Algal Research 33 (2018) 337–344

Contents lists available at ScienceDirect

Algal Research

journal homepage: www.elsevier.com/locate/algal

Techno-economic analysis for the production of novel, bio-derived elastomers with modified algal proteins as a reinforcing agent

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ARTICLE INFO

Keywords:
Microalgae
Proteins
Biomaterials
Biorefinery

ABSTRACT

Shifting from a fossil fuel-dependent economy to modern, sustainable development requires not only the introduction of biofuels, but should also include novel and sustainable materials from renewable feedstocks. In this study, the viability of producing polyurethane-inspired elastomers manufactured through co-polymerization of modified proteins from microalgae with the synthetic monomer poly(ethylene glycol) methyl ether methacrylate (PEGMA) is investigated. Techno-economic evaluation of the process reveals great potential for the technology to be economically feasible, resulting in an investment payback rate of 8.4 years under the given conditions. Sensitivity analysis shows that the process feasibility is highly dependent on the protein availability, price of co-polymer, and protein concentration. Conversely, the relatively minor influence that the price of residual proteins plays in the process economics is very beneficial from the perspective of justifying algal biofuels production. A positive economic balance for the technology is achieved for a variety of different product formulations, prices, and processing techniques.

1. Introduction

Depletion of fossil fuels [1], climate change [2], uncertainty in energy markets [3], and waste disposal issues [4] force us to reconsider our approach to how we utilize the Earth's resources. A traditional petroleum biorefinery separates the fractions of crude oil, which after upgrading form a variety of products such as fuels, plastics, and chemicals. Therefore, sustainable development conducted through shifting the economy from fossil fuels to bio-based resources should consider all of these groups of commodities. Bio-derived plastics (bioplastics) are defined as plastics containing all carbon atoms derived from renewable, natural feedstocks, hence they have increased biodegradability and/or recyclability [5]. Currently, the global market is highly dependent on fossil fuel-derived plastics. In 2016, only slightly over 4 million tons of both biodegradable and bio-based plastics were produced worldwide, which only makes up to about 1% of total global production (300 million tons). Among different types of biomaterials, polyurethanes are the most predominant group of bioplastics, contributing 41.2% of the global market for biomaterials [6]. In general, polyurethanes have numerous forms and applications, ranging from insulation foams to hard, thermostable plastics used in a variety of commodities. Polyurethanes are synthesized by the condensation of polyols with isocyanates to form urethane bonds between prepolymer segments [7]. A number of approaches to replace polyols by utilizing plant-derived oils have been demonstrated [8], including a study reporting on algal oils successfully incorporated in the process [9]. Due to the hazardous nature of isocyanates [10], a second component of polyurethanes, there has been significant interest in developing non-isocyanate polyurethanes. Some of the examples of alternatives include polyurethanes based on polymerization of cyclic carbonates [11,12] or carbonated oils [13,14] and amines, which contribute to the hardness of the materials. Recently, hybrid materials comprised of proteins and synthetic rubbery polymers have been proposed as alternatives to these engineering plastics, where bio-derived proteins play the role of reinforcing hard domains [15].

In the last decades, large investments were made in the research and development of renewable biofuels. First generation feedstocks (starch-rich) for producing biofuels are often quoted as unsustainable, whereas second generation ones (waste and lignocellulose) are often economically and energetically infeasible [16]. Remarkable interest has been paid into third generation biofuels – microalgae, which are aquatic organisms that convert sunlight energy and carbon dioxide into lipids, which further can be used as substrates for biodiesel production. This concept has numerous benefits: algae have much higher lipid productivity per area than terrestrial plants [17], they can be used in carbon dioxide sequestration and waste water treatment, they have

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https://doi.org/10.1016/j.algal.2018.06.012
Received 18 October 2017; Received in revised form 24 May 2018; Accepted 10 June 2018

