Industrial Crops & Products xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Industrial Crops & Products

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

Epoxidized sucrose soyate—A novel green resin for crop straw based low density fiberboards

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A R T I C L E I N F O

Keywords:
Epoxidized sucrose soyate
Biobased resin
Wheat straw
Soybean straw
Fiberboards
Physical and mechanical properties

A B S T R A C T

A study was conducted to evaluate the mechanical properties of low density fiberboard produced with combinations of two fibers soybean straw (*Glycine max*), and wheat straw (*Triticum aestivum*) and two resins methylene diphenyl diisocyanate (MDI) and epoxidized sucrose soyate (ESS) resin as binders. ESS is a high performance, soybean oil based epoxy that has shown promise as a highly biobased adhesive. Six formulations of panels were produced using various combinations of straw and resin binder. Mechanical testing of sample boards was conducted using ASTM standard D1037-12. Test results showed that type of resin did not influence soy straw or wheat straw board's stiffness and strength properties but had a major impact on water resistance, screw withdrawal strength and internal bond strength. The study demonstrated the potential of ESS as a novel binder for fiberboard system if a suitable crosslinker and catalyst is utilized. It also showed that increasing ESS content over 50% in a MDI blend lowered the performance characteristics of boards. However, analytical testing of the resin systems showed limited reactivity between ESS soyate and MDI, indicating other compatible resin chemistries should be explored for achieving superior board properties. Overall, a resin blend with 25–50% ESS in MDI appears favorable for low density fiberboards. ESS can be a promising bio-based resin as it has the potential to meet California Air and Resources Board (CARB) standards while providing acceptable properties as an adhesive.

1. Introduction

Conventional dry-process medium density fiberboard (MDF) is composed of wood particles that have been pressed together under high temperature and pressure with a resin binder to form a homogeneous board (American National Standard for Particleboard, 2002). In recent years, alternate lignocellulosic materials have gained much attention. Several researchers have evaluated the viability of corn, rice, wheat, bagasse, deoiled sunflower cake, and soybean fibers for use in fiberboard (Sitz and Bajwa, 2016; Halvarsson et al., 2010; Reddy and Yang, 2005; Iñiguez-Covarrubias et al., 2001; Evon et al., 2015; Ye et al., 2007). Utilizing agricultural residues in fiberboards provides the advantage of adding value to sustainable resources. It also helps to reduce pressure on traditional woody biomass, which has the potential for ethanol and other bio-fuels (White, 2009).

The most commonly used resins in the fiberboard industry in dry process fiberboard production include phenol formaldehyde (PF), urea formaldehyde (UF), and methylene diphenyl diisocyanate (MDI) (Healthy Building Network, 2008). None of these resins are biobased or derived from sustainable sources. However, these resins are economical and provide excellent adhesion properties, and improve the moisture resistance of the boards (Wood Handbook, 2010). The main disadvantage with these resins is the health hazards they pose to workers in the fiberboard industry and end use consumers. Formaldehyde is a known carcinogen. Fiberboards made with UF and PF produce volatile emissions after production, while MDI has been designated as a potential carcinogen and irritant that can potentially cause asthma and dermatitis (Healthy Building Network, 2008). This health hazard, along with the California Air and Resources Board (CARB) phase 2 changes to composite board standards motivates the research into alternative resins (CARB, 2007). The development of bio-based materials from renewables continues to be promising alternative to replace petrochemical. Some of the alternative resin choices that have been investigated are either vegetable oils or proteins based. These can be further broken

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http://dx.doi.org/10.1016/j.indcrop.2017.04.057
Received 14 February 2017; Received in revised form 26 April 2017; Accepted 28 April 2017

down to glycerol ester-based or other ester based. Soybean oil and proteins have been used as adhesives (Kuo et al., 1998; Liu, 2005). Recently, the protein containing dried distiller's grains with solubles was exploited as adhesive in particleboards (Sundquist and Bajwa, 2016). Alternative resins that utilize epoxidized vegetable oils derived from linseed, safflower, and soybean have also been found to have high performance, and have general designation of an epoxidized sucrose ester of fatty acids (ESEFAs) (Pan et al., 2011a,b). ESEFAs have shown promising results in a number of applications ranging from biobased thermosets by crosslinking of the epoxy groups, to further derivatization by reaction of the epoxy groups. A 100% bio-based thermosetting coating system were developed from epoxidized sucrose soyate cross-linked with blocked bio-based dicarboxylic acids (Kovash et al., 2014). Similarly highly functional biobased methacrylate oligomers were synthesized via the reaction between methacrylic acid and epoxidized sucrose soyate (Yan and Webster, 2015). A recent study reported acceptable creep strain properties of methacrylated epoxidized sucrose soyate based flax fiber composites (Amiri et al., 2016).

Sucrose ester of fatty acid from soybean oil is produced commercially by Proctor and Gamble under the trade name SEFOSE, which is also referred as sucrose soyate. Due to their low viscosities (300–400 mPa s), SEFOSE sucrose esters can be used as binders and reactive diluents for air-drying high solids coatings. Expoxidized sucrose soyate (ESS) has epoxide groups, which has reactive intermediates that can produce functional groups and promote bonding and crosslinking between other appropriate functional groups (Pan et al., 2011b). A fully substituted molecule of ESS resin is composed of a sucrose molecule that has its eight hydroxyl groups substituted with (epoxidized) fatty acids from soybean oil (Monono et al., 2015). It has been shown that epoxide groups can react with the functional isocyanate group present in MDI to create an oxazolidone ring (Uribe and Hodd, 1984; Caille et al., 1990; Zlatanic et al., 2004) this reaction allows for the mixture of both ESS and MDI resins to potentially create a high-performance resin that does not need additional cross-linkers and utilizes a readily available renewable resource. The reactions between isocyanate and epoxide groups have two competitive reactions that form two potential products; oxazolidone rings and isocyanurate. Oxazolidone is a heterocyclic ring that produces improvements in both thermal stability and mechanical properties (Caille et al., 1990).

