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SCIENTIFIC PAPER

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PRODUCTION OF BIOPLASTIC MATERIAL FROM ALGAL BIOMASS

Article Highlights

- Algae-based bioplastic possesses very good mechanical features
- Biodegradability is comparable to that of the cellulose-based thermoplastic
- Application of algae biomass for sustainable bioplastic is viable

Abstract

Bioplastic composite material was developed from polylactic acid used as basic polymer and microalgae. Two types of biomaterials were prepared based on the proportion of microalgae and polylactic acid. The mass ratios were set to 5:95 and 10:90. First, spirulina was chosen as initial material and then a mixed culture of microalgae community from the biogas digestate treatment. The aim of the research was to study the characteristics of materials in order to determine whether the algal biomass community could be used in the production of bioplastics. It was found out that microalgae do not significantly impact the properties of the polylactic acid material. The degree of material crystallinity increased, the melting temperature reduced, and the modules of losses increased.

Keywords: PLA, spirulina, calorimetry, biodegradability.

Currently, 80% of polymer material is produced from fossil fuels and the need for plastic increases. Consequently, waste quantity is increasing and the environmental impact increases [1]. The main concern is due to their non-biodegradability. Reduction in plastic use is an option but has proven difficult to regulate internationally [2].

Plastics are the major components in municipal waste [3]. Particularly concerning is the growing quantity of microplastics. One of the alternatives is production of bioplastic from natural biodegradable materials, made from renewable sources [4]. Potentially promising material could be algea [5]. Spirulina and chlorella have been incorporated into thermoplastic blends with high density polyethylene (HDPE). Spirulina gave better results in final thermoplastic blends' properties. Unlike fossil-based plastics, microalgae-based bioplastics can be designed for biodegradability in natural as well as industrial composting settings. Main classes of currently developed bio-based plastics include plastics based on starch, polyhydroxyalkanoates (PHAs), polylactic acid (PLA) and celulose [4]. PLA is one of the most studied bioplastics regarding recyclability [6]. Polylactic acid (PLA) is a thermoplast which results by condensation of lactic acid or ring opening polymerization of lactide [4]. PLA provides high mechanical strength and very good thermal properties in comparison to other fossil-based polymers. The properties of the amorphous PLA glass transition, and the mechanisms involved during the aging process were investigated [7,8]. The high cooling rates enable reaching the thermodynamic equilibrium after a few minutes. Assimilation occurs where microorganisms are supplied by necessary carbon, energy and nutrient sources from the fragmentation of polymers and convert carbon of plastic to CO_2, water and biomass [9]. Parameters, such as pH, temperature, moisture and the oxygen content are among the most significant environmental factors that must be considered in the biodegradation of polymers [10]. The aim of this paper was to use the algal biomass community form the biogas digestate treatment for the production of novel composite biodegradable material. For this purpose, PLA was used and blended

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with algal biomass community from the biogas digestate treatment plant for the first time. The mechanical, thermal and rheological properties of the obtained materials were characterized by the static tensile test, TGA, DSC and DMA analysis. Finally, the biodegradability of the prepared samples was tested.

EXPERIMENTAL

Materials

The biomass was taken from anaerobic biogas digestate treatment (BDT). It was air-dried for 24 h at 29 °C. Dry biomass was grinded. Spirulina was purchased from Algen Company, Slovenia. It was powdered in a glass mortar. The resulting fine blue powder was stored at room temperature until analysis.

The blends were prepared first from spirulina with polylactic acid (PLA) and then from biomass with PLA. Polylactic acid type 2003D in pellet form was supplied by Nature Works LCC (Minnetonka, MN, USA). The density was determined at 1.24 g/cm^3.

5 different granulated samples were prepared:

- Sample PLA: 100% PLA
- Sample PLA-A-5: 95% PLA and 5% of algal biomass community
- Sample PLA-A-10: 90% PLA and 10% algal biomass community
- Sample PLA-S-5: 95% PLA and 5% of spirulina
- Sample PLA-S-10: 90% PLA and 10% of spirulina.

The dried material blends were placed into a co-rotating twin-screw extruder (Laboratory extruder LTE20-44, LabTech, USA). The temperature was set to 175 °C. The screw speed was between 20 and 50 rpm.

