Polymer Degradation and Stability 133 (2016) 75–84

Contents lists available at ScienceDirect

Polymer Degradation and Stability

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

Biodegradable soy protein films with controllable water solubility and enhanced mechanical properties via graft polymerization

Yi Zhao [a], Helan Xu [a], Bingnan Mu [a], Lan Xu [b], Yiqi Yang [a, c, d, *]

[a] Department of Textiles, Merchandising & Fashion Design, University of Nebraska-Lincoln, Lincoln, NE, 68583-0802, USA
[b] Department of Agronomy and Horticulture, University of Nebraska-Lincoln, Lincoln, NE, 68583-0915, USA
[c] Department of Biological Systems Engineering, University of Nebraska-Lincoln, Lincoln, NE, 68583-0802, USA
[d] Nebraska Center for Materials and Nanoscience, University of Nebraska-Lincoln, Lincoln, NE, 68583-0802, USA

ARTICLE INFO

Article history:
Received 31 May 2016
Received in revised form
28 July 2016
Accepted 6 August 2016
Available online 8 August 2016

Keywords:
Soy protein
Poly(vinyl alcohol)
Water soluble film
Biodegradation
Graft polymerization
Acrylic acid

ABSTRACT

Graft polymerization of acrylic acid endowed soy protein films with good tensile properties and water solubility without sacrificing biodegradability. In this research, soy protein was grafted with acrylic acid and cast into biodegradable films as substitutes of non-biodegradable Poly(vinyl alcohol) (PVA) films. The grafted soy protein films had 318%, 114%, 60% and 9% higher tensile strength, elongation, dissolving rate and transmittance, compared to ungrafted ones, respectively. Acrylic acid grafting provided soy protein films with biodegradability, flexibility, and adhesion to yarns substantially higher than PVA, while water solubility and abrasion resistance similar to PVA, leading to high potential applications of the grafted soy proteins in the fields of water soluble packaging films and slashing to substitute PVA.

1. Introduction

Using renewable polymers from agricultural byproducts as alternatives to non-biodegradable ones is essential for sustainable industries. Poly(vinyl alcohol) (PVA) figures prominently in the development of water soluble materials, such as fast-dissolving packaging films, oral medicine films and yarns' coating (textile warp sizes), and has a high annual consumption of over 1 million tons worldwide [1]. Due to good mechanical properties and water solubility, PVA films provide anglers' baits [2] or some chemicals, such as laundry detergents, bleach, fertilizers, pesticides, dyes and pigments, with enough protection during storage, and disappear after immersing in water bath for short period of time [3]. PVA coatings also provide warp yarns with protection against external abrasion and tension during high speed weaving, and are easily removed during desizing [4]. However, high amount of desized or released PVA wastewater have led to serious water pollution due to their poor biodegradability [5]. PVA is one of the chemical oxygen demand (COD) contributors to wastewater. In addition, PVA has capability of mobilizing heavy metals from sediments in water body [6,7], leading to irreversible accumulation of these metals in organs of marine creatures, and thereby causes related diseases [8]. Therefore, exploitation of biodegradable polymers with good water solubility to replace PVA in industries is imperative.

Substitutes of PVA for packaging films and textile sizes should have good biodegradability, good tensile strength of films with high elongation, and enough water solubility for laundering or desizing. Soy protein has good biodegradability, film formability, and is readily available in large quantities from edible oil and biodiesel production [9], and thus has high potential to be fabricated into environmentally benign films and textile sizes [10,11]. However, films from soy protein have high brittleness [12] and fail to be directly used in packaging or slashing (textile warp sizing) industries [13,14]. Many physical modifications have been studied to overcome the drawbacks of pure protein films [15,16]. Addition of water soluble plasticizer, such as glycerol [17,18], hydroamine [19,20], sucrose, galactose and fructose [21,22], and sorbitol [23], could increase flexibility of protein films. However, tensile strength of protein-based films has been substantially decreased with the addition of plasticizers [24,25]. In addition, films from hydrolyzed and plasticized soy protein cannot easily disintegrate or dissolve in

* Corresponding author. Department of Textiles, Merchandising & Fashion Design, University of Nebraska-Lincoln, Lincoln, NE, 68583-0802, USA.
E-mail address: yyang2@unl.edu (Y. Yang).

http://dx.doi.org/10.1016/j.polymdegradstab.2016.08.003
0141-3910/

water due to the lack of water-soluble groups on molecular chains.

Chemical modifications have possibility to improve water solubility of proteins, such as sulfonating hydroxyl groups, transforming amine groups into quaternary ammonium salts, transforming hydroxyl groups into carboxyl groups, and diazotizing amine groups and reacting with compounds with hydrophilic groups. However, most of the above modifications strongly destroy protein molecules due to strong reaction conditions and need toxic chemicals during reaction, leading to poor mechanical properties and toxicity of modified protein films. Chlorosulfonic acid was used to transfer hydroxyl groups on aliphatic chains into sulfo groups using dichloromethane as solvent after overnight reaction [26–28]. Sulfonation of hydroxyls groups on benzene rings occurred only with strong acids, such as toxic chlorosulfonic acid or sulfur trioxide [29,30]. Sulfonation of benzene rings, which contain hydroxyl, was carried out using 98% sulfuric acid at high temperature [31]. Diazotization of amine groups occurred under strong acid conditions, such as 4 mol/l sulfuric acid [32]. Hydroxyl groups could also react with chloroacetic acid under 40 wt% alkali condition and form water soluble carboxyl groups by nucleophilic substitution reaction [33]. Also, hydroxyl groups on proteins could react with hydrophilic epoxy compounds to increase their water solubility. However, the reaction only can be carried out under strong alkali conditions [34]. In addition, water solubility of protein has limited improvement via the chemical modifications due to limited reaction sites on proteins. For example, proteins have few tertiary amines, which could be transformed into quaternary ammonium salts.

