Chemically Treated Borneo Sago (*Metroxylon sagu*) Starch Reinforced Poly Lactic Acid Bio-composites

Md. Rezaur Rahman,^{a,*} Sinin Hamdan,^a Rubiyah Binti Baini,^a Muhammad Khusairy Bin Bakri,^{a,*} Muhammad Adamu,^{a,b} Perry Law Nyuk Khui,^a Akshay Kakar,^c and Khairuddin Sanaullah ^{d,e}

Properties of Borneo sago starch reinforced poly-(lactic acid) (PLA) composites were evaluated, with attention to the effects of treatment with acrylic acid, benzene diazonium chloride, and tetrahydrofuran. The PLAsago composites treated with tetrahydrofuran had the highest tensile strength, with a maximum value of 0.85 MPa at 20 wt%; whereas the PLAsago composites treated with benzene diazonium chloride had the highest modulus of elasticity, with a maximum modulus of elasticity of 28 kPa at 5 wt%. Scanning electron microscopy images of the surfaces showed good interfacial contact between the PLA and the sago starch treated with benzene diazonium chloride. The Fourier-transform infrared spectra revealed the functional group characteristics of the chemicals composition of the materials. According to the thermogravimetric analysis results, all of the composites displayed thermal stability up to a temperature of 300 °C. The differential scanning calorimetry analysis revealed that the poly lactic acid-sago composites treated with benzene diazonium chloride had the highest melting point.

Keywords: Treated; Chemical; Poly lactic acid; Borneo; Bio-composites

Contact information: a: Faculty of Engineering, Universiti Malaysia Sarawak, Jalan Datuk Mohammad Musa, Kota Samarahan, Sarawak 94300 Malaysia; b: Nigerian National Petroleum Corporation, NNPC Corporate Headquarters, Abuja, Nigeria; c: Department of Materials Science and Engineering, University of Houston, 4800 Calhoun Road, Houston, Texas 77204, United States; d: Informetrics Research Group, Ton Duc Thang University, Ho Chi Minh City, Vietnam; e: Faculty of Applied Sciences, Ton Duc Thang University, Ho Chi Minh City, Vietnam; *Corresponding authors: rmrezaur@unimas.my; kucaigila@yahoo.com

INTRODUCTION

In the Southeastern region of Asia, sago palm (*Metroxylon sagu*) is highly commercialized, especially in countries such as Malaysia, Indonesia, Papua New Guinea, and the Philippines. A majority of the sago palm tree species grow in extremely wet conditions; however, they are also known to easily adapt to harsh environments (Mohamad Naim *et al.* 2016). Since sago palms have high adaptability towards harsh environments, they do not require extensive monitoring or maintenance. In addition, a majority of the types of sago palm have a relatively high longevity (approximately 25 years) and they may undergo replantation every year (Abd-Aziz 2002).

Currently, Malaysia is the third largest sago palm producer in the world, right after Papua New Guinea and Indonesia (Liestianty *et al.* 2016). In Malaysia, the Borneo island of Sarawak is the largest producer of sago palm, timber, and other sago related products. According to Naim *et al.* (2016), Mukah, Dalat, Matu, and Daro are the four main plantations in Sarawak and are 11,112 hectares, 28,169 hectares, 4,306 hectares, and 3,149 hectares, respectively (Naim *et al.* 2016). Moreover, according to Uthumporn *et al.* (2014), 96% of the supply of sago exported around the world is from Sarawak, Malaysia.

The properties of starch may differ with respect to its gelatinization, physicochemical, retrogradation, rheological, and thermal characteristics. Sago starch has two primary types of applications, food and non-food applications. Examples of food applications include gelling agents, which are used in hard gum candies and jelly gum (Liestianty et al. 2016). Examples of non-food applications include hydrogels-based starches, which are usually applied in pharmaceutical and biomedical applications (Liestianty et al. 2016). Sago starch is known for its hydrophilicity, biocompatibility, and biodegradability (Kumar et al. 2017). It is also non-toxic and is considered a renewable resource. However, sago starch is prone to bacterial attack and has a short shelf life. Furthermore, the native types of sago starch lack mechanical strength and exhibit a high selectivity and sensitivity towards water. The hydrophilic characteristics of the starch cause poor bonding with hydrophobic polymers in starch-polymer blends (Wu 2005). Starch may also cause agglomeration, in the form of starch paste, when acting as an additive to latex type materials (Misman et al. 2016). Thus, to improve the mechanical properties of the composite, sago starch with a reactive functional group was added to a synthetic polymer blend, such as poly lactic acid (PLA).

