The Characteristic Of Biocomposite Film Of Spirulina Residue As Natural Dyes

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Abstract. *Spirulina plantesis* microalgae contain active ingredients in the form of antioxidants and pigments. Currently, the microalgae *Spirulina plantesis* is used as an antioxidant in the food, pharmaceutical and cosmetic industries. This manuscript discusses the utilization of *Spirulina plantesis* microalgae pigment as a natural dye plastic. The need for color plastics for various uses continues to increase. The use of natural dyes for plastics is expected to produce biocomposite films that are safe for the environment or biodegradable and safe to be used. The aim of the study was to determine the effect of adding Spirulina residue as a natural dye on the characteristics of biocomposite films. The variable concentration of Spirulina residue added to the biocomposite film formula was 0.5%,1%, and 1.5%. The film production method used was the solution casting method. In this study, 200ml of distilled water was added with Spirulina residue (SR), then stirred for 30 minutes, and after that successively added 1% Glycerol and stirred for 15 minutes; Carrageenan 1% and stirred for 15 minutes. The solution was heated at 70^{o}C then Polyvinyl Alcohol (PVA) with concentrations of 3%, 4%, and 5%, and Tapioca (3%) were added until complete gelatinization occurred. The solution was poured into a 30 cm x 20 cm mold and dried at 30^{o}C for 48 hours to form a film. Biocomposite films were analyzed for tensile strength and elongation at break based on ASTM D 638, color, and morphology. The results showed that the highest tensile strength and elongation at break of biocomposites were found in biocomposite films with the addition of 0.5% Spirulina residue, namely 96.40±6.04 kgf/m^2 and 47.64±7.48%, respectively. Analysis of the color of the biocomposite films showed the highest greenish and yellowish colors in the biocomposite films with the addition of 1.5% Spirulina residue and 5% PVA. Spirulina residue can be utilized as the plastic dyes.

1 INTRODUCTION

The need for bioplastics is increasing, especially for the packaging industry, and also for the textile industry, automotive industry, and food industry. In the health sector, plastic is used

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for packaging medical equipment and hospital waste bags. However, after its use, plastic causes environmental problems and creates waste, because it cannot degrade naturally. One way to reduce plastic waste is to use biodegradable plastic (bioplastic). Bioplastics can be produced from cassava starch (1),(2). Then, to improve the performance of starch-based bioplastics, modified starch derived from nuts, glycerol, distilled water, and vinegar is used (3). Apart from that, dragon fruit and turmeric have been used as natural dyes in making bioplastics (4). Additional materials in the form of natural dyes from pine flower waste can be used as bioplastic dyes for food packaging because they do not harm the environment (5).

Other potential materials, such as microalgae are used to make bioplastic because they grow quickly and are not intended as food, which results in their availability (6). Microalgae can be used directly as biomass to produce bioplastics or indirectly using the poly hydroxybutyrate (pHBs) extraction process and also by combining starch with microalgae or it can also be done by producing a mixture of microalgae and polymer through hot molding, melt mixing, solvent casting processes, injection molding or twin screw extrusion (7).

Other than starch, bioplastics can be produced from microalgae that are high in protein, such as the *Spirulina plantesis* microalgae. Spirulina, or blue-green algae, is high in protein (between 50 and 60 percent), antioxidants, vital fatty acids, and other nutrients, it is being used as a nutritional supplement all over the world. Spirulina protein has a higher amino acid content than soy protein, making it one of the best in the plant kingdom (8). The byproduct of *Spirulina platensis* extraction is a solid residue. The analytical results of Spirulina Residue were for components C (41.36 wt%), H (6.60 wt%), and N (7.17 wt%), O (35.33 wt%), while, for the proximate analysis, the lipids (0.09 wt%) were very low (9). The Spirulina residue has been utilized as bio-oil for renewable energy (9), protein source for Cordyceps militaris culture (10), and so on.

