Mechanical Properties of Gracilaria Lichenoides Reinforced Bioplastic Film

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Abstract. In this study, the mechanical properties of gracilaria lichenoides with additional of plasticizer and filler were evaluated. For samples with the addition of 5.5% of plasticizer, produced low tensile strength and this results is vice versa with elongation at break results. The tensile strength of the bioplastic continuously decreases from 14.8 to 2.7MPa as the plasticizer increases up from 1.5% to 5.5%. This phenomenon was analyses under scanning electron microscope (SEM), it shows that, the formation of pores and crystal agglomeration at sample with 5.5% glycerin. To alter these flaws, squid bone is introduce as filler to the bioplastic. Based on the analysis, additional of 6% filler content did alter the tensile strength up to 8 MPa with 3% of the elongation at break.

1. Introduction
Almost every commercial type of plastic currently used in industry is based on petrochemical which is chemical products derived from petroleum [1]. However, petroleum is a finite resource because it formed over millions of years and is being used faster than it is being formed. They will eventually run out. Besides, as the petrochemical based polymers produced, consumed and discarded into the environment, they ending up as non-degradable waste [1,2]. Recently, concerns focus on the potential impact of artificial substances on human health, waste management and environmental damage. While recycling and incineration represent as the alternatives to landfill disposal of plastic products, they understandably also have their own weaknesses [3]. Recycling plastics will deteriorate the quality of the plastic itself and at the same time the costs can also be high. Therefore, intensive research and industrial efforts have focused on the movement in the plastics industry towards sustainability by production of biopolymers as a green alternative to synthetic polymers. Basically, there are four main types of biopolymer based respectively on which are starch, sugar, cellulose and synthetic materials. The main strategies may be followed in syntheszing a polymer which is to build up the polymer structure from a monomer through chemical polymerization. The alternative is to use a naturally occurring polymer and chemically modify it to give it the desired properties. The current and future
development in plastics industry is mainly concerned with using these biopolymers to form more viable materials for mass plastic production by increasing its availability and reducing prices. Algae based bioplastics have been a recent trend in the era of bioplastics compared to traditional methods of utilizing feedstock of corn and potatoes as plastics [4]. While algae-based plastics are in their commencement, once they are into commercialization they are likely to find applications in a wide range of industries. Algae are an interesting natural resource because they proliferate quickly and not impinging on food production [5]. They need nothing but sunlight and a bit of waste water to grow on. Hence, Algae are not harmful to marine’s life, instead considered unsightly and customers want to control or eliminate it. They serve as an excellent feedstock for plastic production owing to its many advantages such as high yield and the ability to grow in a range of environments.

2. Experimental Procedures
The gracilaria lichenoides powder used for preparation of biopolymer plastic and plasticizer which was glycerin (99.0-101.0%, HmbG Chemicals) were purchased from Progressive Scientific Sdn Bhd. The acetic acid used as additive was purchased from local market. Squid bone used as filler was obtained from Pasar Besar Gombak, Selangor Malaysia. The gracilaria lichenoides powder, water, acetic acid and glycerin were mixed together in a single beaker. After that, the mixture was heated on the hot plate, set temperature of 90°C and magnetic stirrer velocity of 3 rpm. Different formulations were prepared by varying glycerin content in each formulation. A series of agar blends were processed into films by casting method. Pure gracilaria lichenoides films were prepared as a control. The film-forming solution was cast into a square mold. After drying in an oven at temperature of 50°C for 10h, the film was obtained. Meanwhile, with the addition of squid bone filler, the squid bone was washed and dried in the lab dryer for temperature of 40°C within 30 min. Then, it was ground by using blender, model Panasonic MX-798S. Then, it followed the same process took place was same as making algae based matrix biopolymer.

Tensile test was applied according to the technical standard method ASTM D882 using the tensile machine (SHIMADZU, Autograph AGS-X). Measurements were carried out at 25°C and crosshead rate of 5 mm/min with the load of 5 kN. For each sample, 7 specimens were tested. The sample preparation first been done by using Tensile Cutter machine (Standard Toggle Press) to form dumbbell cut. Morphological analysis for the thin film of algae based bioplastic samples were carried out by using Scanning Electron Microscope (JEOL JSM 5600). Before the electron microscopy observation, the surfaces were placed on the aluminum stubs by using two-sided adhesive tape and sputter coated with an alloy of 60% gold (Au) and 40% palladium (Pd) using (JEOL JFC-1600). SEM imaging was performed at an acceleration voltage of 7 kV.

