

Short communication

Surface modification of zein films

Atanu Biswas^{a,*}, Gordon W. Selling^a, Kristen Kruger Woods^a, Kervin Evans^b^a Plant Polymers Research Unit, USDA/Agricultural Research Services, 1815 N. University Street, Peoria, IL 61604, United States^b New Crops and Processing Technology Research, USDA/Agricultural Research Services, 1815 N. University Street, Peoria, IL 61604, United States

ARTICLE INFO

Article history:

Received 20 October 2008

Received in revised form 23 January 2009

Accepted 4 February 2009

Keywords:

Zein

Surface energy

Hydrophilic reagents

ABSTRACT

A novel method to derivatize the surface of zein is devised that can modify the water absorption and surface wetting behavior. The reagents used to impart the desired properties in a reasonable amount of time include octenyl succinic anhydride and alkyl and alkenyl ketene dimers. The method is easy to apply and involves baking with an appropriate concentration of a derivatizing agent. Decreased water absorption and increased contact angle with water relative to control demonstrate the advantages this methodology provides. Atomic force microscopy was used to demonstrate that after derivatization the surface of the film became much different, having large globular domains that extended as much as 122 nm above the lowest surface. Given the hydrophobic character of the reagents and their relative incompatibility with zein, it was anticipated that derivatization would be somewhat inhomogeneous.

Published by Elsevier B.V.

1. Introduction

Zein is a natural polymer obtained as a product of industrial corn processing (Lawton, 2002; Momany et al., 2006). With the growth of the bio-ethanol industry, the amount of zein potentially available has grown considerably, to the extent that techniques are needed to develop new uses for this material. It has been widely studied and has historically had many industrial and food uses (Wang and Padua, 2003; Padua et al., 2005; Ghanbarzadeh et al., 2007). Previously the main application has been in the textile fibers market, but now it is used as a coating for candy, nuts, fruit, pills, and other encapsulated foods and drugs. Zein can also be incorporated into resins and other bioplastic polymers (Lai et al., 1997; Padua and Santosa, 1999; Lawton, 2004; Selling et al., 2004; Selling and Sessa, 2007).

A major drawback in the use of zein as a renewable raw material is the lack of amine moieties (lysine amino acid) which limits the number of typical protein derivatizing techniques available. Another major problem in modifying and derivatizing zein is its lack of solubility. It dissolves in an ethanol/water (90:10) mixture, but this mixture cannot be readily used for chemical modification because alcohol and water may react faster with electrophilic reagents than zein does. In spite of these shortcomings, a number of articles have been reported over the years on zein reactions. For example, a method has been devised to prepare zein acetate in order to increase the water resistance, strength, and flexibility of

zein films (James, 1944) and fibers (Zhang et al., 1997). Likewise, zein has been crosslinked (Veatch, 1941) with cyanuric chloride, formaldehyde, carbodiimide, glyoxal (Woods and Selling, 2007), and glutaraldehyde (Sessa et al., 2007). Biswas et al. reported the acylation of zein with anhydrides and acyl chlorides in dimethylformamide (Biswas et al., 2005a,b) and ionic liquids (Biswas et al., 2006). Wu et al. (2003) synthesized zein/nylon copolymer in dimethylformamide. In all of the techniques described, the derivatization has taken place in solution. However, at times only the surface may need to be derivatized in order to impart value to the article. Additive, non-bound coating techniques have been utilized to vary the surface properties of zein (Wang and Padua, 2006). However, given that additives and coatings can be deposited or removed at various points during processing of the article a technique that bonds the reagent to the zein film has merit.

In this work, we sought to find a new method to derivatize zein. Since a major application of zein is in the form of films and fibers, we believe a surface reaction of zein would be useful. There are several advantages of this approach. First, there is no need to alter the current processes for making films, coatings, or fiber. The reaction can be carried out after the film, coating, or fiber is made. Secondly, we can keep the desirable properties of the film, coating, and fiber and only impart additional desired properties onto the surface. Thirdly, as the reaction only takes place on the surface, less derivatizing agent is consumed, thereby decreasing the cost of the reaction. In addition by chemically bonding the desired agent onto the film, the agent cannot be easily removed physically from the article. Finally, the reaction is easy to do and effective. To our knowledge, there is no prior report of similar surface modification of zein films, coatings, or fibers.

* Corresponding author. Tel.: +1 309 681 6406; fax: +1 309 681 6691.
E-mail address: atanu.biswas@ars.usda.gov (A. Biswas).

2. Experimental

2.1. Materials

The zein samples were obtained from Freeman Industries. Octenyl succinic anhydride (OSA) was purchased from Aldrich. Two ketene dimer samples were obtained from Hercules Incorporated (Wilmington, DE): alkyl ketene dimer (AKD) is derived from saturated fatty acids and alkenyl ketene dimer (ALKD) is derived from unsaturated fatty acids. Deuterated sodium hydroxide and water were purchased from Cambridge Isotope Laboratories (Andover, MA). The other chemicals were procured from Aldrich Chemical Co.

2.2. Procedures

Zein was dissolved in a 90:10 ethanol/water mixture and cast into films of an approximate thickness of 0.21 mm. Solutions of OSA, AKD, and ALKD were dissolved in methylene chloride at 10% concentration. The solutions were then applied onto the zein surface as a thin film of roughly 0.25 mm thickness and 10 mm by 40 mm area. The film and the derivatizing agent were first air-dried, and then placed in an oven at 100 °C overnight. The reaction product was then washed with toluene and methylene chloride to remove any free, unbound chemicals. The final products were characterized with ATR, ^1H NMR, water absorption, and contact angle measurement.

