting Kelang, 53300 Setapak, Kuala Lumpur, Malaysia.*
**Corresponding Author E-mail: yenmin91@gmail.com*

Abstract
Thermoplastic starch (TPS) has been studied to replace the conventional petroleum-derived plastics in the last decade for its biodegradability, low production cost, availability and is a renewable agricultural resources. However, it has limited performance due to its hydrophilic nature, poor mechanical properties and poor long-term stability. Blending fillers into TPS matrix has shown improvements in the mechanical properties of TPS such as cellulose, clay, fiber, fly ash and carbon nanotubes for widening the range of their applications. Most of the fillers that have been studied are not readily biodegradable or incompatible with the hydrophilic characteristic of TPS. Hence, this research aimed to introduce a brand new bio-filler, grinded used-coffee-waste into the combination of *cassava* starch and glycerol via solution casting method in order to improve the compatibility between the fillers with TPS. Critical mechanical properties of the TPS composites, maximum tensile stress, elongation at break and Young's modulus were evaluated using tensile test machine according to ASTM D882-12. Presence of coffee fillers demonstrated sharp increments in elongation at break up to 106 % but slight decrement in both maximum tensile stress and Young's modulus with 0.67 MPa and 4.11 MPa respectively. The elongation at break of the TPS composites increased with the loading levels of coffee fillers from 1 to 5 wt. %, while maximum tensile strength and Young's modulus showed adverse effect with the increase of coffee loading levels.

Keywords: Thermoplastic starch, Coffee-waste-derived fillers, Mechanical properties, Solution casting.

1. Introduction

The daily usage of plastics in the modern society cannot be overlooked due to their plentiful applications ranged from food and merchandise packaging industries to medical technologies. Plastics not only permit modern lifestyles, it also promotes higher standards of living and the overall welfare through the contributions in research and innovation. The global annual production of plastics is predicted to exceed 300 million tonnes by 2015, as it is subjected to a steady growth for more than 50 years and a 2.8 % increment from year 2011 to year 2012 [1-2]. The current plastic films are derived from petroleum and the non-biodegradable characteristic has become their intrinsic deficiency which result in a vast environmental accumulation and pollution problem that lasts for centuries. According to the report from Environmental Protection Agency (EPA) in United States, plastics has made up 12.4 % of municipal waste in year 2010, which is accounted for 24 times of the amounts generated in year 1960, and only 8.2 % of plastic waste was recovered [3].

Hence, in the last decade, there are increased interests and research efforts on developing the biodegradable and renewable plastic films to substitute the petroleum-based films, which is generally known as bioplastics. A recent report presented by Shen et al. [4] revealed that the bioplastics market is gradually growing at a rate of 30 % annually to capture the plastics market. Starch for this context has becoming a promising natural renewable resources to produce bioplastics due to its abundant availability, extremely low cost and biodegradable nature. Starch can be obtained from a great variety of crops since it is the natural carbohydrate storage materials in the form of granules. It composes two structural classes, amylose, the linear poly (α-1,4-glucopyronosyl) polysaccharide molecules and amylopectin, the branched molecules, with abundant of α-1,6-glucopyronosyl linked branch points, as shown in figure 1 [5]. There is a vast hydrogen bonds network in starch as it is a multi-hydroxyl polymer and hence, starch is not readily to be used as a bioplastic alone. However, it poses similar characteristics to the conventional plastics with the addition of suitable plasticizers, such as glycerol, sugars and sorbitol, prepared under the conditions of high temperature (90-180 ºC) with moderate shearing [6]. This is due to the gelatination process that taken place during the mixing of starch with the plasticizer at high temperature and the presence of shear. During the process, the bonds of hydrogen chains are broken, and the structure of starch molecules are disrupted, leading the starch becomes plasticized.

The plasticized starch is known as thermoplastic starch (TPS). Utilization of suitable plasticizer is critical for the synthesis of TPS. In this context, water is reported as a good plasticizer as a gelatinization temperature at a range of 60-70 ºC is given by adequate amount of water, particularly 10-30 wt. % with the destruction of crystalline organization due to the swelling of the granules in starch [7]. However, water is not encouraged to be used as plasticizer solely for its high dependence of final properties to the ambient humidity as well as high volatility that produces a brittle TPS in return. Glycerol is hence applied in this research for its hydroxyl-rich properties and compatibility with *cassava* starch as its application is successfully reported by several studies [8-10]. According to Janssen and Moscicki [11], glycerol is the most excellent plasticizer in reducing the friction between starch molecules. In addition, it has been generated in a large quantities as the by-products in biofuel industries and therefore the utilization of glycerol can address environmental issue simultaneously. The ideal ratio of starch to glycerol (w/w) was claimed to be 70:30

according to Zullo and Iannace [10]. The same result was presented by Pushpadass el al. [12] as the optimal conditions of TPS in terms of tensile strength and Young's modulus are achieved by the addition of 35 wt. % of glycerol.