Bioplastics produced from mixing polyvinyl alcohol (PVA) and Spirulina can reduce the costs and the use of non-biodegradable materials. Bioplastics from *Spirulina plantesis* have mechanical properties that are almost the same as commercial bioplastics (11). Bioplastic film from *Spirulina plantesis* has stronger tensile strength than commercial plastic bags, but its elongation at break is low. This bioplastic can be used for food, pharmaceutical, and cosmetic packaging materials (12). Bioplastic can also be produced from spirulina residue by adding polyvinyl alcohol (13). Bioplastic made from 95% Poly Lactic Acid (PLA) and 5% algae shows good mechanical properties, especially for tensile strength (81 MPa) and elongation at break (4%), this bioplastic can be decomposed in 45 days (14).

Biodegradation of plastic depends on the physical properties, chemical structure of the polymer bonds, both functional groups and crystallization properties, and also on the environment, such as water content, oxygen, temperature, and pH. One method of using natural materials to make bioplastic is using vegetable waste, which can be converted into bioplastic film with mechanical properties similar to other bioplastics (15).

This research aims to determine the effect of adding spirulina residue as a natural dye on the characteristics of biocomposite films based on polyvinyl alcohol, starch, glycerol and carrageenan. Spirulina residue is residue from the spirulina extraction process using CO_2 extraction to obtain carotenoids.

2 MATERIALS AND METHODS

2.1 Material

This research used materials consisting of spirulina residue (residue from the carotenoid extraction process from *Spirulina plantesis* using supercritical CO_2), tapioca flour (Orang

Tani brand), polyvinyl alcohol (Bratachem), glycerol (Bratachem), Carragenan (Swallow brand).

2.2 Biocomposite film manufacturing process method

In this stage, the process of making a biocomposite film is carried out, with variable concentrations of spirulina residue (0.5%, 1.0% and 1.5%) and variable concentrations of polyvinyl alcohol (3%, 4% and 5%). 200 ml of distilled water was added with spirulina residue (0.5%, 1.0% and 1.5%) stirred until homogeneous for 30 minutes, then 1% glycerol was added, stirred for 15 minutes, then 1% carrageenan was added for 15 minutes, after that the solution was heated at 70°C. added polyvinyl alcohol (3%, 4% and 5%). Then add 3% tapioca and then heat until complete gelatinization occurs. After that, pour the solution into a mould measuring 30 cm x 20 cm. Dry at 30°C for 48 hours. Cool at 27°C, remove the film from the mould and store in a desiccator. The biocomposite film formula made in this research is presented in Table 1.

Table 1. Bicomposite films formulation and code.

Code	PVA	Spirulina Residue
F1	3%	0.5%
F2	4%	0.5%
F3	5%	0.5%
F4	3%	1%
F5	4%	1%
F6	5%	1%
F7	3%	1.5%
F8	4%	1.5%
F9	5%	1.5%

2.3 Characterization of biocomposite films

The biocomposite films formed were analysis for mechanical properties (tensile strength and elongation at break), colour analysis, and morphology.

2.3.1 Analysis of mechanical properties and morphology

Mechanical properties and morphology structure Parameters observed were tensile strength and elongation, using UTM, based on ASTM. The film sample was measured into 20 mm long and 2 mm wide, given a 500 N load with the speed of 1 mm/minute and range of 10 mm. The analysis was done 5 times. The morphology structure was observed using Scanning Electron Microscope (SEM).

2.3.2 Colour analysis

Colour intensity analysis with chromameter based on the Harder's lab colorimetric system Hunter's colour notation system is expressed in three values, namely L (lightness), a*(redness), and b* (yellowness). Lightness value, while = 100, green =0, a* value (+a*=

red, -a*= green), while b* (+b* = clear, -b* = blue). Before use, the tool needs to be calibrated using a while calibration plate. The sample is in the form of 25 gram of powder.

