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Potential Red Algae Fibre Waste as a Raw Material for Biocomposite

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ABSTRACT

Red algae are abundant worldwide, and their exploitation for the development of agar products has developed into a significant industry in recent years. Industrial processing of red algae produces a significant amount of solid fibre waste, which contributes to substantial environmental problems. Agar from red algae is mostly used in the food, cosmetic, and pharmaceutical industries. There has been very limited research on the use of red algae in lignocellulosic composites so far. As such, this project aims to fabricate red algae reinforced with polylactic acid (PLA) as composite materials and to investigate the composite's mechanical, physical, and durability properties, as well as its characterization. The composite is fabricated using an extruder and a hydraulic hot press machine in three different composition ratios: 200:0, 180:20, and 160:40 (PLA: fibre (g)). Each sample was subjected to tensile testing for mechanical properties, melt flow index (MFI), scanning electron microscopy (SEM) testing for physical properties, and thermogravimetric analysis (TGA) testing for thermal properties. For durability testing, the samples were buried underground to determine the weight loss of composites over two weeks. The results indicate that while red algae have exceptional thermal properties, however, the strength and durability of the composite decrease with the inclusion of fibre. It is recommended that fibres be treated with an alkaline solution to improve their characteristics before being used as a composite.

1. Introduction

Biodegradable and ecologically friendly materials are becoming increasingly important for the future generation of composite materials in response to global environmental concerns [1-3]. Natural fiber-reinforced composites are being employed in several applications to minimize greenhouse gas emissions. Green composites are a great alternative to petroleum-based materials, which can have harmful environmental effects. However, natural fiber composites also have certain disadvantages, including high moisture content and poor fiber-matrix compatibility, limited fire resistance, reduced durability, and lower impact strength [3-5].

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In recent years, synthetic fibers such as glass fibers, carbon fibers, and boron fibers have been commonly used to provide high strength and stiffness to polymer composites. However, the use of synthetic fibers is non-biodegradable, which raises environmental concerns due to the significant amount of waste produced after disposal [6,7]. To overcome these effects, solutions such as the usage of natural fiber as reinforcement have been formulated and proposed. Natural fibers offer several advantages, such as being biodegradable, widely available, easily obtained, relatively cheap, low density, lightweight, and very flexible during processing [8,9].

Red algae (*Kappaphycus alvarezii*) have the potential to make biocomposites since they can provide a rich source of solid fiber waste, which is generated during the commercial production of red seaweed and is a significant source of pollution [10,11]. Red algae have the advantages of being eco-friendly, lightweight, low-cost, biodegradable, and energy-saving. Seaweed production has been increasing year by year, and it offers many great qualities, such as great processing properties, good elasticity ability, and effective heat protection due to its great heat insulation and heat capacity properties. It can also be recycled and has a strong carbon dioxide (CO2) fixation [12].

There has been a continuous rise in interest in using natural resources to build more ecologically friendly polymers. Polylactic acid (PLA) is a thermoplastic polymer made from sugar cane and other renewable resources, and it is considered one of the most promising resources for biopolymer manufacturing due to its variety of benefits [13,14]. PLA is an eco-friendly, compostable, and biodegradable material, which makes it an ideal candidate for sustainable packaging and disposable products. In addition, PLA has good thermal stability, high mechanical strength, and excellent printability, which makes it suitable for 3D printing applications. PLA has gained considerable attention as a promising alternative to petroleum-based plastics in various industrial applications. Therefore, PLA has great potential to be useful in short-term applications where biodegradability is critical [15]. This work aims to develop red algae-reinforced fiber with PLA as composite materials and to investigate the mechanical properties, physical properties, durability properties, and characterization of the composite of red algae fiber waste. PLA was chosen to keep the composite 100% biobased and natural.

2. Methodology

Polylactic acid (PLA) was purchased from Urich Technology, based in Sungai Petani, Kedah. It has a melting temperature of around 160-180℃. Red algae were collected from Semporna, Sabah. Red algae with the species name of *Kappaphycus alvarezii* were dried using an oven at a temperature of 50 ^{0}C for 24 hours, ground, and then sieved using a sieve shaker to mix with a polymer matrix. Red algae were sieved with a 0.425mm size, 200 diameter sieve to get fine and precise powder. About 60g of red algae was produced.