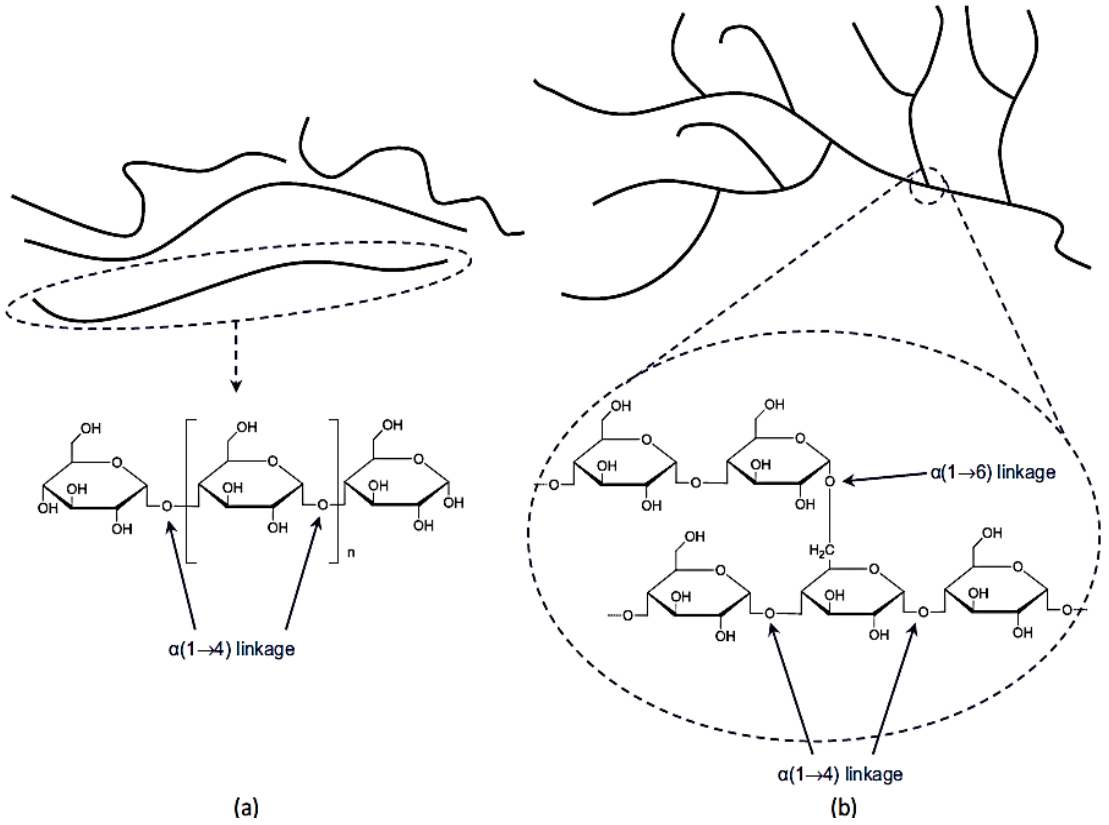

Figure 1. Molecular structure of amylose (a) and amylopectin (b) [13].

Despite the potential of starch to be the substitution for conventional plastic films, it has limited performance due to its major drawbacks such as hydrophilic nature, poor mechanical properties and poor long-term stability. This is because the crystalline phases or highly ordered region hindered the binding between the plasticizers with the hydroxyl groups, resulting in the TPS matrix tends to retrograde after a certain period [14]. Incorporation of foreign body that compatible with the TPS matrix is believed to reinforce the films as it has been proven by some of the fillers such as cellulose nanofillers, nanoclay and carbon nanotubes.

Cellulose nanofillers had brought significant improvement in mechanical properties to the reinforced TPS composites by providing good adhesion in the matrix [15]. This statement is proven by Martins et al. [16] who used bacterial cellulose produced from *Acetobacter Xylinum* as the reinforcement fillers with the loading level from 1 to 5 wt. %. The Young's modulus and tensile strength increasing with the cellulose contents shows 30 times higher than that of non-reinforced TPS. On the other hand, TPS composites with the addition of only 0.055 wt. % of multi-walled carbon nanotubes (MWCNTs) shows increments of 35 % in ultimate tensile strength, up to 70 % in stiffness and 80 % in elongation before failure in a recent works done by Famá et al. [17]. MWCNTs achieved good compatibility with the TPS matrix due to excellent dispersion and adhesion between the phases as proven by SEM micrographs. Another research from Huang et al. [18] reported the improvements in mechanical properties of TPS composites with the addition of nanoclay, activated

montmorillonite (MMT) minerals. The tensile stress is increased from 4.5 MPa to 24.9 MPa with the addition of 10 wt% of MMT while the optimum tensile strain, 134.5 % is achieved by the addition of 5 wt% of MMT. In spite of the potential demonstrated by the mentioned fillers in improving the mechanical properties of TPS composites, high priced and complex preparation process of the fillers turns out to be the major drawbacks which are not economically feasible and hence limit the potential of reinforced TPS in substituting the conventional petroleum-based plastics.

Grinded coffee waste for this context is considered as a good candidate to be utilized as the bio-filler for TPS composite because it is abundant, low cost, biodegradable, and is a renewable resource. Spent coffee grounds have become a major waste in food industries as 650 kg of spent coffee grounds are produced from the processing of one ton of green coffee, leading to an annual generation of 6.0 million tonnes [19]. Hence, valorization of grinded coffee waste in TPS composites can address the environmental issue brought by spent coffee grounds. In addition, the constituents of grinded coffee waste, namely carbohydrates (38-42 %), melanoidins (23 %), lipids (11-17%), protein (10%), minerals (4.5-4.7 %), caffeine (1.3-2.4 %) and etc. show a great potential to share the chemical similarities with starch and hence improve the compatibility with TPS [20]. As cellulose and hemicellulose are the main ingredients of the formation of carbohydrates due to the polymerization of sugars according to Mussato et al. [21], improvement of mechanical properties of TPS composites can be estimated by blending in coffee waste, providing that cellulose had been proven as an effective filler in the enhancement of properties of TPS. On the other hand, melanoidins, the nitrogen-containing brown pigments consist of carboxyl group, as shown in Figure 2 as well as numerous hydroxyl groups with sugar derived skeleton which are predicted to develop strong hydrogen bonds with starch molecules of TPS, and hence improve the compatibility of coffee waste in TPS matrix [22]. Another major constituents, lipids consist of three fatty acyl residues with glycerol served as the backbone for the molecules [23]. As glycerol is an effective plasticizer for TPS, lipids are assumed to exhibit good interaction with the starch molecules in TPS matrix.

