Composites: Part A 84 (2016) 435–441

Contents lists available at ScienceDirect

Composites: Part A

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

Activating relaxation-controlled diffusion mechanisms for tailored moisture resistance of gelatin-based bioadhesives for engineered wood products

Kristen M. Hess, Wil V. Srubar III *

Department of Civil, Environmental, and Architectural Engineering, University of Colorado Boulder, ECOT 441 UCB 428, Boulder, CO 80309-0428, USA

ARTICLE INFO

Article history:
Received 20 November 2015
Received in revised form 9 February 2016
Accepted 11 February 2016
Available online 27 February 2016

Keywords:
A. Resins
B. Environmental degradation
C. Analytical modeling
D. Moisture

ABSTRACT

The feasibility of tailoring the moisture resistance of bioadhesives by activating relaxation-controlled diffusion mechanisms is demonstrated herein using gelatin, a hydrophilic biopolymer, as a model biobased resin for engineered wood products. The effect of gelatin-to-water concentration and tannin addition on the governing kinetics of water transport in gelatin-based bioadhesives was investigated in this work. Time-dependent flexural mechanical properties of laminated (a) gelatin and (b) gelatin–tannin wood veneer composites conditioned at both moderate and high humidity were characterized and compared to oriented strand board and plywood. Results indicate that increases in both gelatin and tannin content not only decrease rates of water uptake, volumetric swelling, and maximum moisture contents of gelatin-based resins, but also increasingly induce relaxation-controlled moisture diffusion behavior, which implies short-term moisture resistance and long-term moisture affinity. This behavior could be leveraged to address both in-service (i.e., strength, stiffness) and out-of-service (i.e., rapid biodegradation) requirements for engineered wood products.

1. Introduction

1.1. Adhesives for engineered wood products

Approximately 60% of all adhesives manufactured worldwide are used in the fabrication of engineered wood products [1]. The annual global demand for engineered wood, including oriented strand board (OSB) and plywood, has doubled over the past three decades and is projected to double again to 5.2 billion cubic meters by 2050, due to factors such as rising populations, stricter building codes, and diminishing supplies of old-growth timber [2].

Engineered wood products are fabricated using predominantly synthetic adhesives, such as phenol formaldehyde (PF), urea formaldehyde (UF), or polymer isocyanates (PMDI) – materials that have been identified as allergens and toxic carcinogens [1,3–5]. The negative effects of formaldehyde and the pressure to decrease reliance on petroleum-based resources have recently prompted a resurgence in research on alternative adhesives from natural, biorenewable sources.

Historically, adhesives derived from animal proteins, including gelatin, were used in wood composites until their replacement by synthetic, low-cost, high-performing adhesives [6,7]. Comprised mainly of the amino acids proline, glycine and 4-hydroxyproline [8], gelatin is a partially degraded form of collagen, a protein found in the skin and bones of animals [9–11]. Commercial gelatin is obtained via thermochemical degradation of collagen's triple-helix structure into random coils, which are stabilized by hydrogen bonds and covalent crosslinking [11–13]. When dissolved in an aqueous (water) solution at elevated temperatures (>50 °C), gelatin exists in a disordered, relaxed coil formation. However, as the solution cools below 30 °C, gelatin becomes more ordered and partially reforms helical structures similar to its parent collagen.

In addition to advantages such as biorenewability, biodegradability, global abundance, and nontoxicity [10,11,14,15], dehydrated gelatin resins exhibit high elastic moduli, tensile strengths, and adhesive properties compared to other biopolymers (e.g., starch, acacia gum) and conventional synthetic adhesives [5,16,17]. While the majority of gelatin-based materials are currently used in the food, packaging, pharmaceutical, and biomedical industries [11,18,19], recent studies demonstrate that gelatin exhibits sufficient adhesive binding properties for use as a bioadhesive for engineered wood products [5,17].

* Corresponding author. Tel.: +1 303 492 2621; fax: +1 303 492 7317.
E-mail address: wsrubar@colorado.edu (W.V. Srubar III).

http://dx.doi.org/10.1016/j.compositesa.2016.02.013
1359-835X/

1.2. Improving the moisture resistance of gelatin-based bioadhesives

As a hydrophilic biopolymer network, gelatin has a high propensity to swell or shrink due to the absorption or desorption of water [20]. While moisture affinity is preferred for out-of-service biodegradation of engineered wood products, moisture resistance is required, especially in the short term, for temporary applications (e.g., concrete formwork, scaffolding, disaster-relief housing). Given that pure gelatin is well known to uptake moisture and lose mechanical integrity immediately upon exposure to high-humidity or wet environments, in-service moisture resistance requirements render pure gelatin a problematic candidate bioadhesive. However, recent research has explored the incorporation of additives, such as polyols, starch, chitosan, tannins, and oligosaccharides, to improve the moisture resistance of gelatin resins [8].

Tannins are polyphenolic compounds derived from vegetables that have recently been investigated as a potential replacement for hazardous phenols in the adhesives industry. In addition to being nontoxic, renewable, and biobased, tannins have a strong affinity for the amino acid proline found in gelatin. Tannin and gelatin are also soluble in water, which eliminates the need for organic solvents during preparation [8]. In addition to the successful implementation of tannin in other formaldehyde-based wood adhesives (i.e., phenol–formaldehyde) [21], tannin has exhibited compatibility with wood substrates and the potential ability to enhance short- and long-term moisture-resistance in gelatin-based bioadhesive networks.