Biodegradable thermoplastic polyesters, such as PLA, are manufactured via biotechnological processes extracted from renewable resources. PLA has a good set of properties, *i.e.*, biodegradability, biocompatibility, comparable strength, and transparency plate. According to Talbamrung et al. (2016), under a certain minimum conditions and moisture content, PLA and a copolymer can be degraded into non-toxic breakdown products; such degradation can be achieved with non-enzymatic hydrolytic processes. Plasticizers, lubricants, and impact modifiers are several types of additives used during the processing of PLA (Pivsa-Art et al. 2016). According to Ali et al. (2017), the starch-based composite films reinforced with corn/wheat hulls, apricot pits, and walnut shells (Ali et al. 2019), is an example of natural food resources by-products that were converted to rigid particles. After addition of the rigid fillers, the results showed that the materials became stronger. The additives also improved the gas barrier properties when higher density and higher crystallinity was used. Chen et al. (2019) also stated that by adding laver, starch/laver composites improved the gas permeability of starch film significantly. The laver flack (fiber) also acted as reinforcing agent, which improved the mechanical properties of the starch matrix by increasing its modulus and tensile strength.

Most of the applications for PLA are based on biomedical and food packaging such as containers, syringes, basins, *etc.* However, there are a few drawbacks, such as a low deformation at break and a high cost of production and maintenance, noting that the products are intended for hygienic situations (Setiawan 2015). Furthermore, the growing issue of waste disposal has motivated the contributions of researchers to develop new sustainable materials. Notwithstanding the many advantages, there are some drawbacks of implementing starch as a filler for PLA. Sago starch is hydrophilic in nature, which leads to poor adhesion with the hydrophobic polymers in starch-polymer blends. Due to these properties of sago starches, chemical modifications are needed to the relatively weak can der Waals forces that form when sago starch is bonded with a hydrophobic polymer. Hence, the solution was chemically treated *via* copolymerization, which is the most common technique for modifying polysaccharides (Ekabafe *et al.* 2016). Chemical treatment *via* copolymerization causes minimal loss of the native properties of starch (Celli *et al.* 2016). In this study, the modification of sago starch was conducted with three different chemicals: acrylonitrile, benzene diazonium chloride, and tetrahydrofuran. The modified sago starch acted as filler to improve the mechanical, thermal, and morphological properties of the PLA bio-composites.

EXPERIMENTAL

Materials

Polylactic acid (4043D grade) powder had a density of 1.24 g/cm³ and a melting point of 145 °C to 160 °C. Reagent grade acrylic acid (99% purity) was supplied by Sigma Aldrich Co. (St. Louis, Mo) and stored in the dark at 5 °C before it was used. Sago starch was obtained from a sago palm plantation in Mukah, Sarawak. Analytical grade cerium ammonium nitrate and other reagents used were supplied by Sigma Aldrich. The chemicals used to prepare the benzene diazonium chloride were as follows: aniline (99.4% purity), sodium nitrite, and hydrochloric acid. Tetrahydrofuran (91.4% purity) was purchased from J. T. Baker Chemical (Phillipsburg, NJ, USA).

Methods

Sago starch treated with acrylic acid

Five grams of dried sago starch was added to 50 mL of distilled water at 75 °C for 30 minutes in a conical flask. The slurry was cooled to 30 °C, and the temperature was maintained for 10 min. Then, 10 mL of 0.01 M ceric ammonium nitrate (CAN) was added, followed by 10 mL of 0.01 M acrylic acid. Next, another 30 mL of distilled water was added into the conical flask. The solution was left for 10 min before it was heated to 60 °C. After that, the mixture was neutralized with 5% sodium hydroxide, with constant stirring, until the solution turned into a reddish-brown color. It was then allowed to further react at 60 °C until the solution turned a pale yellow. The slurry was cooled down to 25 °C before it was adjusted to a pH of 7 *via* glacial acetic acid. The precipitate was later washed with methanol and ethanol and dried in an oven at 70 °C for 24 h before it was powdered.