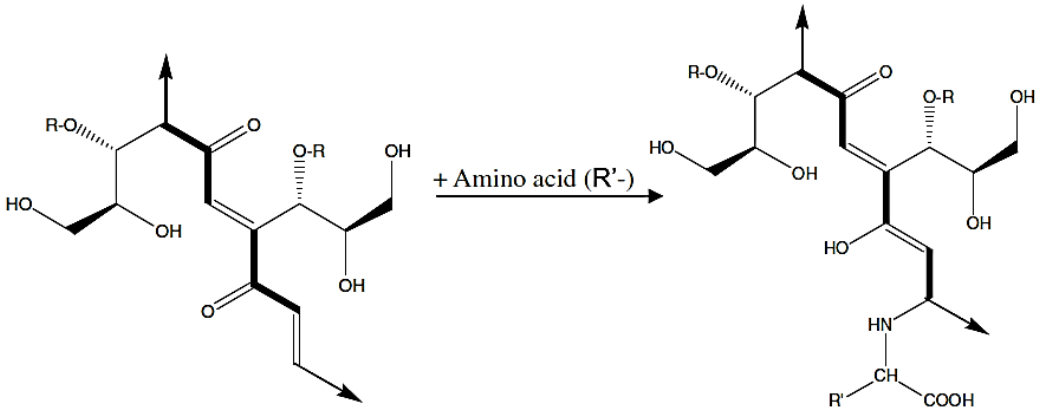

Figure 2. Carbohydrate-based melanoidin structure [24].

2. Experimental

2.1 Materials

The *cassava* starch, normally denoted as tapioca starch that containing around 17 % of amylose was purchased from SCS Food Manufacturing Sdn. Bhd. and utilized as the main ingredient for the preparation of TPS. Tapioca is abundantly cultivated in Malaysia and hence *cassava* starch was served as the native starch in this research in order to reduce the feedstock cost. The plasticizer, glycerol with 98 % of purity was purchased from R & M Marketing (Essex, U.K) and it was used without pre-treatment or further purification [25]. The grinded coffee waste was kindly supplied by Starbucks Sdn. Bhd. in Taylor's Lakeside Campus for the convenient purpose. The grinded coffee waste was washed with distilled water to remove impurities and dried in oven with 70 ºC for 24 hours until a constant weight was obtained and sieved with a sieve shaker to obtain a particle size of 500 µm. The dried starch and grinded coffee waste were kept in desiccator prior to use.

2.2 Design of Experiments

The research was mainly based on experimental and quantitative study. Experiments were carried out with respect to two different parameters, namely, loading level of glycerol and grinded coffee waste filler. Full factorial design was applied for this context as the parameters were manipulated into three different levels, namely low, medium and high. Consequently, there were altogether 9 runs for the experiments according to 3^2 full factorial design. The loading level of glycerol was ranged from 40 to 60 wt. % as this particular loading level of glycerol was believed to produce the desirable properties of TPS [7], [9], [26]. The loading level of coffee filler on the other hand was ranged from 1 to 5 wt. %. This range was set according to the similar research works as grinded coffee waste was a novel filler [8], [27]. Three replicates were tested for each experiments to get the average results in order to increase the accuracy. The composition of each formulation and controlled sample is as shown in **Table 1**.

Table 1. Formulation of TPS/grinded coffee waste filler composites.

Formulation	Loading level of glycerol (wt. %)	Loading level of coffee filler (wt. %)
TPS	50	0
T1-1	40	1.0
T1-2	40	3.0
T1-3	40	5.0
T2-1	50	1.0
T2-2	50	3.0
T2-3	50	5.0
T3-1	60	1.0
T3-2	60	3.0
T3-3	60	5.0

2.3 Preparation of TPS/coffee-waste-derived Fillers Composites Films

TPS composites films were prepared using solution casting method. 20 g of *cassava* starch was added into 800 ml of distilled water with 40, 50 and 60 wt. % of glycerol and 1, 3 and 5 wt. % of coffee waste fillers according to the corresponding run of experiments. The suspensions were heated at 70 ºC and 800 rpm using magnetic plate stirrer (SMHA-3 WiseStir) for 1 hour. The suspensions were then poured into Teflon-coated carbon steel plates and left to dry in the oven at 70 ºC for 24 hours in order to obtain the TPS composites films. The TPS composites films were left to cool until room temperature and kept in polyethylene zip lock bags with silica gels for further testing purpose.

2.4 Tensile Testing of TPS Composites Films

Maximum tensile strength, elongation at break and Young's modulus of the TPS composites films were determined using Tensile Tester Machine STM-SERVO according to ASTM D882-12 (Standard Test Method for Tensile Properties of Thin Plastic Sheeting) with a 5 kN load cell. During the tensile test, the specimens were gripped at one end of the tensile testing machine and pulled until failure with a crosshead speed of 50 mm/min, as suggested by ISO 527 standards (1993). Before testing, the TPS composites films were cut into strips with dimension of 8 x 5 mm while the thickness of the specimens were measured using a digital micrometer. The original gauge length, L_0 was set as 6 mm and the cross-sectional area of the specimens was calculated and recorded in order to obtain the load per unit area of the specimens.