1.3. Scope of work

In this study, the feasibility of engineering a bioadhesive resin with initially protracted rates of water uptake followed by rapid water absorption was explored by investigating the effect of gelatin concentration and tannin addition on the governing diffusion behaviors of gelatin-based bioadhesives. First, the moisture diffusion behaviors of gelatin (G) and gelatin–tannin (G–T) bioadhesive resins prepared with varying gelatin-to-water (g/w) and tannin-to-gelatin (T/g) concentrations were experimentally determined. The kinetic diffusion behaviors were classified as Fickian or non-Fickian (i.e., relaxation-controlled) and modeled using empirical constants obtained from the diffusion experiments. To demonstrate improvements in initial moisture resistance of engineered wood composites fabricated with G and G–T resins, the time-dependent flexural mechanical properties of eight-ply laminated gelatin-wood veneer (GWV) composites were characterized and compared to two commercial engineered wood products, namely OSB and plywood, after conditioning samples in both moderate and high humidity conditions.

2. Materials and methods

2.1. Materials

Gelatin was commercially obtained from Knox (Kraft Foods, Inc.) in granular form. Dried tannin powder derived from the *Castanea Sativa* chestnut tree was supplied by LD Carlson, Company. White oak wood veneer was supplied by Sauers & Company Veneers. 7/16″ OSB and 7/32″ plywood were obtained from a local hardware store.

2.2. Experimental methods

2.2.1. Gelatin film preparation

A 100 mL beaker of deionized (DI) water was heated to 60 °C on a Corning PC-420D hotplate. Powdered gelatin, measured in weight percent of gelatin to water (g/w), was added to the water and allowed to dissolve for 15 min under continuous agitation by a magnetic stir bar. For tannin (T) addition, powdered T was measured in weight percent of gelatin (T/g), added to the 60 °C gelatin-water solution, and allowed to mix for 45 min under continuous agitation.

Each mixture was then poured into a 14 × 8 cm rectangular form for gelation. Upon gelation (approximately 20–60 min depending on the g/w ratio), the material was removed from the form and placed between two pieces of cheesecloth and two grated plates that were secured with ties to prevent warping as the films dehydrated. The films were cured in ambient conditions at a temperature of 21 ± 2 °C. Four classes of gelatin films with varying g/w ratios (10%, 20%, 30%, and 40%) and three classes of films with 40% g/w and varying T/g ratios (2.5%, 5%, and 10%) were prepared. The naming convention for the G films is G10, G20, G30, and G40 for g/w ratios of 10%, 20%, 30% and 40%, respectively. For the G–T films, the convention is G40–T2.5, G40–T5, and G40–T10 for a g/w ratio of 40% with tannin additions of 2.5%, 5%, and 10% by weight percent of gelatin, respectively.

2.2.2. Moisture absorption behavior of gelatin-based films

The moisture absorption behaviors of the four (4) classes of G films and three (3) classes of G–T films were characterized according to a modified ASTM D5229 test method. The G and G–T films were first prepared as described in Section 2.2.1. After curing for 3 days in ambient conditions, the films were placed in an oven at 60 °C to remove any free water that remained in the gelatin films. The initial (dry) masses of the specimens were obtained using a Mettler Toledo XS105 DualRange scale in 12-h time increments until mass loss was negligible (~1% change). The films were then laser cut into 15 by 15 mm squares using an Epilog Legend 36EXT laser system. The specimens were massed and dimensioned using calipers before immersion in DI water at room temperature (21 ± 1 °C).

Specimen masses were obtained at subsequent time intervals until equilibrium was reached or the specimen degraded. The moisture content, *MC*, was calculated according to the following:

$$MC = \frac{m_t - m_0}{m_0} \times 100\% \quad (1)$$

where m_t is the mass of the swollen sample at a given time, and m_0 is the initial mass of the sample after preconditioning (dehydrating). The dimensions of samples that reached equilibrium were measured to obtain the final change in volume. Samples were tested in triplicate.

2.2.3. Laminated gelatin wood veneer (GWV) composite preparation

Laminated GWV composites were prepared with G and G–T resins, namely G40 and G40–T10. The resins were prepared as described in Sections 2.2.1. The GWV composites consisted of eight (8) plies of white oak veneer. A layer of resin was applied to the surface of the wood veneer. A second wood veneer was placed on top and pressed to ensure good bonding over the entire surface. This process repeated until an eight-ply composite had been fabricated. The composite was placed between two grated plates that were tightly secured with ties to prevent warping. The composites were allowed to cure in ambient conditions at a temperature of 21 ± 2 °C.

2.2.4. Flexural mechanical properties of engineered wood products

After curing, the laminated GWV composites were trimmed using a table saw to dimensions specified by ASTM D790. The flexure specimens are shown in both plan and section view in Fig. 1a and b, respectively. The 7/16″ OSB and 7/32″ plywood were also cut to dimensions specified by ASTM D790. The flexural