Sago starch treated with benzene diazonium chloride

To prepare benzene diazonium chloride, 15 mL of aniline was dissolved into a mixture of 40 mL of concentrated hydrochloric acid and 40 mL of water. The solution then was filled in a flask and cooled to 5 °C by immersing it into a mixture of ice and water. Next, 12.5 g of powdered sodium nitrite was dissolved in 30 mL of water, and was added dropwise to the aniline hydrochloride solution, and was further cooled to 5 °C. After that, 10 g of dried sago starch was added into the solution. The reaction was allowed to react for one hour in an ice-water bath. Finally, the treated sago starch was filtered and dried at 25 °C for 24 h.

Sago starch treated with tetrahydrofuran

A total of 50 g of PLA and 10 g of sago starch was mixed in a beaker; 10 mL of tetrahydrofuran solvent was added. The mixture was stirred for 12 h before casting. The casted plates were dried at ambient temperature for 12 h and peeled from the casting surface.

Preparation of the Bio-composites

The PLA-based sample plates were prepared using a hot press machine under a pressure of 6.89 MPa at 150 °C for 3 to 5 min, and the molds were then quenched in water under room temperature 24 ± 1 °C for curing purposes. The weight percentage of the biodegradable fillers are 5, 10, 17.6, 20, and 33.3 wt%. In order to prepare the biocomposites, 15 samples were prepared with different amounts of treated starch and PLA matrix (by weight percentage).

Testing

Tensile test

The tensile strength and modulus of elasticity were analyzed and compared by referring to the weight percentage of the treated sago starch. The tests were conducted with a Universal Testing Machine (Shimadzu, Kyoto, Japan) with a loading capacity of 300 kN and a cross head speed of 1 mm/min. The test was conducted according to ASTM standard D638-14 (2014) and analyzed at room temperature with a stretch rate of 1 mm/min (similar to the crosshead speed). The average values of the tensile strength and the MOE were tabulated in Figs. 1 and 2, respectively.

Fourier transform infrared (FTIR) spectroscopy

The main purpose of the FTIR test was to differentiate the strong bonds from the weak bonds present in the sample, based on the functional group and chemical bond info from the FTIR results. A Fourier Transform Infrared Spectrophotometer (IRAffinity-1CE, Shimadzu, Kyoto, Japan) was used. The samples were cut into small square pieces with a dimension of 1 cm by 1 cm. The analysis of the specimens was conducted at 27 °C with 20 repeated scans at a spectra resolution of 1 cm⁻¹ and a range of 400 cm⁻¹ to 4000 cm⁻¹ to analyze the interaction between the PLA and the treated sago starch. The tests were conducted according to ASTM standard E168-16 (2016) and ASTM standard 1252-98 (2013).

Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) was conducted to determine and identify the interfacial contact between the PLA matrix and the treated sago starch. The morphology of bio-composites was studied using a tabletop scanning electron micrograph (TM3030, Hitachi, Tokyo, Japan). The dispersion of the bio-composites was observed and captured. The samples were fractured in liquid nitrogen and coated with a thin gold plate. Three different magnitudes of magnification (500x, 1000x, and 1500x) were observed. The test was performed according to ASTM standard E2015-04 (2014).

Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was used to determine the loss of weight of a material, either as a function of time or a function of temperature. The TGA was conducted using a TGA machine (Perkin Elmer, Waltham, MA). The conditions for testing were as follows: 20 mg of each sample was analyzed from ambient temperature to 650 °C at a heating rate of 10 °C/min⁻¹, under a nitrogen environment at a rate of 20 mL/min⁻¹. The test was performed according to ASTM standard E1868-10 (2015) and ASTM standard E1131-08 (2015).

Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) was conducted to analyze the type of response given by the bio-composites *via* heating. The main purpose of the DSC was to investigate the melting of the crystalline polymer or the glass transition of a material. The DSC analysis was done using a DSC machine (Perkin Elmer, Waltham, MA). Approximately 5 mg of each sample was sealed in an aluminum pan and heated from 10 $^{\circ}$ C to 200 $^{\circ}$ C at a rate of 10 $^{\circ}$ C/min⁻¹. The test was performed according to ASTM standard D3418-15 (2015) and ASTM standard E1269-11 (2018).

RESULTS AND DISCUSSION

Mechanical Properties

The mechanical properties were investigated based on the results of the tensile test. Figures 1 and 2 showed the tensile strength and the modulus of elasticity of the PLA-sago composites treated with acrylic acid, benzene diazonium chloride, and tetrahydrofuran.