2.1 Composite Preparation

250g of red algae were cut and dried in an oven at 80℃ for 2 hours before grinding into the powder phase. Restch Cutting Mill SM100 machine was used for the grinding process and ground for about 2 hours to get a fine powder. Then, the algae powder was sieved for about 10 minutes. Thermo Scientific EuroLab 16 Twin-Screw Extruder was used to mix red algae and PLA at 175℃ with a rotation speed of 80 rpm. The composition of composites which are 200g of PLA, 180g of PLA and 20g of algae, 160g of PLA and 40g of algae were used to mix the composite. All samples were cut into the pellet before being pressed using a hydraulic hot press machine.

2.2 Mechanical Testing

Dumbbell shape bars of 17cm x 2cm dimension of samples were prepared according to ASTM D638 using the hot press molding technique. Tensile tests were carried out on a tensile testing machine (INSTRON 3367 Universal Testing Machine (UTM)), and the samples were tested to measure the elongation of the specimen before it reaches its breaking point. At least 9 samples of each composition were tested. The mechanical characteristics are discussed for this observation.

2.3 Thermogravimetric Analysis (TGA)

TGA was performed and carried out using TA instruments Q500 analyzer. Each sample was heated from 20℃ to 700℃, in a nitrogen atmosphere, with a heating rate of 10℃.min-1, 50 mL.min-1 flow.

2.4 Scanning Electron Microscopy (SEM)

Samples were analyzed using SEM machine (FEI Quanta 450) to obtain the surface morphology of red algae and the ground fractures of biocomposite. With magnification ranging from 20x to around 30,000x and resolutions of 50 to 100nm, a region with a width of approximately 1 cm to 5 microns can be imaged.

2.5 Melt Flow Index (MFI)

The samples were placed in the Melt Flow Indexer Dynisco-LMFI 5000 machine, with a small amount of each sample placed in the barrel with 180℃ of temperature used with a 1.2 kg load. The molten composites were applied force through the die, and the 30 seconds timer begin to slice 5 cycle times. The sample was sliced for each cycle, and its weight was measured and recorded. Once the cycle is complete, re-insert the weight of each sample's cycle into the machine to obtain the Melt Flow Rate (MFR) for each sample.

2.6 Durability Test

To test the composite's durability, the sample was buried in the soil for a period of time. The purpose was to assess the biodegradability of the sample composite. The samples were buried for 2 weeks. After 2 weeks, the samples were weight, and calculate the percentage of weight loss was according to Formula 1:

2.7 Water Absorption Test

For the water absorption test, all the samples were soaked in the water and left for 24 hours. To observe the rate of water absorption, and change toward all of the samples, the dry weight and weight after soaking were recorded. The purpose of this testing is used to determine the amount of water absorbed under specified conditions. The calculation as Eq. (2).

Percentage weight lost (% weight lost)

$$= \frac{Initial\ weight\ (g) - after\ buried\ weight\ (g)}{initial\ weight\ (g)} \times 100 \tag{1}$$

Percentage water absorption (% water absorption)

$$= \frac{after\ weight\ (g) - initial\ weight\ (g)}{initial\ weight\ (g)} \times 100 \tag{2}$$

3. Result and Discussion

3.1 Tensile Test Analysis

The results of tensile testing are presented in Figure 1 and Table 1 for composite from red algae and PLA. Three composites from each sample were tested to determine and observe the properties of strength and stiffness of each sample. Tensile tests are used to determine how materials will react while under tension. In a simple tensile test, a sample is pulled to its breaking point to determine the material's ultimate tensile strength.

Table 1
Stress and Young's modulus results of each sample

	Sample 1 (200g PLA)	Sample 2 (20g algae, 180g PLA)	Sample 3 (40g algae, 160g PLA)
Stress (N/mm^2)	0.235 (0.09)*	0.132 (0.12)	0.118 (0.05)
Young's modulus	34.74 (0.72)	33 (0.57)	23.6 (0.75)

*Value in parenthesis is the standard deviation

Table 1 shows the strength of red algae/PLA composite on strength and stiffness against pure PLA. However, the strength of the sample added with red algae shows a decreasing value of the strength. This is due to the weak interfacial strength between polar hydrophilic red algae and non-polar hydrophobic PLA [11]. In order to improve the tensile strength, treatment such as alkaline treatment can be considered before red algae are added to a mixture of composite

3.2 TGA Analysis

In TGA analysis, those samples were continuously weighted while it heats in the presence of an inert gas environment. The residual mass was recorded. The thermal behavior of algae and PLA is shown in Figure 1.