3 RESULT AND DISCUSSION

3.1 Environmentally Friendly Plastic Formulation

In this research, the method used is the solution casting method, where Spirulina residue functions as a natural colour additive. Spirulina residue is obtained from the by-product of the *Spirulina plantesis* extraction process using a super critical CO_2 extractor to obtain carotenoids (16). The composition of Spirulina residue can be seen in Table 2. It shows that Spirulina residue contains quite high total carbohydrate levels (59.94/100g). In the process of making biocomposite films, water is used as a solvent, because spirulina residue can dissolve well in water. It is also easy to get the water, and it is safe as well as environmentally friendly solvent. The spirulina residue used was in concentrations of 0.5%, 1.0% and 1.5%. Stirring was done for 30 minutes, this aimed to obtain Spirulina residue dissolved homogeneously in water. The plasticizer used is glycerol, 1% glycerol is used because glycerol can dissolve well in water. Fiber in biocomposites can function as reinforcement by using 1% carrageenan and 3% tapioca starch. The biocomposite matrix uses polyvinyl alcohol polymer with variables, namely 3%, 4% and 5%, because polyvinyl alcohol is a synthetic polymer that can dissolve in water, so it can mix homogeneously with Spirulina residue and tapioca starch and carrageenan. Polyvinyl alcohol is easily decomposed, so the resulting biocomposite film will decompose easily and is environmentally friendly. Making bicomposites will produce biocomposite films that can be used for packaging.

Table 2. Spirulina residue composition.

No	Parameter	Analysis Results
1	Moisture	14.65 g/100g
2	Total ash	12.47 g/100g
3	Protein	3.16 g/100g
4	Total carbohydrate	59.94 g/100g
5	AEAC	14.78 g/100g
6	IC 50	0.32 mg vit C/g sampel
7	Inhibition value	27.25 mg/ml
8	Total fat	2.08 %
9	Vitamin B1	132.49 mg/kg
10	Vitamin B2	-
11	Vitamin B6	80.27 mg/kg
12	Na, Sodium	2840.33 mg/kg
13	K, Potassium	43.93 mg/kg
14	Ca, Calcium	12172.95 mg/kg
15	Mg, Magnesium	4655.96 mg/kg
16	P, Phospor	11624.80 mg/kg
17	Zn, Zinc	55.03 mg/kg
18	Mn, Manganese	3.77 mg/kg

3.2 Mechanical Properties of Biocomposite films

Analysis of the mechanical properties of biocomposite films is to determine the homogeneity of the mixture of materials used in making biocomposites, consisting of tensile strength and elongation at break. The results of tensile strength analysis show that the biocomposite film uses Spirulina residue 0.5% and PVA 4% is stronger than a biocomposite film with Spirulina residue concentration of 1.0% and 1.5% and PVA concentration of 3% and 5%, as seen in Figure 1. Spirulina residue containing fiber (calculated as carbohydrate) can effect the tensile strength of the biocomposite film.

The analysis of elongation at break of biocomposite films, shows that biocomposite films using Spirulina residue with a concentration of 0.5% and PVA with a concentration of 3% produce biocomposite film with higher elongation at break compared to biocomposite films using Spirulina residue 1.0% and 1.5% in PVA 4% and 5% (Figure 2). This shows that the higher the concentration of Spirulina residue will result in a lower elongation at break. It's interesting to observe that the elongation value for biocomposite film of RS 0.5% in PVA 3% and 4% show similar value. It shows that in lower concentration, Spirulina residue can help the stress tranfer in PVA matrice with concentration of 3% and 4%. It also shows that Spirulina residue can affect the elongation at break properties of biocomposite films. Based on the composition of the residue, Spirulina contains ash, usually in the form of minerals which can affect the flexibility of the biocomposite film.

To increase the flexibility of the plastic produced from *Spirulina plantesis*, glycerol was added at different concentrations (15-30%). Higher tensile strengths and lower elongations were observed from this bioplastic with addition of 30% glycerol compared to commercial plastic bags. These results showed that this bioplastic can be used for food packaging in pharmaceutical applications or cosmetics, where high elongation is not needed (9). The use of a compatibilizer also increased the elongation capability of the plastic and enabled smoother surface (8). The microalgae biomass particles which have particles diameter of 5 micrometers did not show efficient strengthening ability. The smaller particles were able to blend with the other materials more efficiently (17). Composite film surface appears to be rough and uneven. In addition, rigidity of the composite film by means of elasticity could affect the tensile strength (18). Bioplastic film produced from *Spirulina plantesis* and PVA mixture which has the most similar mechanical properties is bioplastic which uses 6 wt% compatibilizer (8).