Figures 1 and 2 show the tensile strength and the modulus of elasticity of the PLAsago composite specimens treated with acrylic acid. The optimal performance for the tensile strength and the modulus of elasticity was found with a composition of 17.6 wt% starch content, for both properties. The tensile strength and modulus of elasticity increased as the sago starch load was increased, from 5.0 wt% to 17.6 wt%, and then it decreased as the load was increased past 17.6 wt%. The highest values for the tensile strength and the modulus of elasticity were 0.33 MPa and 1.4 kPa, respectively, which was attributed to the increased molecular weight and entanglement density of the polymer matrix structure. After the load by weight percentage was increased to more than 17.6 wt%, the tensile strength decreased. The trend of the graphs (as shown in Figs. 1 and 2) showed the ductile properties. Thus, the best overall composition for a PLA matrix with acrylic acid treated sago was a load of 17.6 wt%. The presence of sago starch as a filler acted as an obstruction that separated the molecular chain in the poly lactic acid matrix (Apopei *et al.* 2012). However, a further increased in the filler load (past 17.6 wt%) did not improve the mechanical properties of the PLA matrix.

For the PLA and sago starch treated with tetrahydrofuran, a load of 20 wt% was shown to be the optimal concentration. The addition of sago starch treated with tetrahydrofuran at lower percentages yielded a lower overall tensile strength and modulus of elasticity. The presence of sago starch treated with tetrahydrofuran acted as an obstruction that separated the molecular chain of the PLA. An increase in sago starch as a filler did not improve the mechanical properties of the PLA bio-composites. The trend of the modulus of elasticity also showed an increase in the ductile properties (Jahangir *et al.* 2017).

In terms of tensile strength, a 20.0 wt% load of starch treated with benzene diazonium chloride had the highest value at 0.32 MPa. Loads ranging from 5 wt% to 17.6 wt% yielded a higher ductility than the load with 20.0wt% and 33.3 wt%. However, a 33.3 wt% load showed that the sample was uncharacteristically distorted in terms of the tensile test process. The trend of the graph for the tensile test of a 33.3 wt% load showed elastic deformation that was followed by plastic deformation (Punyamurthy *et al.* 2014).





Fig. 1. Tensile strength of the PLA-sago composites with varying fiber loads (by wt%)







However, a higher modulus of elasticity for sago starch treated with benzene diazonium chloride also showed plastic deformation, which implied that the material was brittle. Thus, the modulus of elasticity of benzene diazonium chloride showed the greatest improvement. A high modulus of elasticity indicated that the sago starch treated with benzene diazonium chloride conferred resistance against elastic deformation when the load was applied on the composites (Punyamurthy *et al.* 2014).

Infrared Spectral Properties

Fourier transform infrared analysis was conducted to analyze the chemical bonding and functional groups formed between the sago starch used as a filler with a PLA matrix. Figures 3, 4, and 5 show the FTIR spectra of the sago starch treated with acrylic acid, tetrahydrofuran, and benzene diazonium chloride, with PLA, respectively. Based on Figs. 3, 4, and 5, the peak assigned to the O-H stretching absorbance (at a range between 3200 cm⁻¹ to 3700 cm⁻¹) was present and intensified. This occurred due to the fact that the -OH group of the starch contributed to the bond stretching vibration (Wu 2005).

A small peak at 1749.44 cm⁻¹ was present, as shown in Fig. 3. The peak was assigned to the ester carbonyl stretching vibration of the copolymer. Based on this observation, branched and crosslinked macromolecules may have been produced, since the copolymer had carboxyl groups to react with the hydroxyl groups of sago starch (Lele 2015). Hence, there was evidence of chemical modifications made by acrylic acid. The - C-H stretch absorbances at 2918.30 cm⁻¹ and 2993.5 2cm⁻¹ were also not present in the FTIR spectra analysis in Fig. 3, when compared with the spectra in Fig. 5. As mentioned above, a 17.6 wt% load of sago starch treated with acrylic acid/PLA was shown to be the best combination. The reason for the disappearance of the stretching was due to the -C-H group in the PLA matrix of the bio-composites showing strong interfacial bonding between the polymer matrix and the sago starch filler.