3. Results and Discussion

3.1 Tensile Testing

The results of vital mechanical properties, maximum tensile stress, Young's modulus and elongation at break obtained from tensile testing are tabulated using graphical method with boxplots to indicate the standard deviations of the data, as shown from Figure 3 to 5. Dotted lines in the graphs show the mean reading given by controlled samples for comparison purpose. Based on Figure 3, the incorporation of grinded coffee waste into TPS matrix did not exhibit a positive effect in enhancing the maximum tensile stress as the results given by most of the TPS/coffee filler composites were slightly lower than the controlled samples. However, TPS composites with the lowest loadings of coffee filler and glycerol, T1-1 yielded an increase in maximum tensile stress up to 0.95 MPa. Hence, it could be considered as the optimum loading levels for both the coffee filler and glycerol in terms of enhancing the maximum tensile stress of TPS composites. In contrary, TPS composites with the highest loadings of coffee filler and glycerol, T3-3 demonstrated the lowest maximum tensile strength, 0.21 MPa. This result is in concordance with the studies performed by Hietala et al. [28] that revealed aggregates of the filler, cellulose nanofibres in the TPS matrix when the loadings were higher than the optimum level, leading to the decline in tensile strength. In addition, it can be observed that the results showed an adverse effect by increasing the loading level of coffee fillers from 1 to 5 wt. %, regardless of the loading level of glycerol. Therefore, lower loading level of coffee filler was preferable to increase the maximum tensile strength of TPS composites. The effect given by the loading level of glycerol on the other hand was

not noteworthy as similar trend of results were obtained at different loadings of glycerol.

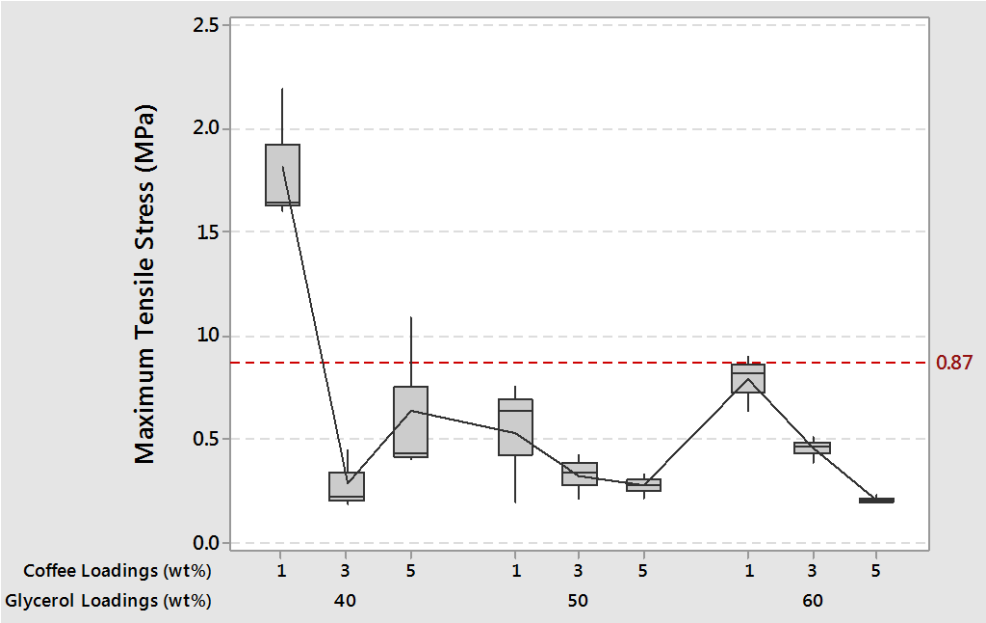

Figure 3. Maximum tensile stress of various formulations.

According to Figure 4, the trend of results in Young's modulus was very similar to that of maximum tensile stress as previously observed. Presence of grinded coffee waste fillers brought down the Young's modulus of TPS composites likewise. Similar to that of maximum tensile stress, formulation with the highest loadings of coffee filler and glycerol, T3-3 exhibited the lowest Young's modulus, which is 0.33 MPa. Formulation with the lowest loadings of coffee filler and glycerol, T1-1 again demonstrated an increase in Young's modulus up to 8.01 MPa, and hence proving that the optimum level of loadings of coffee filler and glycerol had been achieved. Conversely, no specific trend was observed for the effect of increasing the loadings of coffee filler and glycerol in Young's modulus by only observing Figure 4. Hence, further analysis that required to study the effect of individual factors to the responses in detail would be required.

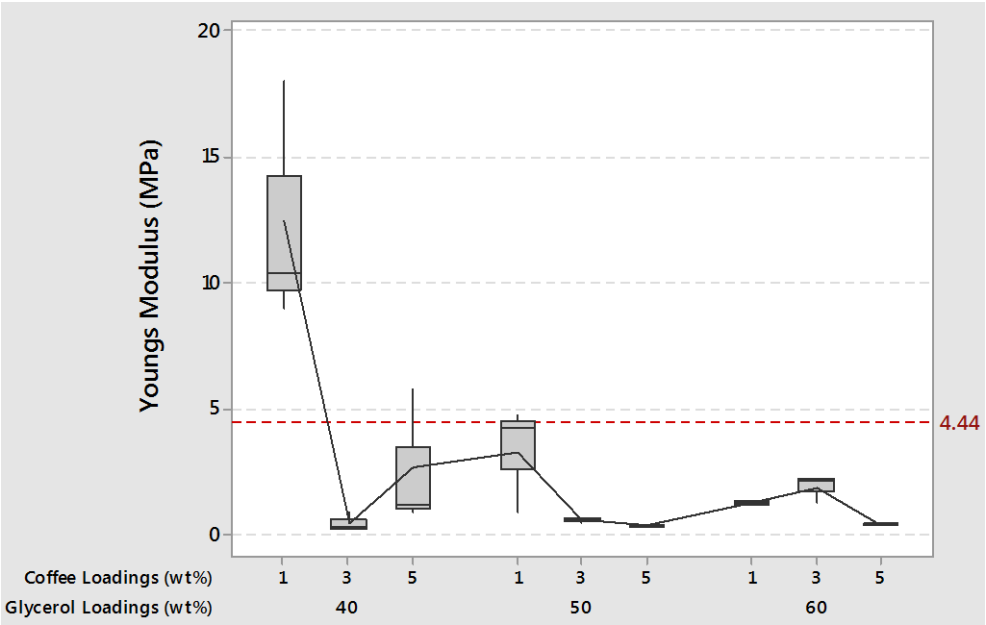

Figure 4. Young's modulus of various formulations.