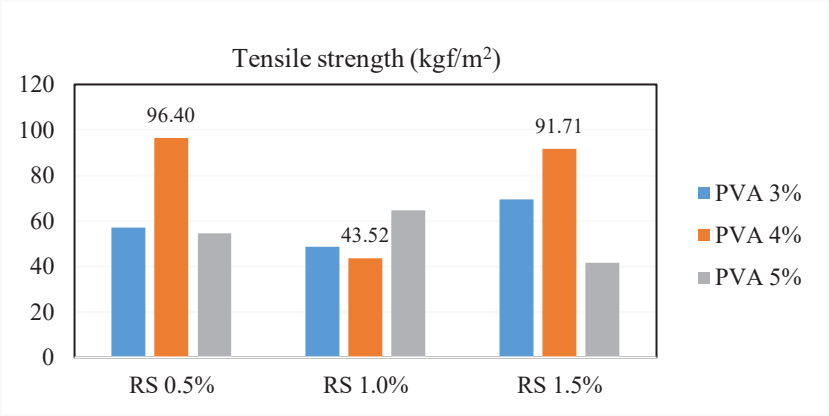


Fig. 1. Tensile strength of biocomposite film at spirulina residue concentration and poly vinyl alcohol concentration.

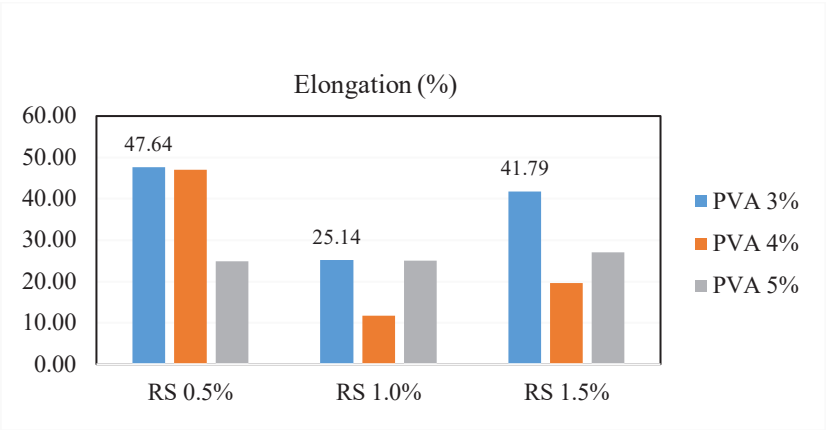


Fig. 2. Elongation at break of biocomposite film at Spirulina residue concentration and poly vinyl alcohol concentration

3.3 Colour Analysis of Biocomposite Films

In this research, the use of Spirulina residue did not only affect the mechanical properties of the biocomposite film, but also give colour to the biocomposite film. In general, Spirulina contains bioactive ingredients which have colours; the green from chlorophyll, the blue colour from phycocyanin, and the orange colour from carotenoids. After the extraction using a CO_2 supercritical process, in order to obtain carotenoids and chlorophyll, spirulina residue still has colour or pigment. This color or pigment is the color of the biocomposite film. The color of the biocomposites observed with the naked eye does not show any real differences, as presented in Figure 3. Therefore, the color differences between the biocomposites produced were analyzed using the Color Reader tool.

