# Effect of seaweed on storage modulus of thermoplastic sugar palm Starch/Agar composites

R. Jumaidin<sup>1,3\*</sup>, S. M. Sapuan<sup>1</sup>, M. S. Zakaria<sup>2,3</sup>, A. F. Ab Ghani<sup>1,3</sup> and M. I.H.C Abdullah<sup>1,3</sup>

<sup>1)</sup> Fakulti Teknologi Kejuruteraan Mekanikal dan Pembuatan, Universiti Teknikal Malaysia Melaka,

Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia

<sup>2)</sup> Department of Mechanical and Manufacturing Engineering, Universiti Putra Malaysia,

43400 UPM Serdang, Selangor, Malaysia

<sup>3)</sup> Fakulti Teknologi Kejuruteraan Mekanikal dan Pembuatan, Universiti Teknikal Malaysia Melaka,

Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia

<sup>4)</sup>Centre for Advanced Research on Energy, Universiti Teknikal Malaysia Melaka,

Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia

\*Corresponding e-mail: ridhwan@utem.edu.my

Keywords: thermoplastic starch; seaweed; sugar palm

ABSTRACT – This paper presents the effect of seaweed on the storage modulus of thermoplastic sugar palm starch/agar (TPSA) composites. The TPSA/seaweed composites were fabricated by addition of 10 to 40wt% seaweed into TPSA matrix. The samples were hot pressed into 3 mm thickness plate using hot compression moulding. Dynamic mechanical testing (DMA) was conducted on all samples at a temperature range of 25 to 150°C. The results show that the storage modulus of all samples decreased gradually when subjected to increasing temperature. Incorporation of seaweed has increased the storage modulus of the material. The loss modulus of the composites was also increased which indicates higher viscosity of the material. In conclusion, the addition of seaweed has improved the storage modulus and loss modulus of TPSA composites.

# 1. INTRODUCTION

In recent, the awareness to reduce environmental pollution from plastic disposal has attracted the attention of many researchers to develop fully biodegradable materials. Biopolymer derived from natural resources is a promising alternative to the conventional petroleum based polymer. Among biopolymers, starch is one of the most interesting material to produce biodegradable plastics namely thermoplastic starch (TPS). TPS has been studied extensively due to the thermoplastic behavior of the material accompanied with its low cost, biodegradable and renewable characteristic [1], [2]. However, the pure thermoplastic starch has poor mechanical properties and very sensitive to moisture.

Eucheuma cottonii (also known as Kappaphycus Alvarezii) is a red macroalga which commercially known for producing k-carrageenan, a sulfated polysaccharide used as thickening agent in food and non-food industry [3]. In the meantime, the production of k-carrageenan from the seaweed also produce enormous amount of solid waste since the content of k-carrageenan varies from only 25 to 35% from the whole seaweed weight which is yet to be utilized.

Sugar palm (Arenga pinnata) is a unique plant which belongs to Palmae family and believe to be native to South East Asia [4]–[7]. According to Ishak et al., [8] apart from producing sugar, this tree is able to produce starch from the trunk. Sahari et al., [9] has developed the thermoplastic starch derived from native sugar palm starch. Nevertheless, the mechanical properties of the material were reported to be poor and further modification is needed. In our earlier study [1], [10], the modification of thermoplastic sugar palm starch with agar has shown significant improvement in the mechanical properties of the material. In addition, further modification of the thermoplastic sugar palm starch/agar blend with Eucheuma cottonii seaweed waste indicate good miscibility of the materials which led to improvement in the mechanical properties and thermal stability of the material [11]. However, the increase in the thermal stability shown in TGA results was reported based on reduced weight loss of the material, whereas, the initial decomposition temperature of the material suffers slight loss following the incorporation of seaweed waste

Therefore, it is important to study the dynamic mechanical properties of seaweed reinforced thermoplastic SPS/agar blends in order to investigate the behavior of this material when subjected to increasing temperature. Although several studies on the modification of thermoplastic starch has been reported, it is clear from literature that no study carried out the dynamic mechanical analysis of thermoplastic sugar palm starch/agar modified with Eucheuma cottonii seaweed wastes.

# 2. RESEARCH METHODOLOGY

# 2.1 Materials

Sugar palm starch (SPS) was produced from sugar palm tree at Jempol, Negeri Sembilan, Malaysia. The starch was extracted through several process. The tree was cut into section and the interior part was crushed to extract the woody fibers that contain the starch. The woody fibers were soaked and squeezed in fresh water to dissolve the starch from the fiber. The water solution was filtered and the starch was collected after sedimentation process. The wet starch is dried in open air for 48h prior to oven drying at 105°C fo24h.