Figure 1 shows the relationship between the temperature of thermal degradation with percentage derivative weight change for each composite. Compared with pure PLA, its shows that PLA has a low percentage derivative weight change compared with 20g and 40g of red algae/PLA composites, respectively. This proved that PLA tends to easily burn at high temperatures and the polymer has low resistance toward high temperatures. By adding algae fibre, it proved that red algae-PLA composite has a high potential for good thermal degradation. According to the findings, the 20g red algae has high heat resistance. The amount of weight change given to the composite during thermal degradation proved this. Furthermore, the low red algae level indicates that the composite will degrade thermally more quickly, which will increase its overall performance [3,12].

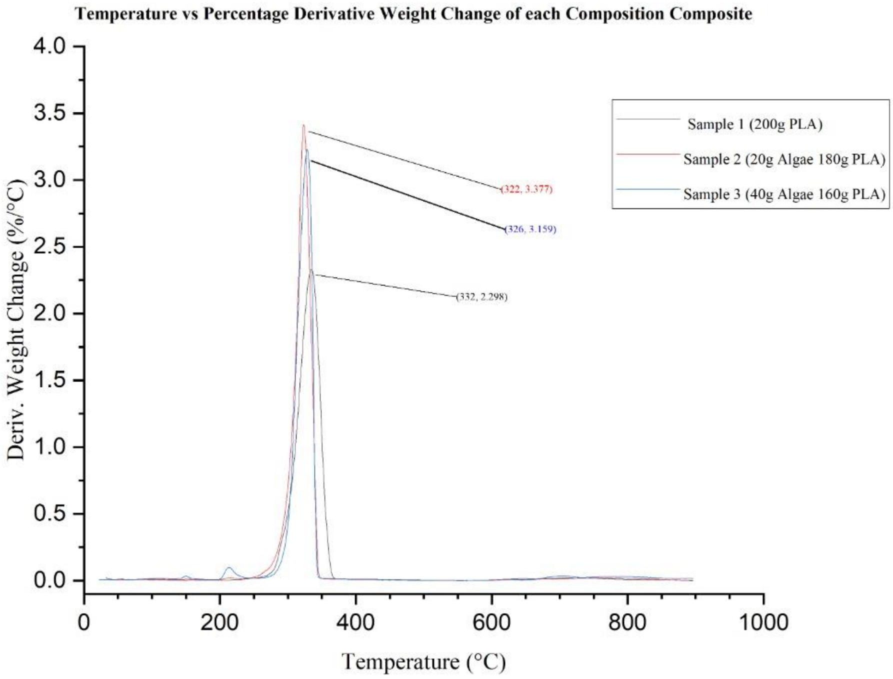
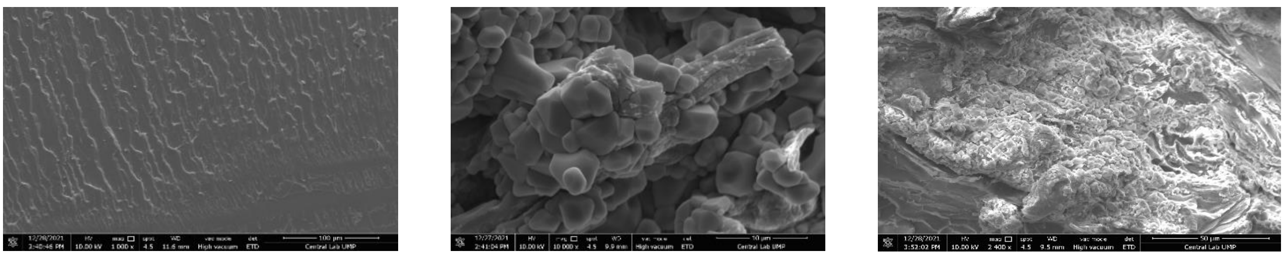


Fig. 1. Result of Percentage Derivative Weight change of each composite.

3.3 SEM Analysis

The surface of PLA and Red algae-PLA composites are shown in SEM micrographs, Figure 2, which can observe the combination of dispersed and matrix phases of composites. PLA is a semi-crystalline material, which means that some of the molecular structure of the material is arranged into crystals while the remainder is disordered or amorphous, like glass. The fracture surface of PLA appears more brittle because less plastic deformation can be seen on the fracture surface. The cell walls of red algae are doubled. The polysaccharides agarose and agaropectin, which may be removed from the cell walls by boiling as agar, are found in the outer layers. By adding the red algae, it could see the grain structure of the material is increased. The combination of red algae and PLA shows a good bonding system between both of materials [2,11].



