Available online at www.sciencedirect.com

ScienceDirect

Bioresource Technology 99 (2008) 2032–2036

BIORESOURCE TECHNOLOGY

Processing and properties of gluten/zein composite ☆

Sanghoon Kim *

National Center for Agricultural Utilization Research, Agricultural Research Service, USDA, 1815 N. University Street, Peoria, IL 61604, United States

Received 14 February 2006; received in revised form 27 February 2007; accepted 27 February 2007
Available online 7 May 2007

Abstract

Polymer composites have been formed by mixing component materials in extruders or compression molds. Agricultural biopolymers are usually mixtures of several compounds; however, high-temperature processing can cause unwanted consequences such as decomposition, gas generation, and phase-separation. This report introduces a new technology to form biodegradable polymer composites that can replace existing petroleum-based polymers. With this newly developed process, polymer composites are produced at room temperature. During the process, micrometer-scale raw materials are coated with zein, which has strong adhesive properties, and are then compressed to form a rigid coherent material. Since this technique does not require purification of the raw materials, various types of compounds can be used as component materials. In this report, wheat protein, gluten, was used as a matrix material. The compressive yield strength of the product formed from gluten is ca. 40 MPa, comparable to that of polypropylene.

Keywords: Biopolymer composite; Biodegradable polymer; Gluten; Zein

---

1. Introduction

There is considerable interest in replacing some or all of the synthetic plastics by biodegradable polymers in many applications. Because petrochemical-based plastic material persists beyond its functional life, a waste disposal problem is facing modern society. Research to alleviate pollution and litter problems includes efforts to develop plastics that degrade more rapidly in the environment. Most of our waste is either stored in landfills or composted. Since most of the natural polymers are biodegradable, the use of natural polymers as a substitute for non-biodegradable synthetic polymers can be environmentally beneficial to some extent. Recently, many research groups have concentrated on the development of biodegradable polymer blends or composites from starch (Gaspar et al., 2005), corn gluten meal (Beg et al., 2005; Wu et al., 2003a), wheat gluten (Domenek et al., 2004; Woerdeman et al., 2004; Kayseriliolu et al., 2003), and zein (Wu et al., 2003b).

In most cases, commercially available biopolymers contain a significant amount of unwanted materials that remain after the extraction/isolation process. Purification of these materials is very costly for the practical utilization of these agricultural products as a component of useful final products. If these agricultural excess products can be used without further purification, we can minimize the use of toxic chemicals, simplify the manufacturing process, save energy, and lower the production cost.

Conventionally, polymer composites had been manufactured by mixing the component materials in an extruder at high temperature. If raw material is a mixture of various components with impurities, phase-separation, decomposition, and gas generation will interfere with the extrusion process. This report introduces a new methodology for the production of biodegradable polymer composites that will potentially replace existing petroleum-based polymers. This newly developed technique requires neither extrusion

---

☆ Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

* Tel.: +1 309 681 6260; fax: +1 309 681 6685.
E-mail address: kims@ncaur.usda.gov

0960-8524/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.biortech.2007.02.050

nor processing at high temperatures. Instead, micrometer-scale raw materials (powders) are coated with zein which has a strong adhesive force, and compressed to form a rigid material. Since this technique does not require purification of raw materials except zein, various types of compounds can be used as component materials. In this report, wheat gluten was used as a matrix material.

Proteins are natural polymers that possess a highly complex structure. Gluten is a mixture of several proteins in which gliadin, glutenin, globulin and albumin predominate. It is the largest protein fraction in wheat and represents about 8–15% of the dry weight of the grain.

Zein, a protein derived from corn, can be used as a biodegradable material (Lawton, 2002; Shukla and Cheryan, 2001), and as early in 1909, it was used to prepare plastics (Goldsmith, 1909). Later, the related research was delayed due to the emergence of petroleum-based plastics. However, within the last two decades, zein has again attracted attention because of its biodegradability. In this report, zein is utilized because of its good adsorption to hydrophilic surfaces and strong adhesive properties.