Figure 4 shows the FTIR spectra for a 20 wt% load of sago starch treated with tetrahydrofuran and a PLA matrix. In addition, the FTIR spectrum of the tetrahydrofuran treated sago starch/PLA (Fig. 4) showed an absorption bond at the wavenumber of 1749.44 cm⁻¹ (Yao *et al* 2019), which indicated the characteristic absorption band of carbonyl groups (C=O) in bio-composites substituents. Hence, this could be the cause of a 20 wt% load of sago starch treated with tetrahydrofuran yielding the optimal results in terms of their mechanical properties.



Fig. 3. FTIR spectra of a 20 wt% load of sago starch treated with acrylic acid/PLA



Fig. 4. FTIR spectra of a 20 wt% load of sago starch treated with tetrahydrofuran/PLA



Fig. 5. FTIR spectra of a 20 wt % load of sago starch treated with benzene diazonium chloride/PLA

Figures 3 and 4 show the presence of a 3200 cm⁻¹ to 3500 cm⁻¹ broad band, which corresponds to the stretching of the O-H bond. Figures 4 and 5 show the peaks between 1665 cm⁻¹ and 1760 cm⁻¹, which corresponded to the stretching of the C=O bonds (Saidi *et al.* 2014).

Figure 5 showed the FTIR spectra for a 20 wt% load of sago starch treated with benzene diazonium chloride/PLA. There were a few common peaks that could be seen, which ranged from 3200 to 3500 cm⁻¹ and 2918 cm⁻¹. Those bonds corresponded to OH stretching and C-H stretching, respectively (Punyamurthy *et al.* 2017). Figures 4 and 5 show a peak at 1749.44 cm⁻¹, which corresponded to C=O carbonyl stretching. The C=O stretching seemed to be dull, which was shown in Fig. 5. This was probably due to the benzene diazonium chloride, which had greater interaction with the carbonyl groups in the PLAs. The benzene diazonium reacted with the hydroxyl groups to produce a nucleophile. This nucleophile was reactive and attacked the electrophile, which was produced from the electron delocalization of the carbonyl group from the PLA matrix (Saidi *et al.* 2014).

Morphological Properties

The interfacial contact at phase boundaries with different percentages of filler loadings for the three different treated sago starches were investigated *via* morphological study. Figure 6 shows an uneven surface through the surface morphologies of a 5.0 wt% load of sago starch with acrylic acid/PLA. The previously stated ductile characteristics were supported by the void fraction displayed in the surface morphologies of the 5.0 wt% load of sago starch treated with acrylic acid/PLA. The poor dispersion of the treated sago starch is shown in Fig. 6.



Fig. 6. Surface morphology of 5.0 wt% load of sago starch treated with acrylic acid/PLA at 200x magnification

Figure 7 shows the SEM images of the uneven surfaces of a 5 wt% load of sago starch with tetrahydrofuran/PLA. The SEM images showed non-uniform cell sizes and

bioresources.com

indicated poor interfacial contact between the treated sago starch and the PLA matrix (Jahangir *et al.* 2017). The gaps that were observed in Fig. 7, indicating that voids were present between the matrix and the treated sago starch, due to the low amount of treated sago starch that filled into the PLA matrix. A large degree of agglomeration of sago starch was observed due to the poor dispersion of the filler; which apparently was the reason that the 5wt.% load of sago starch with tetrahydrofuran exhibited weaker tensile properties when compared to other sample loads (by wt%) (Jahangir *et al.* 2017).



x200 500 µm

Fig. 7. Surface morphology of 5.0 wt% load of sago starch treated with tetrahydrofuran/PLA at 200x magnification



Fig. 8. Surface morphology of 5.0 wt% load of sago starch treated with benzene diazonium /PLA at 200x magnification

Figure 8 shows the surface morphologies of a 5.0 wt% load of sago starch with benzene diazonium chloride/PLA. The ductility improved, and the void fraction was decreased. The void fraction that existed in Figs. 6 and 7 decreased as the holes were filled by sago starch. Thus, there was an interaction between the benzene diazonium chloride treated sago starch and the PLA matrix; whereas no aggregates were observed in Fig. 8, which demonstrated that there was good interfacial contact between the PLA matrix and the sago starch (Punyamurthy *et al.* 2017). In addition, the previously stated ductile properties of the samples could be observed and supported through the surface roughness.