Blends were granulated in Krauss Maffei CX 50--180 Blue Power machine and stored at room temperature. Dark blends with algal biomass community and samples with pure PLA are seen in Figure 1.

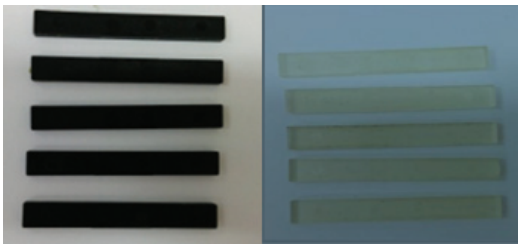

Figure 1. Final spirulina blend samples (left) and 100% PLA samples (right).

Methods

The thermogravimetric analysis (TGA) was performed to record the weight loss as function of temperature. Samples were heated from 40 to 600 °C at the heating rate of 10 °C/min under flow of O_2 (20 ml/min) and then heated from 600 to 990 °C at the heating rate of 10 °C/min under flow of N_2 (20 ml/min).

The tensile test was performed on a Shimadzu Ag-X testing machine according to EN-ISO 527:2004.

Dynamic mechanical analysis (DMA) was performed on a dynamic mechanical analyzer, DMA 8000 (Perkin Elmer).

The thermal properties were characterised by Differential Scanning Calorimetry (DSC) using TGA/ /DSC 3+ Instrument (Mettler Toledo, USA). First, the samples were conditioned at 20 °C for 2 min. Then, measurements were carried out from 20 to 190 °C, at a heating rate of 10 °C/min, under a nitrogen atmosphere.

Biodegradability of composted material samples was studied using a respirometer (ECHO, RESEP 2). The biological activity of organisms was determined by measuring the concentration of carbon dioxide in the exhausted air under controled conditions. Chambers were filled with compost and samples. The time of composting was set to 45 days. Biodegradability was determined for the following samples:

- Sample PLA: 100% PLA
- Sample PLA-A-5: 95% PLA and 5% of algal biomass community
- Sample PLA-A-10: 90% PLA and 10% of algal biomass community
- Sample PLA-S-5: 95% PLA and 5% of spirulina
- Sample PLA-S-10: 90% PLA and 10% of spirulina
- Sample compost
- Sample control.

RESULTS AND DISCUSSION

Thermogravimetric analyses

Thermogravimetric analyses for the samples with algal biomass community and for the spirulina blend are presented in Figure 2.

The one-stage degradation of microalgae is seen from Figure 2a. The degradation peak is seen at 295 °C. The weight loss due to water loss is at 115 °C. From 295 to 590 °C degradation took place with formation of volatile reaction compounds. The total weight loss of 86.9 and 13.1% loss of inorganic remains were determined.

Figure 2b represents the two-stage decomposition of spirulina blends. The weight loss due to water loss was determined at 91 °C. The material degradation peak is seen at 317 °C. From 317 to 590 °C degradation took place with formation of volatile