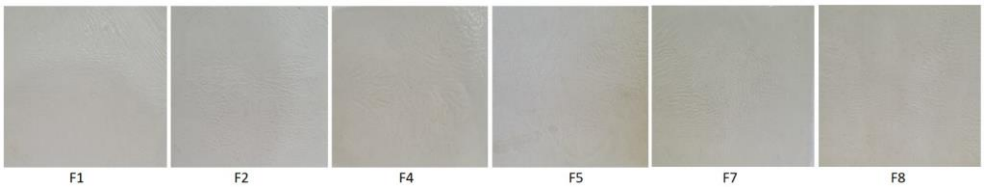


Fig. 3. Biocomposite films of PVA filled with Spirulina residue

Based on colour analysis using a Minolta CR 400 Chromameter, it shows that the variable values "L" (Lightness) and "b" (yellowness) and "a" (Greenness). The colour brightness (L) value shows that the highest 'L" value is in the residue concentration 0.5% spirulina and 3% polyvinyl alcohol concentration of 76.18. This shows that the higher the concentration of spirulina residue will produce a lower "L" colour brightness and the higher the poly vinyl alcohol concentration indicates that the "L" colour brightness value is lower., as shown in Figure 4. The greenish colour value "a" shows that the highest greenish colour value is at a spirulina residue concentration of 1.5% and a 5% poly vinyl alcohol concentration of 6.95. This shows the higher the spirulina residue concentration will produce a higher greenness value and the higher the concentration of poly vinyl alcohol will produce a higher greenness value, as seen in Figure 5. In the yellowness value "b" indicates that the highest yellowness value was at a spirulina residue concentration of 1.5% and a poly vinyl alcohol concentration of 5% at 29.97. This shows that the higher the concentration of spirulina residue will produce a higher yellowness value and the higher the poly vinyl alcohol

will produce a higher yellowness value, as can be seen in Figure 6. These results indicate that the level of colour change that occurs is quite significant and relevant to visual observation. There was a colour change when the concentration of spirulina residue is increased and the concentration of poly vinyl alcohol is increased.

A comparison was conducted from the same natural dyes –carmine, turmeric, indigo and annatto- with and without encapsulation. Injected into the same PVC matrix (19), the possibility of reducing the UV transparency of two commercial and very common food packages after smart coating with commercial and green materials such as P-Coumatic acid and quinine for PLA matrix (20). Dyeing polyethylene (PE) plastic waste with bioactive photoacid phycocyanobilin (PCB) extracted from the pigment of spirulina blue-green algae the populations of long living photoproduct X*, which are pertinent to deprotonated phyrole species (anionic species) (21).

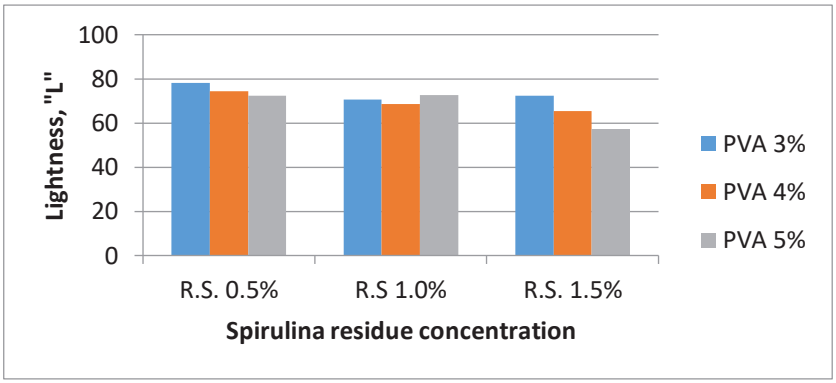


Fig. 4. Colour lightness value "L" of biocomposite film at spirulina residue concentration and polyvinyl alcohol concentration

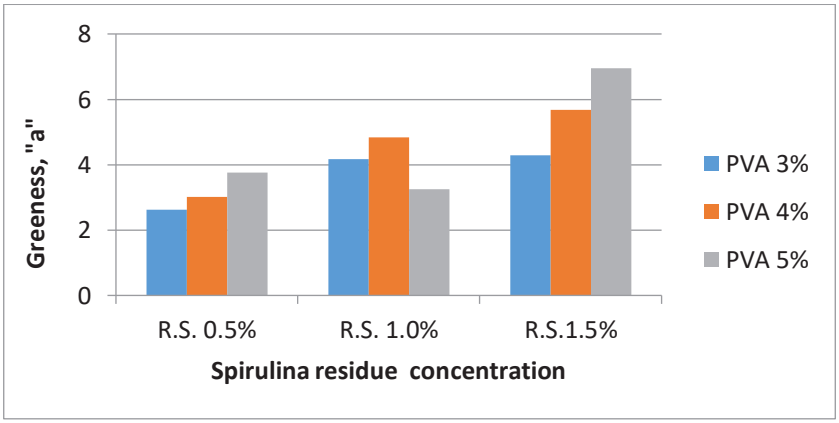


Fig. 5. Greenish colour value "a" of biocomposite film at spirulina residue concentration and polyvinyl alcohol concentration