It was clearly evident from Figure 5 that blending of grinded coffee waste filler enhanced the elongation at break of TPS composites since all formulations demonstrated an increase in elongation at break compared to the controlled samples. Generally, the reduction in elongation at break is very common for polymer reinforcement as it is inversely related with tensile strength [13]. Incorporation of coffee fillers into TPS matrix demonstrated this phenomenon in the other way round, whereby the results showed enhancement in elongation at break of the materials with the decrement of maximum tensile stress. Based on Figure 5, highest elongation at break that up to 140 % was exhibited by the formulation T2-3 while the lowest elongation at break with the value of 42 % was given by the formulation T3-2. As the standard deviation of the data was so huge and no specific trend could be observed from the results with just based on Figure 5, main effects plot is required to further justify the effects of loadings of coffee fillers and glycerol in the enhancement of elongation at break of TPS composites.

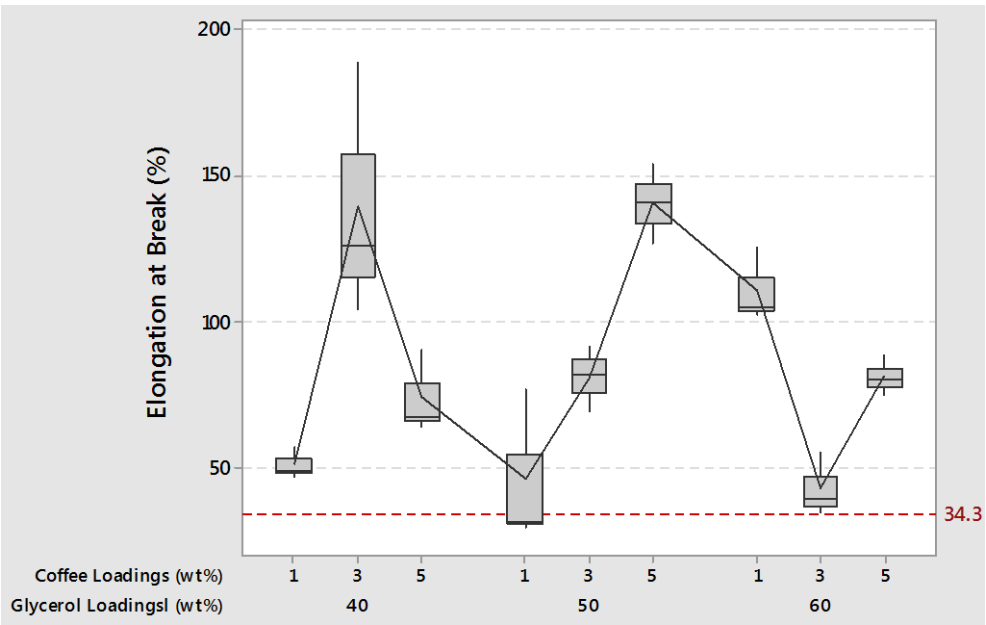

Figure 5. Elongation at break of various formulations.

In order to comprehend the significance of each factors contributing in the mechanical properties of TPS composites, Minitab 17 software was employed in this research to further analyse the individual effects of loadings of coffee filler and glycerol by plotting main effects plots as shown from Figure 6 to 8. Based on Figure 6, it could be observed that the optimum loadings of coffee fillers in enhancing the maximum tensile stress was only 1 wt. %. Maximum tensile stress decreased significantly when the loadings of coffee filler increased from 1 to 5 wt. %. The results obtained were not preferable as the maximum tensile stress lies between the ranges of 0.3 to 0.4 MPa, which were lower than that of controlled sample. Similarly, the main effect plots for Young's modulus as shown in Figure 7 showed the same trend of graphs with that of maximum tensile strength. Increasing the loadings of coffee fillers from 1 to 5 wt. % again demonstrated adverse effect to the Young's modulus as the values were lower than the controlled sample by around 75%.

As this research was only served as a preliminary study for the effect of introduction of coffee filler into TPS films, the particle size of coffee fillers was remained as micron scale instead of nano scale, which was 33 times larger than that of *cassava* starch. The large particle size of coffee fillers might have impeded the embedment of the fillers in TPS matrix and hence worsen the mechanical properties of TPS composites in terms of maximum tensile strength and Young's modulus. The large particle size of coffee filler inevitably caused uneven distribution of the materials in the TPS matrix, which in turns influenced the hydrogen bonding between the starch granules and the fillers. The compatibility of coffee filler with TPS matrix for the context of degree of adhesion and dispersion has to be further analysed using SEM. It was very common to obtain a negative result for the introduction of brand new filler into TPS films, whereby the incorporation of fly ash, a brand new filler showed incompatibility with the hydrophilic characteristic of TPS, proven to worsen the mechanical properties of TPS composite with the research performed by Ma et al. [29].