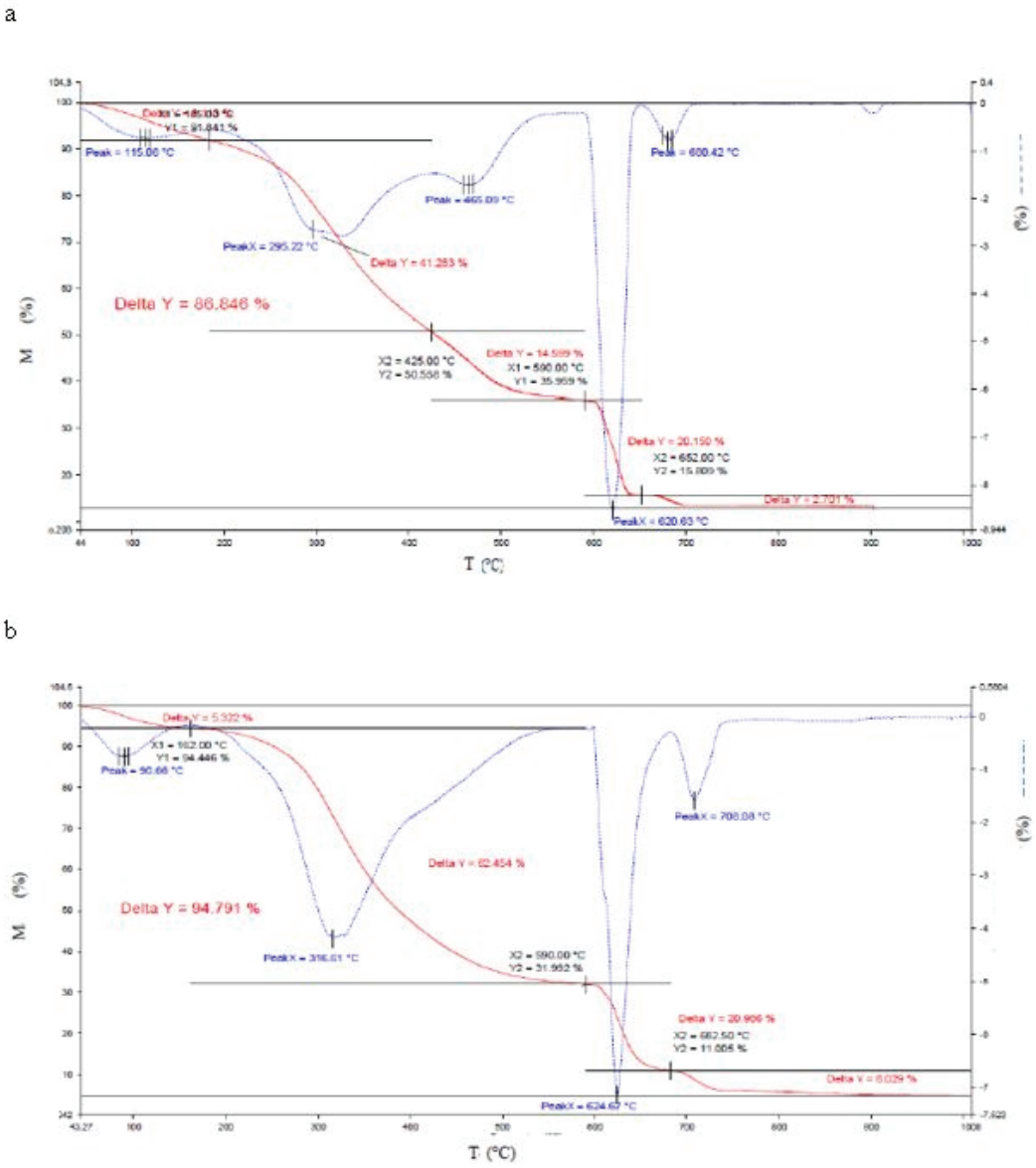

Figure 2. TGA curves: a) for algal biomass community + PLA; b) spirulina.

reaction compounds. The total weight loss of 94.8 and 5.2% loss of inorganic remains were determined.

The spirulina blends showed higher degradation rates and temperature resistance than algal biomass community, and the degradation started at higher temperature. The difference in inorganic residue quantity probably represents the heavy metals which are likely absorbed by algal biomass community [5].

The results of tensile tests are given in Table 1. Tensile strength, elongation and module of elasticity (E module) were determined.

The results showed higher tensile strength than the reported 63.4 MPa [13]. Tensile strength decreases with increasing the share of algal biomass

Table 1. Results of mechanical tests

Composition	Tensile strength, MPa	Elongation at break, %	*E*-module, GPa
PLA	95.52 ± 1.93	4.47 ± 0.05	3.31 ± 0.62
PLA-A-5	81.16 ± 0.48	3.88 ± 0.15	3.28 ± 0.63
PLA-A-10	69.46 ± 0.98	2.91 ± 0.51	3.31 ± 0.75
PLA-S-5	62.67 ± 7.26	2.32 ± 0.56	3.32 ± 0.65
PLA-S-10	77.23 ± 2.78	3.55 ± 0.56	3.37 ± 0.44

community. It seemed that algal biomass community was not compatible with PLA and the adhesion between the polymer matrix and algae seemed to be poor. On the other hand, an elongation increment was observed in contrast with spirulina blends.

Modification of bioplastic by adding a plasticizer such as epoxidized soybean oil (ESO) could improve the tensile strength and elongation properties [11]. Condensation reaction between the oxirane rings in ESO and the hydroxyl groups (starch) improved mechanical properties as well as increase hydrophobicity of biocomposite material.