Agar powder was purchased from R&M Chemicals, Malaysia and glycerol was procured from Science chem, Malaysia.

Eucheuma cottonii solid wastes was obtained after hot

alkaline extraction process to obtain k-carrageenan. The seaweed waste was cleaned with water and dried at 80  $^{\circ}$ C for 24 h. The dried seaweed wastes were ground and sieved then kept in zip-locked bags until further process. The average particle size of the ground seaweed waste is 120 $\mu$ m.

## 2.2 Sample preparation

The biocomposites was prepared using thermoplastic sugar palm starch/agar (TPSA) as the matrix and seaweed waste as the reinforcement. TPSA was prepared by addition of glycerol followed by premixing using high speed mixer at 3000 rpm for 5 min. The ratio of starch, agar, and glycerol was maintained at 70:30:30. The resulting blend was melt-mixed using Brabender Plastograph at 140 °C and rotor speed of 20 rpm for 10 min. This mixture was granulated by means of a blade mill equipped with a nominal 2 mm mesh. Then, the granulate was thermo-pressed for 10 min at 140 °C under the load of 10 tonnes to produce laminate plate with 3 mm thickness. The same processes were used for the modification of TPSA with 10, 20, 30, and 40 wt. % of seaweed. All samples were pre-conditioned at 53% RH for at least 2 days prior to testing.

### 2.3 Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis (DMA) for seaweed reinforced/TPSA were conducted according to ASTM D5023 standard. The measurements were carried out using a DMA instrument (TA Instruments (New Castle, DE) model Q800 V20.24 Build 43) operated in flexure mode at a frequency of 1Hz in a nitrogen atmosphere. The dimensions of the samples were 50 mm x 10 mm x 3 mm. The samples were mounted on a specimen holder in three-point bending condition. The dynamic storage modulus was recorded as a function of temperature from ambient temperature (25°C) to 150°C, at a constant heating rate of 2°C/min.

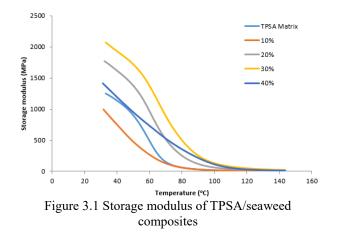
### 3. RESULTS AND DISCUSSION

#### 3.1 Storage modulus

In general, storage modulus is the elastic modulus of a material that defines the recoverable strain energy of the materials. It represent the elastic behavior of materials when subjected to increasing temperature. In addition, this properties also indicates the stiffness of the materials. Figure 2 shows the variation of storage modulus as a function of temperature. It can be seen that the TPSA matrix shows decreasing storage modulus when subjected to increasing temperature. As the temperature increased from 25 to 140°C, the storage modulus of the sample decreased gradually. According to the previous study [12], the decreasing trends is a typical results for glassy amorphous solids. This finding is in good agreement with the previous studies on thermoplastic starch [13].

Incorporation of seaweed into TPSA has led to increase in the storage modulus of the material. The highest value is observed for the composites with 30wt% seaweed. The improvement in the storage modulus of the composites might be attributed to several reasons. Firstly, both seaweed and the TPSA are hydrophilic in nature which led to good adhesion between them. This finding is in agreement with Phan et al [14] which indicates improvement in the mechanical properties of the material following the combination of compatible materials. Secondly, combination of compatible material led to formation of new hydrogen bonding which aid in improving the mechanical properties of the material [11]. Finally, the presence of residual carrageenan in the seaweed waste might form a network with the TPSA, therefore improving the modulus of the material. This might be associated with the previous finding which reported improvement in the tensile modulus of thermoplastic starch following the incorporation carrageenan [15].

However, the addition of seaweed at 40wt% resulted to drop in the storage modulus of the material. This phenomenon might be associated to matrix discontinuity following excessive filler content in the matrix. Another study conducted by Jawaid et al. [16] also reported improvement in the storage modulus of composites following the incorporation of jute and oil palm fiber. The author attributed the improvement to high modulus of elasticity of the fiber than the matrix. Sim et al. [17] reported significant improvement in the loss modulus of poly(lactic acid) composites following the addition of red algae fiber.



#### 4. SUMMARY

This study evaluated the storage modulus behavior of TPSA/seaweed composites. It was found that all TPSA/seaweed composites show decreasing trend of storage modulus with elevating temperature from 25 to 150°C. This was associated with higher mobility of polymer chain at increasing temperature. The incorporation of seaweed has increase the storage modulus of TPSA composites. TPSA/seaweed composites with 30wt% seaweed content shows the highest storage modulus. In general, the incorporation of seaweed into TPSA increased the stiffness of the material by reducing the free movement of the polymer chain.