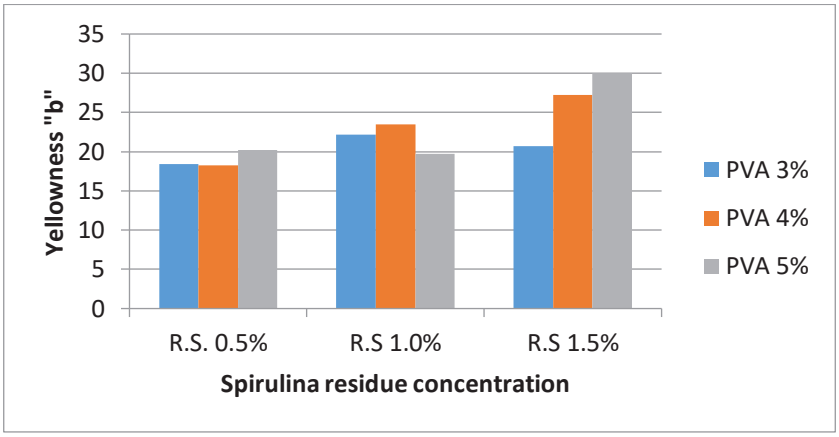
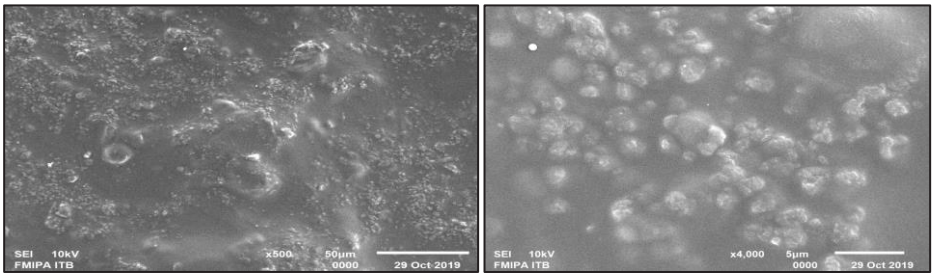


Fig. 6. Yellowness value "b" in spirulina residue concentration and polyvinyl alcohol concentration

3.4 Morphology residue Spirulina in Polyvinyl alcohol matrix

Characteristic of polyvinyl alcohol as a matrix for residue spirulina rheology aimed to observed the form of the polyvinyl alcohol matrix particle. Morphology was analysis by Scanning Electron Microscope (SEM). Figure 7 describes the SEM result with magnification for 500x times and 4000 x times. The particles are isotropic, wavy-round shape, and the particle bond with the matrix. Residue spirulina was very well furthermore, polyvinyl alcohol matrix can protect residue spirulina as natural dyes. The morphology of residue spirulina-polyvinyl alcohol is soft and homogeny. Based on SEM result, the biocomposite film with concentration Spirulina residue of 1.5% in PVA 5%, shows homogeneously shaped and spreading depressively.



3a 3b

Fig. 7. SEM Analysis of polyvinyl alcohol 5 % - residue spirulina 1.5 % with magnification 500x (3a) and analysis of polyvinyl alcohol 5 % - residue spirulina 1.5 % with magnification 4000x (3b)

4 CONCLUSION

Spirulina plantesis microalgae residue from the CO_2 extraction process can be used as a natural dye in biocomposite films. The method used to make biocomposites is the solution casting method. The results of the research showed that the highest tensile strength showed in biocomposite of 0.5% Spirulina residue and 4% polyvinyl alcohol, which was 96.40 kgf/m^2. Meanwhile, the highest elongation at break of the biocomposite made from 0.5% Spirulina residue and3% polyvinyl alcohol was 47.64%. Biocomposite color analysis showed the highest greenish color (6.95) in the biocomposite film of 1.5% spirulina residue dan 5%

polyvinyl alcohol and the highest yellowish color (29.97) in the biocomposite film of 1.5% spirulina residue dan 5% polyvinyl alcohol. Morphology shows homogeneous dispersion of Spirulina residue in polyvinyl alcohol matrice.

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