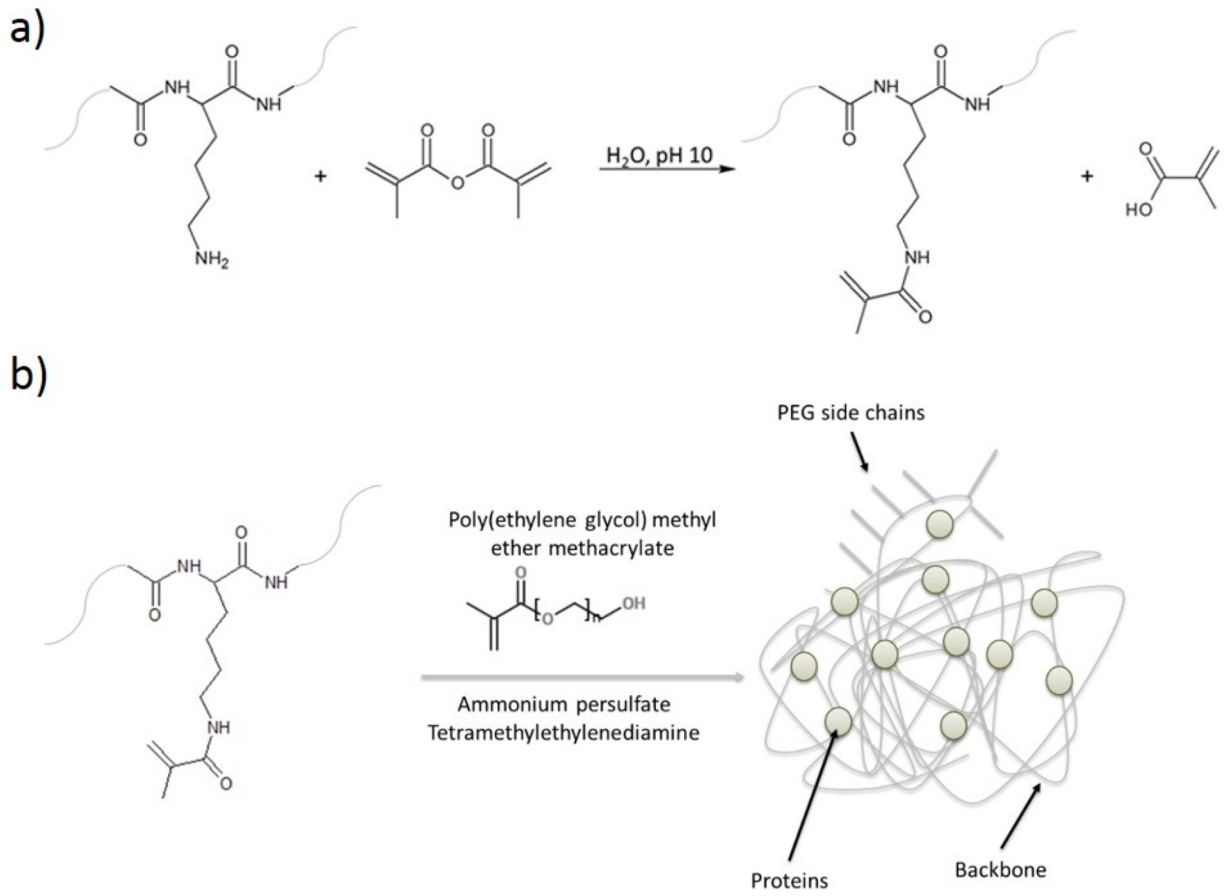

Fig. 1. Two-step reaction for synthesizing polyurethane-like elastomers: a) methacrylation of proteins, b) co-polymerization with PEGMA in the presence of AMPS and TEMED.

relatively low nutrient requirements and can be grown on variety of non-arable lands, and they are not directly competitive with food [18]. However, microalgal fuels have not been commercialized yet, mainly due to high costs associated with producing algal biodiesel [19]. One suggested approach is to incorporate the biorefinery concept into microalgae processing, utilizing other, higher-value compounds that are present in the biomass [20]. It has previously been concluded that algal biodiesel derived from *Chlorella vulgaris* lipids can be sold at a market price if the residual soluble proteins' stream can find its customer and be sold for more than $800 per ton [21].

In order to solve both of the issues explained in the previous paragraphs – a need for sustainable and non-toxic replacements for isocyanate based elastomers and a need for perspective customer for residual algal proteins – we have proposed a novel way to produce strong and tough thermoset materials. The process has been tested out in the laboratory with whey protein [15] and residual algal proteins [22] as feedstock. A two-stage reaction is conducted to obtain the protein co-polymers (Fig. 1). In the first step, proteins undergo reaction with methacrylic anhydride at basic conditions to yield methacrylated proteins and methacrylic acid as a by-product. In this step, primary amine groups located in lysine side chain and in N-terminal amino acids are substituted by methacrylamide groups, making the proteins reactive in co-polymerization. The degree of methacrylation is dependent on the ratio of methacrylic anhydride to crude protein. Variation in this step influences the final properties of the product as it determines cross-linking within the polymer. In principle, proteins are responsible for the stiffness and rigidity of the material, whereas poly(ethylene glycol) methyl ether methacrylate (PEGMA) contributes to its elasticity.

In the second reaction, methacrylated proteins copolymerize with co-monomer in the presence of ammonium persulfate (APS) as initiator and tetramethylethylenediamine (TEMED) as catalyst to create a crosslinked material consisting of stiff proteins and flexible synthetic polymer chains. The likely random copolymerization leads to randomly distributed hard and soft domains. In the course of this process a hydrogel is formed, which requires molding and further drying in order to obtain the final product. Specific data on processing parameters were listed in the relevant studies for whey [15] and algae [22] proteins as feedstocks. The first manifestation of this concept resulted in hydrophilic thermoset materials; however, projected further developments are expected to yield products with variety of characteristics. These can be obtained by changing processing parameters, co-monomer, or the protein modifications.

Based on the currently available data on the first demonstration of this technology, the objective was to perform technical and economic assessment (TEA) whether the suggested method for production of novel protein-based, polyurethane-inspired elastomers is economically feasible at its current technology readiness level (TRL). The process was modelled using appropriate software (SuperPro Designer by Intelligen©) with adjustment of necessary variables. As the technology is expected undergo future improvements, this model serves as a framework for these kinds of processes and allows quick economic assessment. In order to investigate model boundaries and influence of specific parameters on the final model performance, sensitivity analysis was also performed.

2. Approach and assumptions

2.1. Process description

The manufacturing process for polyurethane inspired biomaterials