3. Results and Discussion
The tensile strength and elongation at break of the algae sample without filler and different percentage of glycerin content are shown in figure 1, the tensile strength of bioplastic sample decreases with increasing amount of plasticizer used. As the content of glycerin increase from 1.5% to 5.5%, the tensile strength (TS) values of the bioplastic decreases from 14.8 to 2.7 MPa. Polyol, such as glycerol, has two plasticizing effects; first as a result of its presence in the film and second because its intensively hygroscopic character tends to draw additional water into the matrix [6]. Therefore, as the plasticizer amount increased, the numbers of plasticizer molecules that reside between polymer chains were also increased. Thus, the intermolecular spacing between the polymer chains networks also increased and allowing the water molecules to go through the films, resulting in lowered the tensile strength. In addition, absorption of water vapor from the surrounding due to hydrophilic properties of plasticizer can cause swelling of the polymer film. This can also be the possibility of reduction in interaction between the polymer chains. The results obtained was in agreement with the previous research conducted by Amman Ullah et al.,[2] whereby the weak tensile properties of albumin glycerol
plastics could have been explained through disordered conformations as the relatively large chemical structure of glycerol prevented any long range plasticization to occur and vice versa [7].

![Figure 1. Samples with glycerin content on the tensile strength and elongation at break.](image)

In terms of the extension that occurred before breaking, the sample with higher amount of glycerin used as plasticizer produced higher amount of extension which elongate nearly 18.3% on average before a ductile break. Meanwhile, the other sample with lower amount of plasticizer only extended around 4.1% before breaking. This clearly showed that, the plasticizer molecules affect the strength of the interactions between adjacent molecules, increasing the distance and thus reducing the internal force which gives more flexibility to the films. The possible reason that can be suggested was the bonding that occurred within the structure as plasticization occurred, which had been found in previous research. The study suggested that the tensile test results show incorporating the red algae bioplastics with glycerol did not improved their ductility and the use of glycerol even reduced their tensile strength and energy absorption [8].

Due to higher tensile strength poses by the sample with 1.5% of glycerin, further experimental research had been conducted on it with the addition of squid bone filler to enhance its properties. Based on figure 2, reinforcement of sample by squid bone filler led to increase in tensile strength up to concentration of 3%. At that concentration, squid bone filler seem to form skeleton with interconnected grain in bioplastic that bear mechanical load. However, at concentration of 5%, the mechanical strength was lower. This shows that, maximum amount of filler which gave the highest value of tensile strength was up to 3% only and the value obtained was two times smaller than pure bioplastic matrix. This result in accordance to Sundaram et al. [4] and Zhang et al.[7] that mention the trend of increasing tensile strength of bio-composite does not follow a straight line relationship with filler concentration [9,10]. The filler content affects the interparticle distance and the stress state of matrix polymer surrounding the voids [11]. At low filler concentration, the particle distance is long so the interparticle matrix ligament lies in plane strain state which is hard to yield so that mechanical strength cannot be improved. But if the filler concentration is increased so that the interparticle distances reach the suitable range, the interparticle matrix ligament lies in plane press state which can be plastic yield easily and the mechanical strength can be improved [12].
Figure 2: Sample with filler content on the tensile strength and elongation at break.

It was clear that as shown in figure 2 that increasing content of squid bone filler improved its tensile strength. However, this strength achieved maximum value for sample with 3% of squid bone filler, at 5% the tensile strength was going down due to the limited binder bonding the particle.

When all bioplastic were analyzed through scanning electron microscopy, the images illustrated that samples with 1.5% glycerin content gave more fairly homogenous mixture of algae and the plasticizer microstructure compared to samples with 5.5% glycerin content. The structure of thin film with lower amount of plasticizer is considered as homogenous and dense due to the continuous cross section without defects up to the highest magnification used which was 1000x as in figure 2.

