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Lipid-extracted algal biomass based biocomposites fabrication with poly(vinyl alcohol)

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ABSTRACT

Biodiesel production from microalgae has been recognized as a promising route for sustainable energy supply. The extraction process of oil from microalgae usually generates large amount of lipid-extracted algal biomass (LEA), which has not been economically utilized until now. In order to explore economic potential of the residual biomass, LEA from extraction of microalgae strain, *Nannochloropsis salina*, was employed as the filler in biocomposite fabrication with poly(vinyl alcohol) (PVA). It was noted that the increase of LEA loading reduced mechanical properties, but enhanced the thermal stability of biocomposite materials compared to neat PVA. As poly(diallyldimethylammonium chloride) (PD) was incorporated, mechanical properties of PVA/LEA/PD composites were significantly improved. PD was compatible with negatively charged LEA and PVA matrix as PD possesses positive charges. PVA was compounded with 20% LEA and 12% PD to synthesize the PVA68LEA20PD12 biocomposite. In contrast to neat PVA, this biocomposite recorded the similar mechanical property but the enhanced thermal property. This type of biocomposite film can be applied in commercial industries as specialty materials, for instance, 3D printing material. This helps to improve the economic feasibility of microalgae-based biofuel production.

1. Introduction

Microalgae-derived biofuels (e.g., biodiesel) possess the potential to overcome many challenges of the sustainability which are associated with other biofuels today. There are large amounts of co-products generated during the production of microalgal biodiesel, which is lipid extracted algal biomass (LEA) [1]. LEA is produced when lipid of microalgae is extracted. Several studies have been carried out to utilize LEA as biomass source for hydrogen and methane production via anaerobic digestion [2], fermentable sugar [3], bioethanol production [4], biofertilizer [5], and animal feed [6,7]. However, there have been few studies to utilize LEA into value-added materials such as biocomposites [8,9].

In general, one type of biocomposite materials were formulated by biopolymers with organic fillers or biomass-based fillers, while the other type of biocomposite materials were synthesized by petroleum-based polymers with biomass-based fillers. Both approaches of formulating biocomposite materials have considerably attracted researchers and scholars worldwide [10,11]. Biocomposites comprising natural fibers, bio-resins or biopolymers are the future of green composites as they offer reductions in cost and weight, and give less reliance on fossil resources [12]. Biocomposites are currently used mainly in automobile, construction, furniture and packaging industries [12,13]. Various biomass-based reinforcement materials have been used for biocomposite formulation, which are agro-industrial wastes [14], bamboo fiber [15], chitin [16], cellulose [17], wheat gluten [18], macroalgae [19,20], algae fiber of the strain *Lyngbya* [21]. For microalgae biomass, fillers were developed from several strains such as *Chlorella* sp. [22,23], *Nannochloropsis* and *Spirulina* [24], *Spirulina* and *Chlorella* [25] for polymeric blend formulations. Recently, the well-defined nanofibers with diameters about 110 nm were synthesized from PEO/*Spirulina* mixture via electrospinning process, and subsequently utilized in tissue engineering applications (e.g., cell culture) [26]. Beside, electrospun polycaprolactone (PLC) nanofiber containing *Spirulina* (PCL-*Spirulina*) was successfully fabricated and tested as a potential extracellular matrix for treatment of injured central nervous systems [27]. Polyhydroxyalkanoates (PHAs), an emerging biopolymer, can be produced and extracted from *Spirulina*, following by development of nanostructured scaffolds used in tissue engineering [28].

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In conjunction with biomass-based fillers, a wide range of polymer matrices have been used in composite fabrication, which are mainly petroleum-based thermoplastics such as high density polyethylene (HDPE) [29], polypropylene (PP) [30], and low density polyethylene (LDPE) [31]. Although petroleum-based polymers have been popular, related to relative high strength and easy-to-thermally processible property, most of them are non-biodegradable, and their increasing accumulation in this planet has been a threat to the environment and mankind [32]. As poly(vinyl alcohol) (PVA) possesses relatively high tensile strength, biodegradability and water-solubility, it has been attractive to many research groups in recent years. Thus, PVA has been widely used for synthesizing composites including either inorganic or organic materials, which are multi-walled carbon nanotubes [33], nano hybrid polyhedral oligosilsesquioxane (POSS) macromers [34], graphene/montmorillonite clay [35], macroalgae [20], microfibrillated cellulose (MFC) [36], nanofiber of bacterial cellulose [37], castor oil based waterborne polyurethane ionomer (PUI) [38], etc.

In this work, in order to explore economic potential of LEA, LEA derived from *Nannochloropsis salina* was tested for the synthesis of PVA biocomposites, while poly(diallyldimethylammonium chloride) was used as a plasticizer for composite fabrication. The mechanical and thermal properties of the biocomposites were analyzed using universal testing machine (UTM), thermogravimetric analyzer (TGA) and differential scanning calorimeter (DSC). Interfacial interaction between PVA matrices and the fillers was analyzed by monitoring morphological behavior, using scanning electron microscope (SEM) and Fourier transform infrared spectroscopy (FT-IR).

The experimental results strongly suggest the potential use of microalgal LEA in the production of commercially viable biocomposites.