Thermal Properties

Thermogravimetric analysis

The TGA was conducted to calculate the thermal decomposition process for the three treated sago starches and PLA matrix bio-composites. The TGA curves of the sago starch with acrylic acid/PLA are shown in Fig. 9. As shown, all the bio-composites had similar mass loss at approximately 400 °C to 500 °C. The variations that occurred in the thermal stability indicated that there was increase in the molecular weight of the PLA polymer matrix *via* the addition of starch filler (Zhang *et al.* 2003). Sago starch treated with acrylic acid showed thermal stability at 300 °C. This was due to the addition of the filler, which influenced variation in the stabilization temperatures of the PLA polymer matrixes. This effect from adding fillers to the polymer was confirmed by the delayed peak degradation temperature shown in the bio-composites (Ekebafe *et al.* 2016).



Fig. 9. Thermogravimetric analysis (TGA) of PLA-sago composites with 20 wt% loading

Figure 9 shows the TGA curves for the PLA with sago starch treated with tetrahydrofuran. A drastic drop in weight occurred at 300 °C. Variation could be observed in the thermal stability. The delayed peak for the degradation temperature in the biocomposites demonstrated that the addition of fillers to the PLA matrix effected the thermal stability. The peak degradation temperature of the sago starch treated with

tetrahydrofuran/PLA also started at approximately 300 °C. Figure 9 shows the TGA curves for the sago starch treated with benzene diazonium chloride/PLA. A drastic drop in weight occurred at 300 °C. The peak degradation temperature also started at approximately 300 °C. This was attributed to the presence of a barrier effect, which resulted from the remaining polymer layers acting as a diffusion barrier for the oxygen (Apopei *et al.* 2012). Table 2 showed the weight lost at different temperatures for different loads of sago starch with acrylic acid, tetrahydrofuran, and benzene diazonium chloride, with PLA.

Fiber Loading	Sago Starch Treated with Acrylic Acid/PLA						
20 wt%	Temperature	100 °C	200 °C	300 °C	400 °C	500 °C	600 °C
	Weight Loss (%)	1.53	3.64	12.32	90.84	92.80	93.64
	Sago Starch Treated with Tetrahydrofuran/PLA						
	Temperature	100 °C	200 °C	300 °C	400 °C	500 °C	600 °C
	Weight Loss (%)	1.99	3.66	5.31	94.99	96.63	97.18
	Sago Starch Treated with Benzene Diazonium Chloride/PLA						
	Temperature	100 °C	200 °C	300 °C	400 °C	500 °C	600 °C
	Weight Loss (%)	1.53	3.64	12.32	90.84	92.80	93.64

Differential scanning calorimetry (DSC)

The DSC thermograms of the PLA and sago treated with acrylic acid, tetrahydrofuran, and benzene diazonium chloride are shown in Fig. 10.



Fig. 10. Differential scanning calorimetry (DSC) analysis of PLA-sago composites (20 wt%)

As shown, the sago starch treated with benzene diazonium chloride had the highest melting point temperature, while the sago starch treated with acrylic acid had the lowest melting temperature. This was due to the strong structure of dispersion shown in the Figs. 6 to 8, where there is less void and increase in ductility. This was apparent in Fig 8 for benzene diazonium chloride, while many voids were visible in Figs. 6 and 7. As shown in Fig. 10, the first peak appeared at approximately 100 °C, which was assumed to be the melting temperature of the additive in the polymer matrix, while the second peak appeared to be the melting temperature of the sago starch, and the third peak was the melting temperature of the polylactic acid (Saidi *et al.* 2014).

CONCLUSIONS

- 1. Based on the results obtained, a 17.6 wt% load of sago starch treated with tetrahydrofuran PLA composites yielded the optimum results in terms of mechanical properties, as well as the greatest improvement in tensile strength. A 20 wt% load of sago starch treated with benzene diazonium chloride PLA composites had the highest modulus of elasticity.
- 2. According to the SEM results, benzene diazonium chloride treated sago starch PLA composites exhibited good interfacial contact. Fourier transform infrared testing proved the presence of benzene diazonium chloride in the PLA matrix.
- 3. In addition, based on the TGA, the thermal properties of the PLA and sago treated with benzene diazonium chloride were improved. The DSC showed an improvement in the melting temperature and crystallization temperature of the PLA with the addition of benzene diazonium chloride treated sago starch as a filler.

ACKNOWLEDGMENTS

The authors are grateful for the support from the Universiti Malaysia Sarawak (UNIMAS), Grant No. F02/CDRG/1826/2019.