On the other hand, the optimum loadings of glycerol was 40 wt. % in improving the maximum tensile stress as well as Young's modulus according to Figure 6 and 7 respectively. The maximum tensile stress and Young's modulus of the TPS composites decreased significantly with increasing concentrations of glycerol from 40 to 60 wt. %. The results is in concordance with the studies performed by Pushpadass et al. [30] in which the tensile strength and Young's modulus declined with the increasing of glycerol concentrations in TPS/LDPE composites. The higher loadings of glycerol in TPS/coffee filler composites might form a weak boundary layer between starch and coffee fillers due to phase separation of starch [30]. Increased of free volume in the TPS composites network due to the increasing loadings of glycerol leading to poor interactions between the starch chains as well, attributed to the decreasing values of maximum tensile stress and Young's modulus [31].

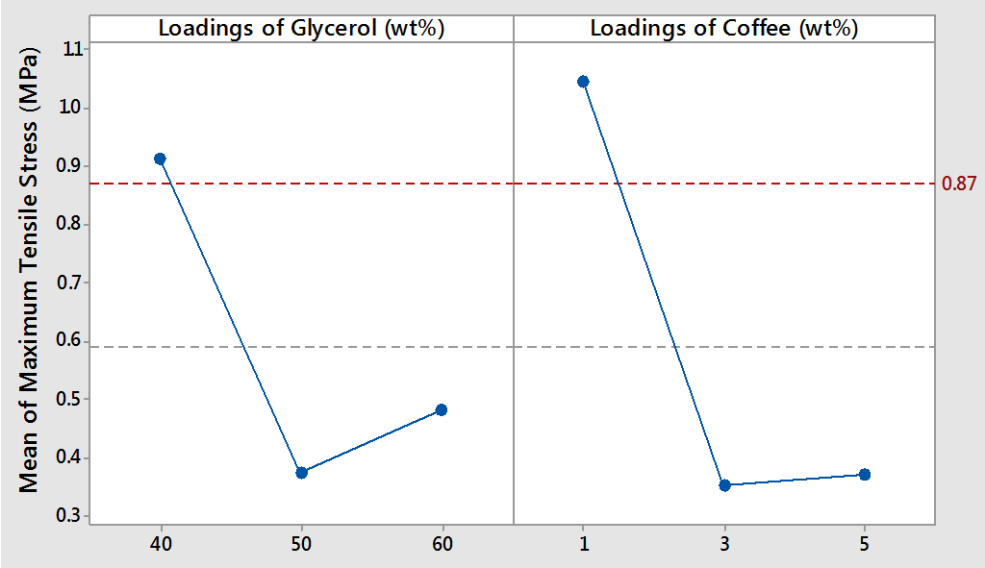

Figure 6. Main effects plot for maximum tensile stress.

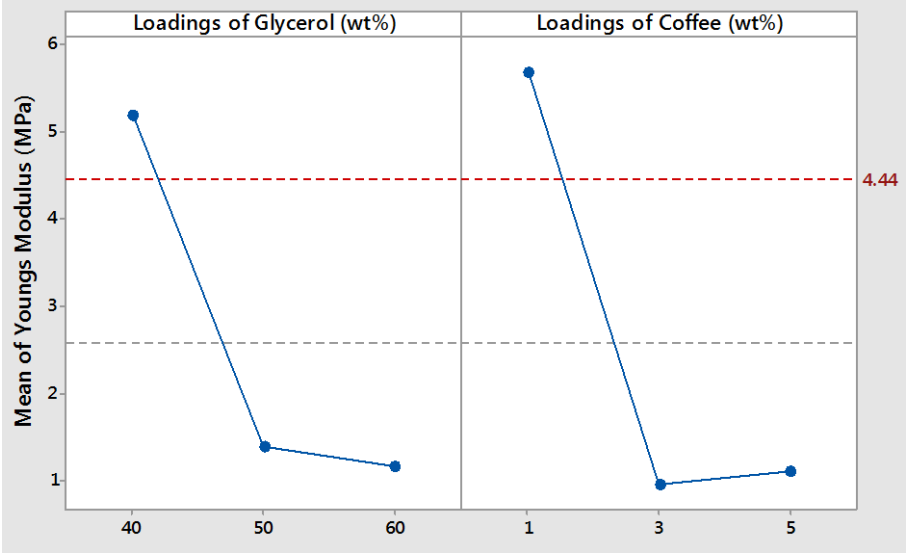

Figure 7. Main effects plot for Young's modulus.

Based on Figure 8, elongation at break of the TPS films were subjected to a slight increment when the concentration of glycerol was increased from 40 to 50 wt. % after which it dropped drastically when the concentration was further increased to 60 wt. %. Hence, the optimum loadings of glycerol was 50 wt. % and it started to exhibit adverse effect when it went beyond this threshold limit. Glycerol for this context was observed as a good plasticizer making the TPS films less brittle. Besides, it could be clearly seen that the elongation at break of TPS/coffee fillers composites increased significantly with the increasing of loadings of coffee fillers from 1 to 5 wt. %, with 5 wt. % as the optimum loading level. The introduction of coffee fillers in TPS composites was more prominent in increasing the elasticity of the materials rather than tensile strength and Young's modulus. The constituents of spent coffee grounds might have led to this behaviour due to the interactions between the lipids contents with the TPS matrix. As glycerol acted as the backbones of lipids molecules in coffee waste and at the same time a good plasticizer in increasing the ductility of

TPS composites, the lipids contents in coffee waste served as the main contributor for this behaviour to be observed [23].