2. Materials and experimental

2.1. Materials

Poly(vinyl alcohol) (PVA) with molecular weight 89,000 ~ 98,000 g/mol and poly(diallyldimethylammonium chloride) (PD) (20 wt% in H_2O) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Microalgal biomass of the strain, *Nannochloropsis salina* was supplied by NLP (Busan, Republic of Korea), which was then used for the lipid extraction process using hexane as solvent and 10% H_2SO_4, at 120 °C and 150 rpm in a 500 L stainless steel high pressure reactor. The reacted mixture was filtered to obtain both liquid-phase containing lipid, and slurry-phase containing lipid-extracted algal biomass (LEA). The biomass slurry was centrifuged at 9000 rpm for 10 min, followed by washing with deionized water three times to further remove liquid-phase containing hexane and H_2SO_4, which resulted in the wet solid biomass. The washed biomass was mixed with distilled water three times for 2 min each using the blender (hmf-995, Hanil Science Industrial, Republic of Korea) to make LEA-water suspension (9% (w/v) solid). The mixture was followed by heating at 90 °C under stirring rate of 400 rpm for 30 min to completely remove hexane. After heating, the mixture was further neutralized with NaOH 2 N and then centrifuged at 9000 rpm for 10 min, followed by freeze-drying at −80 °C and 5MTorr for 72 h. The freeze-dried biomass was then pulverized in a mill (SK-M2, Kyoritsu-Rikou, Tokyo, Japan) in total 9 min (3 times, each 3 min in length and 5 min stop interval) to produce raw LEA powder, which was directly used as the filler in biocomposite fabrication with PVA.

2.2. Preparation of composite materials

Composite materials were prepared by a solution casting method. For the synthesis of PVA/LEA composites, LEA was added to a 250 mL beaker containing water and then mixed under vigorous stirring at 400 rpm for 5 min, followed by sonication using an ultrasonic cleaner (5510R-DTH, Branson Ultrasonics, Danbury, USA) for 15 min. PVA was added to the suspension and kept stirring at 400 rpm for 5 min. For PVA/LEA/PD composites, LEA was added to a 250 mL beaker containing water and then mixed under vigorous stirring at 400 rpm for 5 min, followed by sonication with an ultrasonic cleaner (5510R-DTH, Branson Ultrasonics, Danbury, USA) for 15 min. The suspension was adjusted by adding NaOH 1 N to pH 10.0, which was followed by addition of PD and PVA, then kept stirring at 400 rpm for 5 min to well disperse all components. The LEA filler content was varied at 5, 10, 15, and 20% and PD was added at 4, 8, 12% of PVA biocomposites as a plasticizer, while the solid content over total volume of solution was kept at constant 12% (w/v) (Table 1). After the reacted mixtures i.e. PVA/LEA and PVA/LEA/PD were heated at 90 °C under stirring of 350 rpm for 1 h, the produced heterogeneous solution was casted on a flat glass plate supported by a knife coating device (KP-3000, KEEPAE Co., Ltd., Suwon, Republic of Korea) at room temperature. Then, the film casting frame applicator (JIS K-5400, IMOTO Machinery Co., Ltd., Kyoto, Japan) produced the casting with casting speed of 5 cm/s and coating thickness and width of 1 mm and 150 mm, respectively, which was dried under ambient temperature to obtain thin film with consistent thickness.

2.3. Characterizations

2.3.1. Determination of chemical composition and particle size distribution of LEA powder

The chemical composition of LEA biomass includes both organic and inorganic materials such as carbohydrates, proteins, lipids, and inorganic minerals like ash. The amount of total carbohydrate of LEA is measured by phenol-sulfuric acid assay, which was described by Laurens et al. [39]. The weight percentage of nitrogen and other elements in LEA such as carbon, hydrogen, and sulfur, was analyzed by the elemental analyzer (FLASH 2000 series, Thermo Scientific, USA), and protein content was estimated by using nitrogen-to-protein conversion factor for marine microalgae [40]. Total lipid of LEA was extracted by the modified Bligh-Dyer method and gravimetrically determined [41,42]. Ash was analyzed by using the method, described by Laurens et al. [39]. Dynamic Light Scattering (DLS) (Zetasizer Nano ZS90, Malvern Instruments Ltd., Worcestershire, UK) was used to determine the particle size distribution and the average particle size of LEA powders, which were dispersed in deionized water by the ultrasonic device (5510R-DTH, Branson Ultrasonics, Danbury, USA).

2.3.2. Mechanical properties

The specimens were stamp-cut by using a metallic tool and then they were stored at 25 °C and 43% relative humidity over saturated K_2CO_3, which was in accordance with ASTM E104–02 by maintaining constant relative humidity using aqueous solutions for at least 24 h

Table 1
Biocomposite formulations based on PVA, LEA, and PD produced by solution casting.

Sample	PVA (%)	LEA (%)	PD (%)
PVA95LEA5	95	5	0
PVA90LEA10	90	10	0
PVA85LEA15	85	15	0
PVA80LEA20	80	20	0
PVA91LEA5PD4	91	5	4
PVA86LEA10PD4	86	10	4
PVA81LEA15PD4	81	15	4
PVA76LEA20PD4	76	20	4
PVA87LEA5PD8	87	5	8
PVA82LEA10PD8	82	10	8
PVA77LEA15PD8	77	15	8
PVA72LEA20PD8	72	20	8
PVA83LEA5PD12	83	5	12
PVA78LEA10PD12	78	10	12
PVA73LEA15PD12	73	15	12
PVA68LEA20PD12	68	20	12

PVA: Poly(vinyl alcohol).
LEA: Lipid-extracted algal biomass.
PD: Poly(diallyldimethylammonium chloride).

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