(a) (b) (c)

Fig. 2. SEM micrograph of each composite at 2000x magnification: (a) PLA (b) 20g Red algae-PLA (50 (c) 40g Red algae-PLA

3.4 MFI Analysis

MFI was determined as the average molecular weight of melted thermoplastic materials based on melt viscosity variation. 5g of each composite was used at 180°C temperatures with the same load of 1.2 kg. Each of the dies was cut within 30 seconds for 5 die samples and re-insert the weight of each sample's cycle into the machine once the cycle is complete to obtain MFI for each sample. Table 2 below shows the result of MFI for each composite.

Table 2
The melt flow index results

Sample 1 (200g PLA)	Sample 2 (20g algae, 180g PLA)	Sample 3 (40g algae, 160g PLA)
11.53 (0.76)*	7.781 (0.82)	6.240 (0.65)

*Value in parenthesis is the standard deviation

From the observation, red algae/PLA composite shows a lower value of MFI compared with pure PLA. According to the study, a high MFI corresponds to low molecular weight hence the viscosity of the material is lower too. Red algae/PLA composite shows that the fibres in red algae in the composite increased the viscosity of the composite, resulting in a lower MFI value. Furthermore, the composite's reinforcing served as a structural element. In conclusion, the red algae/PLA composite showed excellent thermal durability at high temperatures. The Red algae/PLA composite can tolerate high temperatures and has a limited capacity to flow under pressure. Furthermore, the composite has a high molecular weight which means have longer chains and it could get harder to flow because they are more tangled [12].

3.5 Durability Analysis

The results of the durability test of each sample are shown in Table 3, where the test was carried out by burying the composites into the soil for 2 weeks. After being buried for two weeks, the composite will be weighed again. The composite's performance is determined by how it responds to the soil, including bacteria and insects. Furthermore, when exposed to natural factors, this investigation will indicate how biodegradable the composite is.

Table 3
Percentage weight lost durability test for each sample's composition

	Sample 1 (200g PLA)	Sample 2 (20g algae, 180g PLA)	Sample 3 (40g algae, 160g PLA)
Initial weight, W_1 (g)	11.45	15.29	10.36
After buried weight, W_2 (g)	10.55	10	0
Weight lost (g)	0.90	5.29	10.36
Percentage of weight lost (%)	7.87	34.623	100

The results show the combination of red algae and PLA gives a positive result on biodegradability. It is proven by the percentage of weight loss of composites after being buried for 2 weeks. When the composites were buried in soil, the process of degradation is happening where the process will break the molecular chain of the red algae-PLA composite and reduced the weight of samples. This may be due to the high cellulose content in red algae tends to make organisms in the soil degraded the composite during the period of study [2,3].

3.6 Water Absorption Analysis

Water absorption of composites was carried out by soaking the entire samples in water for 24 hours. Table 4 shows the result of water absorption for each sample, where there are showing big differences between them. Natural fibre could easily absorb water while PLA can absorb less water due to its hydrophobic properties. PLA is a water-resistant material that can be utilized as a hydrophobic component [9].

Table 4
Percentage water absorption test for each sample's composition

	Sample 1 (200g PLA)	Sample 2 (20g algae, 180g PLA)	Sample 3 (40g algae, 160g PLA)
Initial weight, W_1 (g)	11.41	11.10	9.68
After soaking weight, W_2 (g)	12.58	13.05	12.72
Weight absorption (g)	1.17	1.94	3.04
Water absorption percentage (%)	10.33	14.93	31.40

By adding the PLA to algae fibre, supposedly it will decrease the water absorption of composites. However, due to the much weight of algae in polymer, it corresponds to absorbing more water than repelling water from composites. Sample 3 shows a high percentage of water absorption causing the red algae/PLA composite to have low moisture resistance. Furthermore, sample 2 shows a high corresponding to low water absorption even though not as great as pure PLA. The molecular chain of PLA could hold algae for not to absorb too much water. Except for the low molecular weight polysaccharide isolated from red algae, these abilities were likewise connected to molecular weight, lower molecular weight improved moisture absorption [10]. This means red algae/PLA composite has a high molecular weight corresponding to low water absorption.

4. Conclusions

The Red algae-PLA composites were successfully prepared as natural fibre reinforced polymer composites (NFRPCs). The structural properties of red algae-PLA composite fibre have been characterized by using SEM, TGA, and melt flow index (MFI). The durability test and water absorption test were tested for the physical properties of composite materials and the tensile test was tested for mechanical properties. From all the testing that has been done, it can be concluded that in terms of mechanical strength and physical strength, the red algae/PLA composite shows a decrease in strength, however, the red algae/PLA composite shows good properties in thermal stability. To improve the physical and mechanical properties of this composite, it is suggested for red algae fibre undergo a chemical treatment for improving the fibre properties before being processed into a composite.

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