# REFERENCES

- Jumaidin, R., Sapuan, S. M., Jawaid, M. & Ishak, M. R. (2017). Effect of Agar on Flexural, Impact, and Thermogravimetric Properties of Thermoplastic Sugar Palm Starch. *Current Organic Syntesis*, 14, 200–205.
- [2] Jumaidin, R., Sapuan, S. M., Jawaid, M., Ishak, M.

R. & Sahari, J. (2017). Thermal, mechanical, and physical properties of seaweed/sugar palm fibre reinforced thermoplastic sugar palm Starch/Agar hybrid composites. *International Journal of Biological Macromolecules*, 97, 606–615.

- [3] Khambhaty, Y. *et al.* (2012). Kappaphycus alvarezii as a source of bioethanol. *Bioresourource Technology*, 103, 180–185.
- [4] Huzaifah, M. R. M., Sapuan, S. M., Leman, Z., Ishak, M. R. & Maleque, M. A. (2017). A review of sugar palm (Arenga pinnata): Application, fibre characterisation and composites. *Multidiscipline Modeling in Materials and Structures*, 13, 678–698.
- [5] Huzaifah, M. R. M., Sapuan, S. M., Leman, Z. & Ishak, M. R. (2017). Comparative study on chemical composition, physical, tensile, and thermal properties of sugar palm fiber (Arenga pinnata) obtained from different geographical locations. *BioResources*, 12, 9366–9382.
- [6] Ilyas, R. A., Sapuan, S. M. & Ishak, M. R. (2018). Isolation and characterization of nanocrystalline cellulose from sugar palm fi bres (Arenga Pinnata). *Carbohydrate Polymers*, 181, 1038–1051.
- [7] Ilyas, R. A., Sapuan, S. M., Ishak, M. R. & Zainudin, E. S. (2017). Effect of delignification on the physical, thermal, chemical, and structural properties of sugar palm fibre. *BioResources*, 12, 8734–8754.
- [8] Ishak, M. R. *et al.* (2013). Sugar palm (Arenga pinnata): Its fibres, polymers and composites. *Carbohydrate Polymers*, 91, 699–710.
- [9] Sahari, J., Sapuan, S. M., Zainudin, E. S. & Maleque, M. A. (2013). Thermo-mechanical behaviors of thermoplastic starch derived from sugar palm tree (Arenga pinnata). *Carbohydrate Polymers*, 92, 1711–1716.
- [10] Jumaidin, R., Sapuan, S. M., Jawaid, M., Ishak, M. R. & Sahari, J. (2016). Characteristics of Thermoplastic Sugar Palm Starch/Agar Blend: Thermal, Tensile, and Physical Properties. *International Journal of Biological Macromolecules*, 89, 575–581.
- [11] Jumaidin, R., Sapuan, S. M., Jawaid, M., Ishak, M. R. & Sahari, J. (2017). Effect of seaweed on mechanical, thermal, and biodegradation properties of thermoplastic sugar palm starch/agar composites. *International Journal of Biological Macromolecules*,
- [12] Wu, M., Wang, L. J., Li, D., Mao, Z. H. & Adhikari, B. (2013). Effect of flaxseed meal on the dynamic mechanical properties of starch-based films. *Journal of Food Engineering*, 118, 365–370.
- [13] Zhang, Y. R., Wang, X. L., Zhao, G. M. & Wang, Y. Z. (2013). Influence of oxidized starch on the properties of thermoplastic starch. *Carbohydrate Polymers*, 96, 358–364.
- [14] Phan, D., Debeaufort, F. & Luu, D. (2005). Functional Properties of Edible Agar-Based and Starch-Based Films for Food Quality Preservation. *Journal of Agricultural and Food Chemistry* 53, 973–981.
- [15] Flores, A. C., Punzalan, E. R. & Ambangan, N. G. (2015). Effects of Kappa-Carrageenan on the

Physico-Chemical Properties of Thermoplastic Starch. *Kimika* 26, 11–17.

- [16] Jawaid, M., Khalil, H. P. S. A., Hassan, A., Dungani, R. & Hadiyane, A. (2013). Effect of jute fibre loading on tensile and dynamic mechanical properties of oil palm epoxy composites. *Composites Part B*, 45, 619–624.
- [17] Sim, K. J., Han, S. O. & Seo, Y. B. (2010). Dynamic mechanical and thermal properties of red algae fiber reinforced poly(lactic acid) biocomposites. *Macromolecular Research*, 18, 489–495.