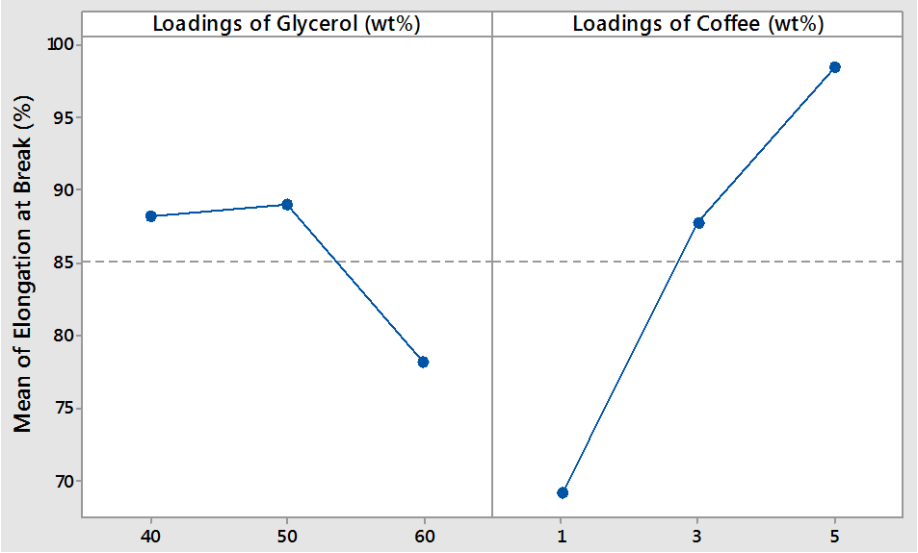

Figure 8. Main effects plot for elongation at break.

4. Conclusions

Incorporation of brand new bio-filler, grinded coffee waste filler into TPS composites films were successfully synthesised via solution casting method with various loadings of coffee fillers and glycerol. The critical mechanical properties, maximum tensile stress, Young's modulus and elongation at break of TPS/coffee-waste-derived fillers composites were evaluated in compliance with international standards as well as compared with non-reinforced control samples to analyse the individual effects of coffee fillers and glycerol on the TPS.

Presence of coffee filler greatly improved the elongation at break accompanied with slight decrement in maximum tensile stress and Young's modulus of the TPS composites. The elongation at break were increased to a maximum of 140 %, while the maximum tensile stress and Young's modulus were declined to 0.21 MPa and 0.37 MPa respectively. However, the positive effect exhibited by coffee filler alone in enhancing the elongation at break of the TPS films showed the potential in producing an elastic material for certain applications such as plastic wrap, simple packaging materials for one time usage and etc. Large particle sizes of coffee fillers might be the main contributor to the decrement in both the tensile strength and Young's modulus. The individual effect of loadings of glycerol on the other hand was insignificant for both maximum tensile stress and Young's modulus, but the elongation an break was improved with increasing loading of glycerol up to 50 wt. % after which adverse changes were observed when the loading was further increased to 60 wt. %. The optimum loadings of coffee fillers and glycerol were found to be 1 wt. % and 40 wt. % respectively in enhancing the mechanical properties of TPS composites as the formulation with this loading level exhibited improved mechanical properties as compared to non-reinforced control samples.

As this research was only designed to serve as the preliminary study of mechanical properties in TPS/coffee-waste-derived composites, it is expected to provide with only the initial studies on the effect of the introduction of coffee fillers in TPS for more detailed research to be carried out in future. The research could be

improved to give more reliable results by producing nano scale coffee waste fillers using planetary ball mile, preceding to the usage for synthesis of TPS composites films. It is suggested to extract the lipids contents of the spent coffee grounds prior to the milling process as clusters of coffee waste could be formed as a result of the vibration and heat generated during the process. Due to the potential of lipids contents of grinded coffee waste in enhancing the elongation at break of the TPS composites, the extracted lipids are necessarily to be transferred back to the nano scale coffee waste fillers for the research purposes. Apart from this, another research that focus on the assessment of water vapour permeation, thermo-mechanical properties and biodegradability of TPS/ coffee fillers composites could be carried out in future in order to further justify the long-term stability of the materials, and hence the applicability in domestic and commercial fields.

References

[1] R. Halden, "Plastics and health risks," *Annu. Rev. Public Health*, vol. 31, pp. 79–94, 2010.

[2] P. Europe, "The Facts 2013: An Analysis of European Latest Plastics Production, Demand and Waste Data," 2013.

[3] U. EPA, "Minucipal solid waste generation, recycling, and disposal in the United States: facts and figures for 2010," *Solid Waste Emerg. Response*, vol. 5350P, p. 12, 2011.

[4] L. Shen, J. Haufe, M. K. Patel, and G. Science, "Product overview and market projection of emerging bio-based plastics," Netherlands, 2009.

[5] D. R. Lu, "Starch-based completely biodegradable polymer materials," *Express Polym. Lett.*, vol. 3, no. 6, pp. 366–375, May 2009.

[6] A. Curvelo, A. De Carvalho, and J. Agnelli, "Thermoplastic starch–cellulosic fibers composites: preliminary results," *Carbohydr. Polym.*, vol. 45, 2001.

[7] Robert Shanks and I. Kong, "Thermoplastic Starch," in *Thermoplastic Elastomers*, A. Z. El-Sonbati, Ed. InTech, 2012, pp. 238–250.

[8] M. Bootklad and K. Kaewtatip, "Biodegradation of thermoplastic starch/eggshell powder composites.," *Carbohydr. Polym.*, vol. 97, no. 2, pp. 315–20, Sep. 2013.

