International Biodeterioration & Biodegradation 129 (2018) 95–101

Contents lists available at ScienceDirect

International Biodeterioration & Biodegradation

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

Hexadecyl ammonium chloride amylose inclusion complex to emulsify cedarwood oil and treat wood against termites and wood-decay fungi☆

F.J. Eller[a,*], W.T. Hay[b], G.T. Kirker[c], M.E. Mankowski[d], G.W. Sellling[b]

[a] United States Department of Agriculture, Agricultural Research Service, National Center for Agricultural Utilization Research, Functional Foods Research Unit, 1815 North University Street, Peoria, IL 61604, USA
[b] United States Department of Agriculture, Agricultural Research Service, National Center for Agricultural Utilization Research, Plant Polymer Research Unit, 1815 North University Street, Peoria, IL 61604, USA
[c] United States Department of Agriculture, Forest Service, Forest Products Lab, Durability and Wood Protection, One Gifford Pinchot Drive, Madison, WI 53726-2398, USA
[d] United States Department of Agriculture, Forest Service, Forest Products Lab, Durability and Wood Protection, Forest Products Laboratory, Starkville, MS 39759, USA

ARTICLE INFO

Keywords:
Juniperus virginiana
Amylose inclusion complex
Wood preservation
Subterranean termite
Wood-decay fungi
Water resistance

ABSTRACT

Cedarwood oil (CWO) has a wide range of bioactivities, including insect repellency and toxicity, as well as conferring resistance against termites and wood-decay fungi. In previous work examining pressure treatment of wood, ethanol was used as the diluent/carrier for CWO. However, it is preferable to use a water-based carrier for environmental, safety and cost considerations. In this research, we describe the use of a hexadecyl ammonium chloride amylose inclusion complex/polyvinyl alcohol (AIC/PVOH) as an emulsifier for CWO to pressure treat wood. Wood samples were subsequently tested for resistance to termites and four species of wood-decay fungi. Wood was also compared for water absorption and swelling. In the termite test, the lowest wood mass losses were for the AIC/PVOH/CWO (5.4%) and EtOH/CWO (5.4%) treatments, which also had the highest termite mortalities (i.e., 100% and 97.6%, respectively). In general, for wood-decay fungi, wood mass losses were lowest for the EtOH/CWO and AIC/PVOH/CWO treatments and were highest for the Water, EtOH, and AIC/PVOH treatments. Wood blocks treated with AIC/PVOH repelled water as evidenced by higher contact angle, lower mass gain (both by submersion and water saturation) and lower swelling. The results indicated that the amylose inclusion complex makes an excellent emulsifier and the AIC/PVOH/CWO mixture inhibits both termites and wood-decay fungi. The amylose inclusion complex alone was as inhibitory as CWO against termites and also inhibits both water absorption and swelling in treated wood.

1. Introduction

There are numerous examples of woods that are resistant to termites and/or wood-decay fungi as well as many examples of extracts from resistant woods that confer resistance to termites and/or wood-decay fungi (Watanabe et al., 2005a,b; Cheng et al., 2007; Abdul Khalil et al., 2009; Santana et al., 2010; Wang et al., 2011; Wahyudi et al., 2012; Kadir et al., 2014; Brocco et al., 2017; Hassan et al., 2017). Eastern red cedar (ERC) (*Juniperus virginiana*) (Cupressaceae) has been demonstrated to be resistant to termites (Kard et al., 2007; Konemann et al., 2014) and extracts from ERC have been shown to decrease mass losses from wood treated with these extracts (Eller et al., 2010; Tumen et al., 2013) for both termites and wood-decay fungi.

Eastern red cedar is an abundant natural resource in the United States and it is the domestic source of cedarwood oil (CWO) (Schmidt and Leatherberry, 1995; Adams, 1987). High quality and yields of CWO have been obtained by CO_2 extraction, using both supercritical CO_2 (Eller and King, 2000) and liquid CO_2 (Eller and Taylor, 2004).