REFERENCES CITED

- Abd-Aziz, S. (2002). "Sago starch and its utilization," *Journal of Bioscience and Bioengineering* 94(6), 526-529. DOI: 10.1016/S1389-1723(02)80190-6
- Ali, A., Yu, L., Liu, H., Khalid, S., Meng, L., and Chen, L. (2017). "Preparation and characterization of starch-based composite films reinforced by corn and wheat hulls," *Journal of Applied Polymer Science* 134(32), 1-9. DOI: 10.1002/app.45159
- Ali, A., Ali, S., Yu, L., Liu, H., Khalid, S., Hussain, A., Qayum, M. M. N., and Ying, C. (2019). "Preparation and characterization of starch-based composite films reinforced by apricot and walnut shells," *Journal of Applied Polymer Science* 136(38), 1-10. DOI: 10.1002/app.47978
- Apopei, D. F., Dinu, M. V., and Drăgan, E. S. (2012). "Graft copolymerization of acrylonitrile onto potatoes starch by ceric ion," *Digest Journal of Nanomaterials and Biostructures* 7(2), 707-716.

- ASTM D3418-15 (2015). "Standard test method for transition temperatures and enthalpies of fusion and crystallization of polymers by differential scanning calorimetry," ASTM International, West Conshohocken, PA. DOI: 10.1520/D3418-15
- ASTM D638-14 (2014). "Standard test method for tensile properties of plastics," ASTM International, West Conshohocken, PA. DOI: 10.1520/D0638-14
- ASTM E1131-08 (2015). "Standard test method for compositional analysis by thermogravimetry," ASTM International, West Conshohocken, PA. DOI: 10.1520/E1131-08R14
- ASTM E1252-98 (2013). "Standard practice for general techniques for obtaining infrared spectra for qualitative analysis," ASTM International, West Conshohocken, PA. DOI: 10.1520/E1252-98R13E01
- ASTM E1269-11 (2018). "Standard test method for determining specific heat capacity by differential scanning calorimetry," ASTM International, West Conshohocken, PA. DOI: 10.1520/E1269-11R18
- ASTM E168-16 (2016). "Standard practices for general techniques of infrared quantitative analysis," ASTM International, West Conshohocken, PA. DOI: 10.1520/E0168-16
- ASTM E1868-10 (2015). "Standard test methods for loss-on-drying by thermogravimetry," ASTM International, West Conshohocken, PA. DOI: 10.1520/E1868-10R15
- ASTM E2015-04 (2014). "Standard guide for preparation of plastics and polymeric specimens for microstructural examination," ASTM International, West Conshohocken, PA. DOI: 10.1520/E2015-04R14
- Celli, A., Sabaa, M. W., Jyothi, A. N., and Kalia, S. (2016). "Chitosan and starch-based hydrogels via graft copolymerization," in: *Polymeric Hydrogels as Smart Biomaterials*, S., Kalia (ed.) Springer, Cham, Switzerland. DOI: 10.1007/978-3-319-25322-0_8
- Chen, Y., Yu, L., Ge, X., Liu, H., Ali, A., Wang, Y., Chen, L. (2019) "Preparation and characterization of edible starch film reinforced by layer," *International Journal of Biological Macromolecules*, 129(1), 994-951. DOI: 10.1016/j.ijbiomac.2019.02.045
- Ekebafe, L. O., Ogbeifun, D. E., and Okieimen, F. E. (2016). "Effect of reaction conditions on the grafting indices of hydrolyzed starch copolymers," *Nigerian Journal of Polymer Science and Technology* 11(1), 75-84.
- Jahangir, M. A., Rumi, T. M., Wahab, M. A., Khan, M. I., Rahman, M. A., and Sayed, Z. B. (2017). "Poly lactic acid (PLA) fibres: Different solvent systems and their effect on fibre morphology and diameter," *American Journal of Chemistry* 7(6), 177-186. DOI: 10.5923/j.chemistry.20170706.01
- Kumar, D., Pandey J., Raj, V., and Kumar, P. (2017). "A review on the modification of polysaccharide through graft copolymerization for various potential applications," *The Open Medical Chemistry Journal* 11(1), 109-126. DOI: 10.2174/1874104501711010109
- Lele, V. (2015). "Ceric ion initiated graft copolymerization of insoluble potato starch with acrylic acid," *International Journal of Applied Research* 1(10), 107-110.
- Liestianty, D., Rodianawati, I., Patimah, and Muliadi (2016). "Chemical composition of modified and fortified sago starch (*metroxylonsp*) from northern Maluku," *International Journal of Applied Chemistry* 12(3), 243-249.
- Misman, M. A., Azura, A. R., and Hamid, Z. A. A. (2016). "The effect of acrylonitrile concentration on starch grafted acrylonitrile (ANS) stability in carboxylated nitrile

butadiene rubber (XNBR) latex," *Procedia Chemistry* 19(1), 770-775. DOI: 10.1016/j.proche.2016.03.083