In this research, soy protein films with good biodegradability, mechanical properties and controllable water solubility have been developed via acrylic-acid graft modification. Under a mild reaction condition, water soluble acrylic acids were grafted onto soy protein, and endowed soy protein with improved film water solubility and mechanical properties without sacrificing biodegradability or destroying protein polymers. Graft polymerization of soy proteins with acrylic acid was characterized. Tensile properties and biodegradability of the grafted soy protein films were studied. Performance properties of the grafted soy proteins, such as effects of grafting ratio on water solubility and transparency of soy protein films, adhesion of grafted soy protein sizes to fibers, and abrasion resistance of the grafted soy protein sized yarns, have been evaluated to explore their potential applications in the field of packaging and textiles.

2. Experimental

2.1. Materials

Soy protein (PRO-FAM 646) was provided by ADM International, Decatur, IL. PVA was purchased from chemical manufacturers in US. The PVA with a hydrolysis degree of 86–89% and 65 kDa molecular weight was purchased from a commercial sizing agent supplier in USA. Viscosity of the PVA at room temperature was 11.6–15.4 mPa at 4% solid content. Other chemicals used in this study were purchased from VWR International.

2.2. Graft modification of soy protein with acrylic acid

Soy protein was grafted with acrylic acid through free radical reaction. Mixture of soy protein and water was deoxygenated by aeration of nitrogen gas for about 20 min. Initiator oxidant (5 wt% $K_2S_2O_8$, based on the weight of soy protein) and reductant (2 wt% $NaHSO_3$, based on the weight of soy protein) were dissolved in distilled water and added into the soy protein mixture within 10 min in sequence. Then neutral acrylic acid monomer (10–70 wt%, based on the weight of soy protein) was slowly added into the flask from dropping pipette within around 45 min. Liquor to soy protein ratio was 9:1. The graft polymerization was carried under a nitrogen atmosphere at 70 °C with stirring at 600 rpm for 4 h. Finally, the graft reaction was terminated by the addition of 0.04 wt% paradioxybenzene (based on the weight of soy protein). Schematic of the graft polymerization of soy protein with acrylic acid is given in Scheme 1. pH of the reaction products was adjusted to isoelectric point of soy protein (pH 4.5) [35]. The precipitate from centrifugation was thoroughly washed and neutralized to about pH 7 and dried at 105 °C. Except of the addition of acrylic monomers, same operations were carried out to prepare ungrafted soy protein as control.

2.3. Determination of grafting parameters

Total amount of residual acrylic acid was determined by titrating the double bonds of residual monomer in the supernatant. % Monomer conversion was calculated using Equation (1) [36].

$$\%\ \text{Monomer conversion} = \frac{W_1 - W_2}{W_1} \times 100 \quad (1)$$

W_1 and W_2: weights of the total and the residual monomer, respectively.

Percent grafting describes the weight percentage of polyacrylic acid branches grafted onto functional groups on the surfaces of soy protein to the original soy protein and % grafting efficiency describes the weight percentage of polyacrylic acid branches grafted onto functional groups on the surfaces of soy protein to the total polyacrylic acid, including grafted polyacrylic acid and ungrafted homopolymers. % grafting and % grafting efficiency were determined by Equations (2) and (3), respectively [36].

$$\%\ \text{Grafting} = \frac{W_a - W_0}{W_0} \times 100 \quad (2)$$

$$\%\ \text{Grafting efficiency} = \frac{W_a - W_0}{W_1 - W_2} \times 100 \quad (3)$$

W_a: weight of grafted soy protein after water wash.W_0: weight of the original soy protein.

2.4. Proton nuclear magnetic resonance (^1H NMR)

Ungrafted soy protein and acrylic acid grafted soy protein (AA-g-SP) were characterized by ^1H NMR in deuterated sodium hydroxide solution to confirm the successful grafting using an Avance 600 MHz Digital NMR spectrometer (Bruker Co. Ltd., Switzerland). Sixty-four scans were acquired to obtain an adequate signal-to-noise ratio. The concentration of each sample was about 1 wt% in alkali solvent.

2.5. Conductometric and potentiometric titration of amine and carboxylic groups

To verify grafting ratio of soy protein, concentrations of carboxylic groups and amine groups were quantified by a pH/conductivity meter (Mettler Toledo Seven Multi TMS47). Thirty grams of grafted and ungrafted soy protein solution with 0.6 wt% concentration of soy protein were prepared, respectively. Standardized 0.024389 mol/l HCl was added into the soy protein solution to adjust pH to 3, under which the carboxylic and amine groups in grafted and ungrafted soy protein were protonated. Standardized 0.026112 mol/l NaOH solution was used in titration. Conductivity and pH values were recorded after addition of about 2 ml NaOH solution.