Junipers are well-known for their resistance to both termite attack and microbial decay (Adams et al., 1988) and extracts from junipers may serve as a source of safe, natural wood preservatives from this abundant renewable resource. Previously, CWO has been demonstrated to confer resistance to susceptible wood species against both termites and wood-decay fungi (Eller et al., 2010; Tumen et al., 2013).

To control the concentration of the preservative used during the pressure treatment of wood, the preservative must be diluted and uniformly dispersed into a suitable liquid carrier. The laboratory pressure treatment procedure also requires 90 min to complete (AWPA, 2012). Therefore, the liquid dispersion must be stable for at least this long. However, after the pressure treatment is completed, it is desirable to

☆ Mention of trade names or commercial products in this article is solely for the purpose of providing scientific information and does not imply recommendation or endorsement by the U.S. Department of Agriculture. USDA is an equal opportunity provider and employer.

* Corresponding author.
E-mail address: fred.eller@ars.usda.gov (F.J. Eller).

https://doi.org/10.1016/j.ibiod.2018.01.010
Received 29 September 2017; Received in revised form 17 January 2018; Accepted 20 January 2018
Available online 07 February 2018
0964-8305/ Published by Elsevier Ltd.

alter the carrier properties to decrease the likelihood of the preservative subsequently being removed (i.e., leached) from the wood. Previously, we used ethanol as the carrier which evaporated and left the CWO behind in the treated wood (Eller et al., 2010; Tumen et al., 2013). Although ethanol was suitable in several ways (i.e., miscible with CWO; readily available; relatively inexpensive; and "green"), an aqueous based carrier is preferrable due to its lower cost and safety advantages. In this study, we investigated the use of an amylose (i.e., corn starch) inclusion complex as an emulsifier in an aqueous carrier to make a better (e.g., nonflammable, less expensive and safer) alternative to ethanol for CWO treatment of wood.

The purpose of this study was to determine if an amylose inclusion complex could be used as an emulsifier for CWO to vacuum impregnate wood and determine how the dispersion components compared for imparting resistance to termites and wood-decay fungi. In addition, we studied how the test materials affect the interaction of water with wood, specifically contact angle, water mass gain and dimensional stability and how these characteristics are related to resistance against termites and wood-decay fungi.

2. Materials and methods

2.1. Cedarwood oil

Heartwood samples were cut from freshly felled Eastern red cedar (Tazewell Co., Illinois) and sawdust was prepared from the heartwood as described by Eller et al. (2014). Cedarwood oil was extracted from this sawdust using supercritical carbon dioxide (70 °C, 27.6 MPa) as described by Eller and King (2000).

All CWO carrier mixtures were formulated to contain 5% CWO by weight. The carrier mixture treatments were prepared using an electric hand blender by mixing on high for approximately 30 s. The five treatments tested were: Water Only; Ethanol Only (EtOH); Amylose Inclusion Complex/Polyvinyl Alcohol (AIC/PVOH); EtOH/CWO; and Amylose Inclusion Complex/Polyvinyl Alcohol/CWO (AIC/PVOH/CWO). The dispersion of CWO in the AIC/PVOH solution was observed to remain uniformly mixed for over 24 h, which was significantly longer than the 90 min needed for the vacuum impregnation of the wood samples described below.

2.2. Preparation of amylose-hexadecylammonium chloride inclusion complexes

High-amylose corn starch (~68% amylose, AmyloGel 03003) was a product of Cargill (Minneapolis, MN). Hexadecylamine (98%); and hydrochloric acid (HCl, 37%) were purchased from Sigma (St. Louis, MO); Polyvinyl alcohol (PVOH) (MW 133,000, 99 mol% hydrolyzed) was purchased from Polysciences, Warrington, PA; Ultrapure water was used for all solutions and was obtained from a Barnstead Nanopure System (ThermoScientific, Asheville, NC).