The success of ESS in coatings and polymeric composites has warranted further research to explore its potential in composition panels. Previous study on the lap shear testing showed that ESS has potential to act as a sole binder (Bajwa et al., 2015). ESS was shown to increase crosslinking and bonding strength considerably when an epoxy-anhydride curing system is implemented as compared to pure ESS. The anhydride system implemented utilized 4-methyl-1,2-cyclohexaneedicarboxylic anhydride (MHHPA) that acted as cycloaliphatic anhydride cross-linker, and 1,8-diazabicyclo[5.4.0]undec-7-end (DBU) that acted as a tertiary amine catalyst. The research was based on the hypothesis that ESS resin has epoxide groups which are reactive intermediates that can react with the functional isocyanate group present in methylene diphenyl diisocyanate (MDI) to promote bonding and crosslinking.

Therefore, the goal of this research was to evaluate the properties of low density fiberboards (640 kg/m^3) manufactured with wheat and soybean fibers and using 1) ESS as a sole binder and 2) ESS blend with MDI and a crosslinker and a catalyst. The main hypothesis was that ESS can bond with MDI resin and produce boards with equivalent properties to that of boards produced using only MDI.

2. Materials and methods

2.1. Materials

The three different resins utilized were: an epoxy-anhydride system composed of ESS, a pure 4,4′-methylene diphenyl diisocyanate (MDI I-Bond, Huntsman Corporation, Woodland, TX, USA) and ESS resin containing a cross linker 4-Methyl-1,2-cyclohexaneedicarboxylic anhydride (MHHPA) and a catalyst of 1,8-diazabicyclo[5.4.0]undec-7-end (DBU). MHPPA was provided by Dixie Chemical Inc. (Pasadena, TX, USA) and DBU (> 99.0% GC) from Sigma-Aldrich (St. Louis, MO, USA). ESS resin was synthesized from sucrose ester of soybean oil, SEFOSE 1618UC (sucrose soyate) supplied by Proctor and Gamble Chemicals (Cincinnati, OH, USA). A detailed list of materials used and the manufacturing process followed to develop ESS can be found in an earlier reported work (Monono et al., 2015). Wheat and soybean straw were obtained from a commercial particleboard manufacturing facility located in Wahpeton, ND, USA. The fibers were screened with 80 mesh sieves to remove fines and dust to improve the adherence of the binding resin to the fibers. The screened material was dried in a convection oven to achieve moisture content between 12 and 15%.

2.2. Manufacture of boards and testing

Low density fiberboards with target density 640 kg/m^3 were manufactured and evaluated for physico-mechanical properties in this study. Typically these boards are used in non-structural applications such as door and window cores. First the oven dried fibers were conditioned in a climate controlled chamber to achieve 10–12% moisture content by weight followed by hot-pressing the fibers to produce fiberboards. Approximately 1 kg of fibers were placed into a rotating drum with paddle mixers. The fibers were then sprayed with resin using an atomizing spray gun such that a batch would contain 4 wt% of resin in the mixture, which remained consistent for each formulation. The resulting resin rich fiber mixture was laid into a mat formed by a two-part aluminum mold that produced 305 mm × 305 mm panels. Resinous fibers were added to the mold such that a target density of 640 kg/m^3 and board thickness of 7.5 mm can be achieved. Sheets of polytetrafluoroethylene were used on the two inner surfaces of the mold to prevent fibers from sticking to the mold surface during pressing. The mold was then placed in Carver Hot Press Model 4122 (Wabash, IN, USA) set at 190 °C and the fiber mat was pressed under 2117 kPa of pressure by manually ramping pressure slowly to prevent mat blowout. The mat was then held to this pressure for 5 min cycle to cure the resin. The pressure was then manually decreased at a slow rate to allow for degassing and to prevent blowout of the formed panel. The board was then removed from the mold and allowed to cool for 24 h at 23 ± 2 °C on an insulated table before cutting it for test samples (Sitz and Bajwa, 2015).

Six formulations (3 resins with 2 fibers types) of fiberboards were pressed to test the effects of resin binders on the physico-mechanical properties of fiberboards (Table 1). The resin formulations were100% MDI, MDI with ESS blend (1:1) by equivalent weight of epoxide to isocyanate, a blend with ratio of ESS:MHHPA:DBU being at 67.5:31.0:1.5. The two fiber types were soybean and wheat straw. Physical and mechanical testing of the sample boards were performed in accordance with ASTM D1037-12 Standard Test Methods for

Table 1
Descriptions of the particleboard formulations.

Resin Composition	Resin Blend	Fiber Type	Sample Labelling
MDI	1	Wheat	Wheat-MDI
MDI + ESS	1:1	Wheat	Wheat-ESS-MDI
ESS+ MHHPA- DBU	67.5:31.0:1.5	Wheat	Wheat-ESS-MHHPA-DBU
MDI	1	Soybean	Soybean-MDI
MDI + ESS	1:1	Soybean	Soybean-ESS-MDI
ESS + MHHPA + DBU	67.5:31.0:1.5	Soybean	Soybean-ESS-MHHPA-DBU

ESS- Expoxidized sucrose soyate, MDI – Methylene diphenyl diisocyanate, MHHPA – 4-Methyl-1,2-cyclohexaneedicarboxylic anhydride, DBU – 1,8-diazabicyclo[5.4.0]undec-7-end.