When higher amount of plasticizer being added in to the biofilm, up to 5.5%, a few irregular particles were visible on the surface of the biofilm. The microstructure observed have pores and cracks which clearly can be seen started at the magnification of 500x and above. From the analysis, it was found that, the important to use the right amount of plasticizer in order to alter the structure and morphology surface of the biofilm. This finding was supported by the fact that glycerol is known to enter polysaccharides chain interior, disrupted intermolecular and intramolecular hydrogen bonds and made the polymer plastic forming a continuous phase of plasticized film [13]. Furthermore, at higher percentage of plasticizer, the surface becomes uneven and heterogeneous as pores and cracks structure appeared especially at the highest magnification as shown in the figure 3. This phenomenon can be
explained with the reference to previous study conducted by Jones et.al.,[12] regarding the moisture and glycerol effect occurred during the SEM been operated [9-12]. According to them, glycerol may leach from the plastic on a much smaller scale with the moisture being removed from the sample when SEM chamber was sealed under high vacuum. As the glycerol slowly released into the environment, it left pores inside the plastic and the pores would be able to absorb water from the surrounding environment. Furthermore, the crack formation resulted when the SEM chamber was sealed and moisture was vacuumed from the testing chamber. This induced strong and rough dehydration on the sample which creates cracks visible in the observation. Based on the results from this morphological analysis, it can be concluded that the properties of plastic thin films may altered as they were able to absorb moisture from the atmosphere and influenced the homogeneity of structure.

Figure 4: SEM micrographs of biofilms reinforced at magnifications of 2000x.

The morphology of squid bone filler and Algae matrix thin films were investigated by SEM. figure 4 shows the surface morphology of Algae bioplastic blends with squid bone filler contents of 1g, 3g and 5g. With the addition of 1g and 3g of fillers, it was possible to see a compatible microphase in the algae matrix biopolymer even though some squid bone flakes appeared on its structure. Generally, these indicate that the two materials are compatible to each other. A quite different morphology was observed for 5g content of filler while there were some small holes may have been caused by the exit of filler and air during the processing procedure. Besides, there were some small particles could be found. This change in behavior means that the adhesion between two components has become poorer as the filler content increases.

4. Conclusion
From the study, it can be concluded that roles of glycerin have a considerable influence on the mechanical properties of algae based bioplastic. Based on the mechanical properties of the bioplastic, it was revealed that the amount of glycerol used as plasticizer at 1.5%, the properties observed of the fabricated thin films were the best by having the highest tensile strength but in reverse effect on the percentage of elongation. In addition, the squid bone as filler for the algae matrix bioplastic gave highest tensile strength when the maximum amount of filler achieved at 3%. The difference in amount of glycerol and filler used did play a significant role affected the mechanical properties of the bioplastic. Evaluation work on morphological study also been carried out under SEM observation which pointed out that the change in surface morphology and increase in amorphous content on the addition of plasticizer and filler.

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References

[1] Coupland, IN., Shaw, N.B., Monahan, FJ., a'Riordan, D. & O'Sullivan, M., 2000 *Journal of Food Engineering* **43** pp 25-30

[2] Aman Ullah T.V., Bressler D., Elias A.L.,& Jianping W., 2011 *Biomacromolecules* **12** pp 3826–3832

[3] M. Nizar Machmud, Reza Fahmi, Rohana Abdullah & Coco Kokarkin., 2013 *J. Sci. Eng.* pp 81-88

[4] Sundaram, J., Durance, T.D., and Wang, R., 1997 *Acta Biomaterialia* **4** pp 932-942

[5] Zhang, Q.; Liu, L.; Ren, L. & Wang, F. 2008 *Journal of Applied Polymer Science* **64** pp 2057–2263

[6] Bartezak, Z., Argon, A.S., Cohen, R.E., and Weinberg. M., 1999 *Polymer* **40** pp 2347-2365

[7] Zhang, S., Cao, X.Y., Ma, Y.M., Ke, Y.C., Zhang, J.K., and Wang, F.S., 2011 *eXPRESS Polymer Letter* pp 581-590

[8] Cides L.C.S., Araújo A.A.S., Filho M.,& Matos., 2006 **84** pp 441

[9] Castelló M., Dweck J., & Aranda. 2009 *J Therm Anal Calorim* **97** pp 627–630

[10] Sudip Mondal, Biswanath Mondal, Apurba Dey, and Sudit S. Mukhopadhyay 2012 *Journal of Minerals & Materials Characterization & Engineering* **11** pp 55-67

[11] Norazowa I, Wan M.Z.W.Y., Maizatulnisa O., Khalina 2011 *Journal of Polymer Reinforced Plastics and Composites* **30** pp 381-388

[12] Jones, A., Zeller, M.A., & Suraj S., 2013 *Progress in Biomaterials* **2** pp 12

[13] Cadman. J., Chen, Y., Zhou, S., Li, Q., 2012 *Mater. Sci. Eng. C-Biomimetic Supramol.*