Water absorption was carried out by immersing 1 cm $\times$ 2 cm films of zein, with or without surface derivatization, in deionized water, samples were run five times. The dry mass of each film was first obtained, and the mass of each immersed film (with excess water removed) was determined at 5, 15, 60, 120, and 1440 min. From this the mass% (water) gained was determined.

The contact angle measurements (measurements were made between two and four times) were made on a First Ten Angstroms FTA4000 Microdrop Instrument. Zein films were held in place with two-sided tape to a glass microscope slide. A 22-gauge needle was used to release a five microliter drop. The initial contact angle (time = 0 s) was calculated using the first stable image of the full drop on the film surface. The second contact angle was calculated using the image captured 2 s after the initial image. Images were recorded every 0.0083 s and a total of 500 images were collected.

The atomic force microscope (AFM) experiments were carried out with a Nanoscope IV microscope and controller (Veeco Instruments, Santa Barbara, CA). Silicon probes (purchased from NanoAndMore Inc., Lady's Island, SC) having a force constant of 1.9 N/m were used. Scans were made in tapping mode in air at rates of 0.1–0.3 Hz. Samples were prepared by slicing pieces of zein treated and untreated thin films with a razor blade and attaching to a steel puck using double-sided tape. Care was taken to scan the samples in the middle in order to avoid scanning over any induced stress fractures caused by the razor blade. Zein films were allowed to adhere to the tape for a minimum of 10 h prior to scanning. Scans were repeated on three separate samples of each film.

3. Results and discussion

The structures of the reagents used in this study are detailed (Fig. 1). Zein was first cast into a film by the conventional method. Solutions of OSA, AKD, and ALKD in methylene chloride (at 10% concentration) were applied to the film surface and heated at 100 °C overnight. Methylene chloride was selected as it can readily dissolve the selected reagents and it is polar enough that it can wet

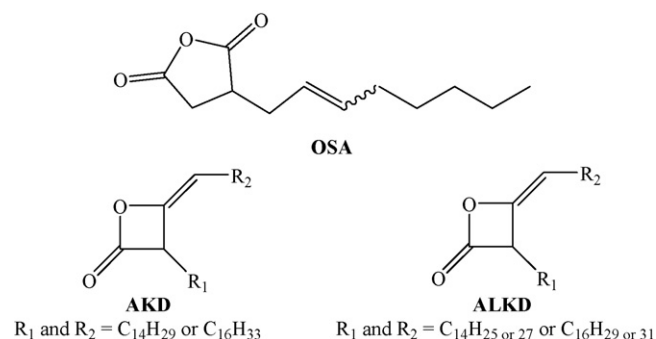
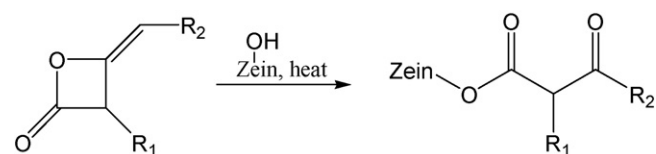


Fig. 1. Structures of reagents used to modify zein surface.

the zein surface. Additional work would be needed to select a more environmentally safe solvent; a solvent such as acetone may also be suitable. These materials have been shown to modify the hydroxyl groups of starch (Qiao et al., 2006). Zein has been shown to have numerous hydroxyl groups due to the presence of many serine and threonine amino acids (Cheryan and Shukla, 2001). Under the reaction conditions it is expected that the ketene dimers (AKD and ALKD) or the anhydride (OSA) will react with the hydroxyl groups located on the surface of the film. The OSA would react in the typical fashion giving an ester moiety bound to the zein and a free carboxylic acid. The ketene dimers would provide β -keto esters on reaction with the hydroxyl groups present in the zein protein (Scheme 1). The terminal amine of zein would react with OSA or the ketene dimer to give an amide or a β -keto amide respectively. Given that this chemistry is occurring at the surface only, it was not surprising to find that differences between test and control could not be found by attenuated total reflectance (ATR) IR or NMR. In ATR the top one or two micrometers is evaluated. In NMR, the bulk material is evaluated. In either case a true surface derivatization would not be detected by these techniques.

After the chemical treatments differences in surface properties were observed. Changes in the hydrophobicity of zein were seen in bulk water absorption experiments. In this case, thin films of zein (0.21 mm thick) were separately immersed in water at different times, and the mass of water absorbed was measured. Care was taken to remove free water droplets on the film surface. The results for different samples of zein are detailed in Fig. 2. It is clear that the surface reaction with OSA, AKD, and ALKD has decreased the water absorbency of zein films. At 120 min, zein films modified with ALKD only absorbed 40% of the water of the unmodified zein. The trend towards decreased water absorbency is ALKD > AKD > OSA except at very long soaking times. Although the reactions of OSA, AKD, and ALKD are only on the zein surface, their effect on bulk water absorption is significant.

As an indication of the change in surface properties, we measured the contact angle of the modified and unmodified zein surface. The results are shown in Fig. 2. The contact angle was larger immediately after the water droplet is deposited on the zein surface ($t = 0$ s) and decreased in time as the droplet equilibrates on the surface. For comparison, the contact angle data for waxed paper and



Scheme 1. Formation of zein alkyl β -ketone ester from reaction of zein with ketene dimer.

Download English Version:

<https://daneshyari.com/en/article/4514945>

Download Persian Version:

<https://daneshyari.com/article/4514945>

[Daneshyari.com](https://daneshyari.com)