Mechanical properties such as compressive yield strength, modulus of elasticity, and yield strength at 0.2% offset of the polymer composites produced from gluten were evaluated. In order to show the universal applicability of the developed technique, the same process was also applied to milk powder, amylose, and two types of soy proteins, and their mechanical properties were evaluated.

2. Methods

2.1. Materials

Gluten, normal maize starch, and ethyl ether were purchased from Sigma (St. Louis, MO). Regular grade zein (F4000) was purchased from Freeman industries (Tuckahoe, NY). The reported protein content for the F4000 Zein was 90–96% (dry basis). Oily impurities of zein were extracted with ether. Ethanol was from Aaper Alcohol (Shelbyville, KY). Soy proteins were obtained from DuPont Soy Polymer (St. Louis, MO). Milk powder (Low Heat Nonfat Dry Milk) was purchased from Dairy America (Dublin, CA).

2.2. Transmittance measurement

Transmittance of zein solution in aqueous ethanol was measured with a custom-built turbidometer that is composed of a He–Ne laser, temperature-controlled sample block, stirrer, neutral density filter, laser powermeter, and laptop computer. The 633 nm beam from the He–Ne laser passes through sample solution in a scintillation vial, the diameter of which is 2.5 cm. During the transmittance measurement, the sample solution was continuously stirred with a digitally controlled magnetic stirrer. The intensity of the transmitted laser beam was monitored with a laser powermeter, the output of which is interfaced with a laptop computer.

2.3. Preparation of protein composites

Test specimens from protein composites were prepared by using molds fabricated from aluminum. Typical manufacturing procedure for test specimens is as follows (example composites with 20% zein). Both 6 g of Gluten and 1.5 g of zein powder were dispersed and mixed thoroughly in 13.5 g of ethanol. Then 1.5 g of distilled water were added and stirred until the zein was fully dissolved. After that, 50 g of ethanol were added with vigorous stirring. During this time, proteins aggregated to form a large chunk. Excess aqueous ethanol was decanted, and the aggregate was poured into an aluminum mold. Compression pressure was adjusted to 75 lbs/cm^2 for 2 min. The manufactured specimens were air-dried for 72 h, and stored at $50 \pm 5\%$ relative humidity until mechanical property was measured.

2.4. Mechanical property measurement

The sample specimens were prepared by the conditions specified in the American Society for Testing and Materials (ASTM) standard, D695. The test specimens were conditioned at 23 ± 2 °C and $50 \pm 5\%$ relative humidity for no less than 40 h prior to testing in accordance with Procedure A of Practice D618. The samples were tested with Instron Universal Testing Machine (Model 55R1122, Canton, MA) equipped with 500 kg reversible load cell. Merlin software handled data recording and manipulation. For all the tested samples, a crosshead speed of 1.3 mm/min was used. Compressive yield strength, modulus of elasticity, and yield strength at 0.2% offset were compared between sample specimens.

3. Results and discussion

The new technology presented in this report makes use of the powerful adhesive properties of zein to bind the matrix materials. The first step of the process is to disperse the matrix material and zein in ethanol. The matrix material must be a powder of micrometer-scale particle size, and most of the spray-dried biopolymers satisfy this condition. The second step is dissolving zein in the mixture by adding a small amount of water. The final composition of the solvent has to be 85–90% aqueous ethanol. After the zein is completely dissolved, ethanol is added to make the ethanol content of the solvent greater than 95%. At this moment, zein molecules are adsorbed to the surface of the matrix particles, and the sticky characteristics of zein induce agglomeration of the particles. The final step is squeezing out the solvent from the chunk material in the mold and recovering the ethanol.

The optimum solvent composition of zein for this process had been found by measuring the transmittance of the zein solution. Zein is soluble in 70–90% aqueous etha-