The *E*-module does not change much if different samples are compared, as seen from Table 1. The sample rigidity did not change by adding more algal biomass community (see samples PLA-A-10 and PLA-S-10) to the blends.

DMA and DSC analyses

Dynamic mechanical analysis (DMA) results are presented in Table 2.

The higher the dynamic elastic module the higher the degree of crystallinity. With both spirulina samples the dynamic module of elasticity (E_{dm}) increases with the spirulina share at 30 and 80 °C, and *vice versa* with DTP algal biomass community. Therefore, the degree of crystallinity has a decreasing tendency with algal biomass community, and the amorphosity of the material increases.

In Table 3, the thermal properties of blends are summarized. The value of glass transition temperature Tg of PLA was measured at 76.8 °C, which is a little higher in comparison with the reported data, Tg = = 66.2 °C [12] and Tg = 56.1 °C [13]. Tg of blends did not change significantly regardless of the algae share. All Tg remained in range of 72.2-74.3 °C. PLA melting temperature was determined at Tm = 153.3 °C, which coincide with the earlier reported value of Tm = 151.6 °C [13]. The share of spirulina (5 and 10 mass%) did not affect the Tm, while Tm of PLA-A-5 decreased for 4 °C in comparison with pure PLA. The reason could be due to the immense increase in the degree of crystallinity. It increased from 50% for PLA up to 86% in PLA-A-5. Algae act as a nucleation core which influences the increase in crystallisation.

Table 3. The thermal properties of blends

Sample	Tg / °C	ΔCp / Jg^{-1} K^{-1}	Degree of crystallinity, %	Tm / °C
PLA	76.8	0.228	50.32	153.5
PLA-A-5	72.2	0.306	86.64	149.5
PLA-A-10	73.3	0.211	39.61	152.3
PLA-S-5	74.3	0.106	41.35	153.4
PLA-S-10	74.3	0.075	55.20	153.3

Heat capacity step ΔCp is in accordance with literature [7], where the value 0.25 J/(g K) was reported. High cooling rate in PLA/algae samples leads to higher enthalpy, and more free volume in the blend, and consequently Tg is lower. Thus, the diffusion related to the structural recovery is higher. In blends with spirulina, a lower cooling rate was observed.

As already mentioned, some results of material properties could be the consequence of heavy metal content in the algal biomass community. Therefore, analysis on metals which are most likely present in real algal biomass community was performed. The results of metal measurements in algal biomass community (w_A), in spirulina (w_S) and maximum allowed values of first-class compost (w_C) are presented in Table 4. As seen from Table 4, the concentration of metal in algal biomass community is higher compared with spirulina. We can accept the suspicion that algae absorb metals from water streams. However, for composting, only the concentration of Zn is problematic in blended algal biomass community. Zhao [15] found out that Zn does not cause any changes in the germination index. In samples with spirulina, the measured concentrations are very low. Zhang proposed the mixing ratios which were safe for land application [14]. In our case, the mixing ratio should be 1:5 between algal biomass community (w_A) and spirulina (w_S).

A biodegradable material is converted to CO_2, water, inorganic compounds and biomass [17]. During 45 days of incubation, most samples reached the plateau in producing CO_2. Figure 3 represents the CO_2 production in time dependence.

Table 2. Results of dynamical mechanical analyses

Sample	E_{dm} at 30 °C, GPa	E_{dm} at 80 °C, GPa	Module losses at 30 °C, MPa	Module losses at 80 °C, MPa
PLA	3.86	18.33	37.4	11.9
PLA-A-5	3.06	53.20	75.1	26.3
PLA-A-10	2.26	36.76	57.2	17.4
PLA-S-5	2.86	32.61	50.4	18.2
PLA-S-10	3.55	42.36	61.1	20.3

Table 4. Determination of metal ions concentrations in real algal biomass community and in spirulina, in comparison with compost

Metal	w_A / mg kg^{-1}	w_S / mg kg^{-1}	w_C / mg kg^{-1}
Cu	56.5	<2	100
Zn	2110	14.1	400
Cd	<1	<1	1.5
Cr	67.6	<2	100
Ni	43.0	<2	50
Pb	8.6	<2	120