- Naim, H. M., Yaakub A. N., and Hamdan, D. A. A. (2016). "Commercialization of sago through estate plantation scheme in Sarawak: The way forward," *International Journal of Agronomy* 94(1), 1-6. DOI: 10.1155/2016/8319542
- Pivsa-Art, S, Kord-Sa-Ard, J., Pivsa-Art, W., Wongpajan, R., O-Charoen, N., Pavasupree, S., and Hamada, H. (2016). "Effect of compatibilizer on PLA/PP blend for injection molding," *Energy Procedia* 89(1), 353-360. DOI: 10.1016/j.egypro.2016.05.046
- Punyamurthy, R., Sampathkumar, D., Ranganagowda, R. P., Bennehalli, B., Dadyankal, P., and Venkateshappa, S. C. (2014). "Surface modification of abaca fiber by benzene diazonium chloride treatment and its influence on tensile properties of abaca fiber reinforced polypropylene composites," *Ciência & Tecnologia dos Materiais* [Science and Technology of Materials] 26(2), 142-149. DOI: 10.1016/j.ctmat.2015.03.003
- Punyamurthy, R., Sampathkumar, D., Ranganagowda, R. P. G., Bennehalli, B., and Srinivasa, C. V. (2017). "Mechanical properties of abaca fiber reinforced polypropylene composites: Effect of chemical treatment by benzenediazonium chloride," *Journal of King Saud University - Engineering Science* 29(3), 289-294. DOI: 10.1016/j.jksues.2015.10.004
- Saidi, M. A. A., Rahman, W. A. W. A., and Majid, R. A. (2014). "Effect of different solvents on the thermal, IR spectroscopy and morphological properties of solution casted PLA/starch films," *Malaysian Journal of Fundamental and Applied Science* 10(1), 33-36. DOI: 10.11113/mjfas.v10n1.67
- Setiawan, A. H. (2015). "Determination of crystallization and melting behaviour of polylactic acid and polypropyleneblends as a food packaging materials by differential scanning calorimeter," *Procedia Chemistry* 16(1), 489-494. DOI: 10.1016/j.proche.2015.12.083
- Talbamrung, T., Kasemsook, C., Sangtean, W., Wachirachuttapong, S., and Thingpin. C. (2016). "Effect of peroxide and organoclay on thermal and mechanical properties of PLA in PLA/NBR melted blend," *Energy Procedia* 89(1), 274-281. DOI: 10.1016/j.egypro.2016.05.035
- Uthumporn, U., Wahidah, N., and Karim, A. A. (2014). "Physicochemical properties of starch from sago (*Metroxylon sagu*) palm grown in mineral soil at different growth stages," in: 2014 Global Conference on Polymer and Composite Materials 27-29 May, Ningbo, China, pp. 12-26. DOI: 10.1088/1757-899X/62/1/012026
- Wu, C.-S. (2005). "Improving polylactide/starch biocomposites by grafting polylactide with acrylic acid characterization and biodegradability assessment," *Macromolecular Bioscience* 5(4), 352-361. DOI:10.1002/mabi.200400159
- Yao, J., Ji, H., Lu, H., and Gao, T. (2019). "Effect of tetrahydrofuran extraction on surface functional groups of coking coal and its wettability," *Journal of Analytical Methods in Chemistry* 2019(1), 1-8. DOI: 10.1155/2019/1285462
- Zhang, L., Gao, J., Tian, R., Yu, J., and Wang. W. (2003). "Graft mechanism of acrylonitrile onto starch by potassium permanganate," *Journal of Applied Polymer Science* 88(1), 146-152. DOI: 10.1002/app.11614

Article submitted: Nov. 27, 2019; Peer review completed: Dec. 31, 2019; Revised version received: Jan. 7, 2020; Accepted: Jan. 12, 2020; Published: January 21, 2020. DOI: 10.15376/biores.15.1.1641-1655