[9] È. Mylla, R. Partanen, and J. Seppa, "Effect of glycerol on behaviour of amylose and amylopectin films," *Carbohydr. Polym.*, vol. 50, pp. 355–361, 2002.

[10] R. Zullo and S. Iannace, "The effects of different starch sources and plasticizers on film blowing of thermoplastic starch: Correlation among process, elongational properties and macromolecular structure," *Carbohydr. Polym.*, vol. 77, no. 2, pp. 376–383, Jun. 2009.

[11] L. Janssen and L. Moscicki, "Thermoplastic starch as packaging material," *Acta Sci. Pol., Tech. Agrar.*, vol. 5, no. 1, pp. 19–25, 2006.

[12] H. A. Pushpadass and M. A. Hanna, "Age-induced changes in the microstructure and selected properties of extruded starch films plasticized with

glycerol and stearic acid," *Ind. Agric. Prod. Cent.*, vol. 48, no. 18, pp. 8457–8463, 2009.

[13] F. Xie, E. Pollet, P. J. Halley, and L. Avérous, "Starch-based nano-biocomposites," *Prog. Polym. Sci.*, vol. 38, no. 10–11, pp. 1590–1628, Oct. 2013.

[14] M. R. T. Rahman, "A Report On Starch Granule : Plant Source Course Title: Advances in Carbohydrate Chemistry," Jiangnan, 2014.

[15] R. Bodîrlău, C. Teacă, and I. Spiridon, "Green Composites Comprising Thermoplastic Corn Starch and Various Cellulose-Based Fillers," *BioResources*, vol. 9, no. 1, pp. 39–53, 2013.

[16] I. Martins, S. Magina, and L. Oliveira, "New biocomposites based on thermoplastic starch and bacterial cellulose," *Sci. Technol.*, vol. 69, pp. 2163–2168, 2009.

[17] L. M. Famá, V. Pettarin, S. N. Goyanes, and C. R. Bernal, "Starch/multi-walled carbon nanotubes composites with improved mechanical properties," *Carbohydr. Polym.*, vol. 83, no. 3, pp. 1226–1231, Jan. 2011.

[18] M. Huang, J. Yu, and X. Ma, "High mechanical performance MMT-urea and formamide-plasticized thermoplastic cornstarch biodegradable nanocomposites," *Carbohydr. Polym.*, vol. 63, no. 3, pp. 393–399, Mar. 2006.

[19] S. Obruca, P. Benesova, S. Petrik, J. Oborna, R. Prikryl, and I. Marova, "Production of polyhydroxyalkanoates using hydrolysate of spent coffee grounds," *Process Biochem.*, vol. 49, no. 9, pp. 1409–1414, Sep. 2014.

[20] P. Esquivel and V. M. Jiménez, "Functional properties of coffee and coffee by-products," *Food Res. Int.*, vol. 46, no. 2, pp. 488–495, May 2012.

[21] S. I. Mussatto, L. M. Carneiro, J. P. a. Silva, I. C. Roberto, and J. a. Teixeira, "A study on chemical constituents and sugars extraction from spent coffee grounds," *Carbohydr. Polym.*, vol. 83, no. 2, pp. 368–374, Jan. 2011.

[22] R. Shi, Z. Zhang, Q. Liu, Y. Han, L. Zhang, D. Chen, and W. Tian, "Characterization of citric acid/glycerol co-plasticized thermoplastic starch prepared by melt blending," *Carbohydr. Polym.*, vol. 69, no. 4, pp. 748–755, Jul. 2007.

[23] L.-C. Wu and C.-M. Cheng, "Flow-injection enzymatic analysis for glycerol and triacylglycerol.," *Anal. Biochem.*, vol. 346, no. 2, pp. 234–40, Nov. 2005.

[24] H.-Y. Wang, H. Qian, and W.-R. Yao, "Melanoidins produced by the Maillard reaction: Structure and biological activity," *Food Chem.*, vol. 128, no. 3, pp. 573–584, Oct. 2011.

[25] R. Bodirlau, C.-A. Teaca, and I. Spiridon, "Influence of natural fillers on the properties of starch-based biocomposite films," *Compos. Part B Eng.*, vol. 44, no. 1, pp. 575–583, Jan. 2013.

[26] A. L. Da Róza, A. J. F. Carvalhob, A. Gandinia, and A. A. S. Curveloa, "The effect of plasticizers on thermoplastic starch compositions obtained by melt processing," *Carbohydr. Polym.*, vol. 63, no. 3, pp. 417–424, 2006.

[27] P. Müller, K. Renner, J. Móczó, E. Fekete, and B. Pukánszky, "Thermoplastic starch/wood composites: interfacial interactions and functional properties.," *Carbohydr. Polym.*, vol. 102, pp. 821–9, Feb. 2014.

[28] M. Hietala, A. P. Mathew, and K. Oksman, "Bionanocomposites of thermoplastic starch and cellulose nanofibers manufactured using twin-screw extrusion," *Eur. Polym. J.*, vol. 49, no. 4, pp. 950–956, Apr. 2013.

[29] X. Ma, J. Yu, and N. Wang, "Fly ash-reinforced thermoplastic starch composites," *Carbohydr. Polym.*, vol. 67, no. 1, pp. 32–39, Jan. 2007.

[30] H. Pushpadass, P. Bhandari, and M. Hanna, “Effects of LDPE and glycerol contents and compounding on the microstructure and properties of starch composite films.,” *Carbohydr. Polym.*, vol. 82, no. 4, pp. 1082–1089, 2010.
[31] D. Lourdin, H. Bizot, and P. Colonna, “Antiplasticization in starch-glycerol films?,” *J. Appl. Polym. Sci.*, vol. 63, pp. 1047–1053, 1997.