The most CO_2 was produced by the spirulina blend sample PLA-S-10, which contained the highest share of spirulina (10%), followed by the sample with a little lower share of spirulina (5%). Samples with 100% PLA also produced a lot of CO_2. PLA is susceptible to biodegradation by compost, and isolated soil microorganisms were capable of degrading PLA as well, such as *Amycolatopsis* sp. The strain represented the highest enzyme activity toward the PLA and PCL bioplastics [15]. As seen from Figure 3, the production of CO_2 is fastened by algae addition: the higher the share of algal biomass community, the faster the digestion. Spirulina speeded up the process of CO_2 conversion more than algal biomass community due to certain microorganism strains [16]. The CO_2 production of samples with WWTP sludge (PLA--A-5 and PLA-A-10) was slower. The result could be attributed to the fact that algal biomass community contained some metals (see Table 4) which inhibit the CO_2 production.

CONCLUSIONS

Bioplastic composite material was developed from polylactic acid (PLA), which represent a basic polymer and microalgae. After extraction, the solid matrix was dried.

Algae-based bioplastic possesses very good mechanical features, with tensile strength and elongation at break over 81 MPa and over 4% elongation, respectively, for 95% PLA and 5% algae sample. Based on presented results of the mass loss test, the new bioplastic is demonstrated to be totally decomposed within 45 days. In terms of the biodegradability of this material, data showed that CO_2 production was comparable to that of cellulose-based thermoplastic. These results highlight the possibility to obtain a new sustainable bioplastic. Algal biomass community can also be easily managed because it does not require any separation from other waste. Therefore, the application of algal biomass community for bioplastic production appears to be realistic.

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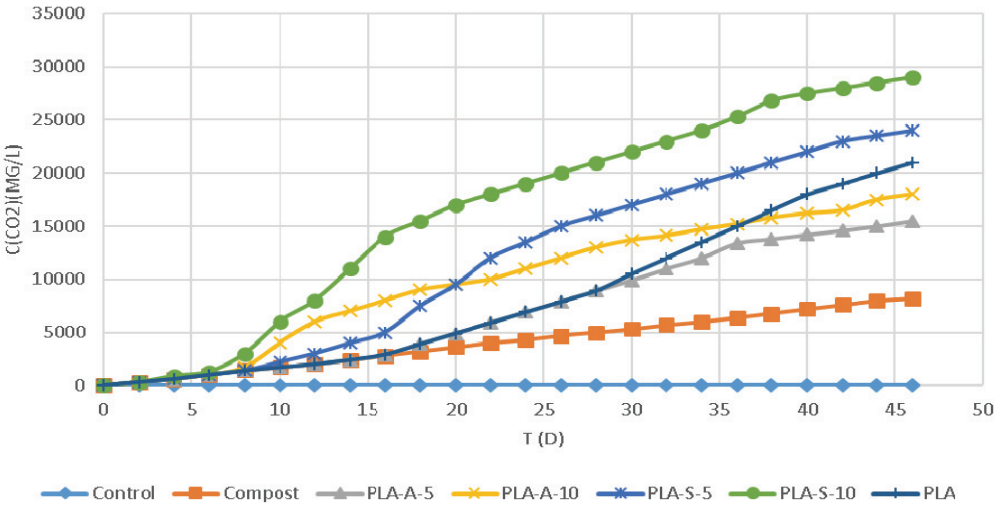

Figure 3. Dependence of CO_2 production on time.

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NAUČNI RAD

PROIZVODNJA BIOPLASTIČNOG MATERIJALA IZ ALGALNE BIOMASE

Bioplastični kompozitni materijal je razvijen od poli(mlečne kiseline) (PLA), koja se koristi kao osnovni polimer, i mikroalgalne biomase. Dve vrste biomaterijala su pripremljene na osnovu udela mikroalgi i PLA. Korišćeni su maseni odnosi 5:95 i 10:90. Najpre je korišćenabiomasa spiruline, a zatim mešana kultura mikroalgi iz proizvodnje biogasa. Cilj istraživanja bio je proučavanje karakteristika materijala, kako bi se utvrdilo da li se biomasa zajednica algi može koristiti u proizvodnji bioplastike. Otkriveno je da mikroalge ne utiču značajnije na svojstva materijala PLA. Stepen kristalnosti materijala i moduli gubitaka su se povećali, a temperatura topljenja smanjila.

Ključne reči: PLA, spirulina, kalorimetrija, biorazgradivost.