The procedure for producing the amylose-inclusion complexes was the same as that reported earlier (Hay et al., 2017a). The high-amylose corn starch (100 g) was dispersed in 1800 mL of deionized water within a 2-L stainless steel Waring blender (Waring Products division, New Hartford, CT). After high shear mixing the dispersion was subsequently passed through a Penick and Ford (Penford Corp., Englewood, CO) laboratory model steam jet-cooker operating at excess steam conditions (Klem and Brogly, 1981). The temperature in the hydroheater was 140 °C, steam back pressure was 380 kPa, and the steam line pressure was 550 kPa and the dispersion was pumped through at a rate of 1 L/min. The jet cooked solution was collected in a 4-L stainless steel Waring blender container (Waring Products division, New Hartford, CT). A solution of hexadecylammonium chloride was prepared, 5.25 g of hexadecylamine was dispersed in 217.42 g of 0.1 N HCl and fully dissolved by heating to 90 °C. The hexadecylammonium chloride solution was then immediately added to the hot starch dispersion after jet-cooking. The solution was sheared in the Waring blender for 1 min, and then quickly cooled in an ice bath to 25 °C. The solution was then freeze dried using a Labconco Freezone 6 L freeze dryer (Labconco, Kansas City, MO).

A solution containing 1% amylose-hexadecylammonium chloride complexes and 1% PVOH was prepared as reported previously by dispersing the polymers in nanopure water and heating the dispersions to 80 °C (Hay et al., 2017b).

2.3. Termite resistance

Using a no-choice test (i.e., only one treatment per container), vacuum impregnated wood blocks were tested for resistance to eastern subterranean termites, *Reticulitermes flavipes* (Kollar) (Isoptera: Rhinotermitidae) using Standard Method for Laboratory Evaluation to Determine Resistance to Subterranean Termites E1-06 (AWPA, 2016). Workers and soldiers of *R. flavipes* were collected from dead logs present at Sam D. Hamilton Noxubee National Wildlife Refuge (Starkville, Mississippi) and maintained in the laboratory at 25 °C in the darkness in cut sections of the collected logs in 30-gallon trashcans. The day of the test setup, termites were removed from the collected log sections by breaking the rotting wood open and shaking the termites out of the wood through a screen to catch large debris. Termites were placed in plastic tubs with moistened paper towels for 2 h before being counted with an aspirator. Screw top jars were filled with 150 g sand along with 27 mL distilled water and held for 2 h to equilibrate. For the no choice test, blocks were conditioned (33 °C, 62 ± 3%), weighed and placed on a square of foil on top of the damp sand with one block in each jar. A total of 400 termites (396 workers and 4 soldiers) were released in each jar (Fig. 1) and jars were kept in the conditioning chamber at 27 °C and 75 ± 2% relative humidity for 28 days. After four weeks, the number of live termites were counted. Blocks were brushed to remove sand, conditioned for one week, and re-weighed to determine weight loss as described in the AWPA E1 standard.

Spruce/Pine/Fir (SPF) blocks were prepared from a board milled to 2.54 cm × 2.54 cm × 0.64 cm. The wood blocks were conditioned to a constant mass at 25 °C and 50% relative humidity (RH) and weighed prior to vacuum impregnation. Wood samples were submerged under a given treatment solution and held under vacuum (−0.088 MPa) for 30 min and then pressurized to 0.69 MPa for 60 min. After impregnation, wood samples were reweighed, the solvent was allowed to evaporate and the blocks re-conditioned to a constant mass at 25 °C and 50% RH. Wood weight loss and termite mortality were determined after a 28 day exposure to the termites. There were six replications of each treatment. The five treatments tested were the same as described above.

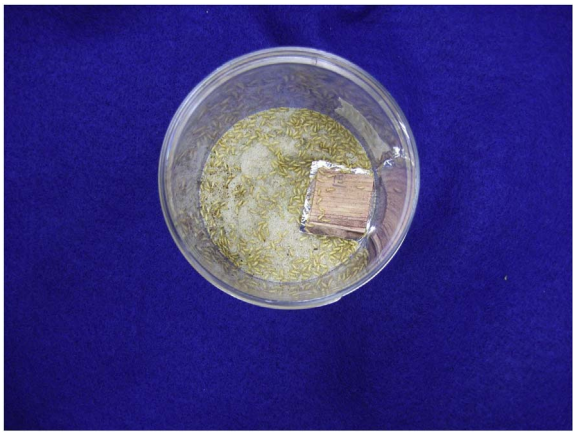

Fig. 1. Photograph showing termite resistance bioassay.