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Study of dextrin-derived curing agent for waterborne epoxy adhesive

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ABSTRACT

In this study, a water-soluble dextrin derivative was synthesized by reacting dextrin with trimellitic anhydride. The chemical structure of the dextrin-derived curing agent was confirmed by FT-IR and ^{1}H NMR. The dextrin derivative contained free carboxylic acid groups and was used as curing agent for waterborne epoxy in wood bonding test. The adhesion of wood bonded by this waterborne epoxy system was studied and compared with that of wood bonded by phenol–formaldehyde resin. Results showed that the two adhesive systems displayed very similar block shear strengths and specimen failures. The two types of adhesives also showed similar extents of resin penetration into the wood substrate. This study demonstrated that starch or dextrin could be used as an economic feedstock for synthesis of curing agents for waterborne epoxies in the effort to develop formaldehyde free and volatile organic compounds (VOC)-free wood adhesives.

1. Introduction

Urea–formaldehyde (UF) and phenol–formaldehyde (PF) have been the dominant adhesive resins in wood composite industry during the last several decades due to their low costs, aqueous nature, low viscosities and overall satisfactory properties (Sellers, 2001). However, formaldehyde is deemed as a human carcinogen. Formaldehyde emissions, particularly from the UF resin, during resin production and use of wood composites could present a serious threat to public health (Baumann, Lorenz, Batterman, & Zhang, 2000; Heck, Casanova, & Starr, 1990). The enforcement of the strict formaldehyde emission standard will gradually restrict the use of UF resin, and PF resin. Moreover, phenol and formaldehyde are produced from petrochemical feedstocks. There is a great interest in developing cost and performance competitive formaldehyde-reduced or formaldehyde-free adhesives from renewable resources. Soy protein-based adhesives, once the major adhesives for plywood bonding before being replaced by the stronger and more water-resistant UF and PF (Johnson, Myers, & Burden, 1984), reignites the interest of adhesives from renewable resources. Soy protein-based adhesives are mainly based on various alkaline hydrolyzates of soy proteins and demonstrate relatively low strength and water resistance compared to UF and PF resins. To meet the stringent performance requirement of wood composites, soy protein-based adhesives were either co-used with synthetic adhesives, e.g. diphenylmethane diisocyanate (Riebel, Torgusen, Roos, Anderson, & Gruber, 1997) and PF (Kuo et al., 2001; Yang, Kuo, Myer, & Pu,2006) to co-crosslink during curing or chemically modified, e.g. by grafting with dopamine (3,4-dihydroxyphenylalanine) (Liu & Li, 2002) and by forming complex with polyamide–epichlorohydrin copolymer. However, the water resistance of soy protein-based adhesives does not meet the industry requirement yet.

Although epoxy adhesives have good wetting ability on cellulosic materials and form very strong bonds, they are limited to certain special joining applications such as bonding wood to metals. Epoxies have not been used as wood composite adhesives due to their relatively higher cost, high viscosity, use of organic solvents, and slow curing. Waterborne epoxy resins demonstrate advantages similar to that of UF and PF resins, such as low viscosity and good wetting and penetration, and are potential substitutes for formaldehyde-based adhesives in wood composites industry. However, the current waterborne epoxy resins are expensive and use petroleum-based waterborne polyamidoamine (Gagliano & Frazier, 2001) or aromatic polycarboxylic acids (Anderson & Bohr, 2000) as curing agents. Wood industry will greatly benefit if a cost competitive eco-friendly waterborne epoxy or curing agent could be produced from renewable feedstocks.

Starch is an abundant and inexpensive crop product. Starch and its hydrolyzate dextrin have long been used for adhesives. Because of low bonding strength, low water resistance and sensitivity to biological degradation, starch-based adhesives are mostly used as various glues for book-binding, wallpaper, envelop, bottle labeling, etc. (Lazarus, 1983) in the last two decades. To the best of our

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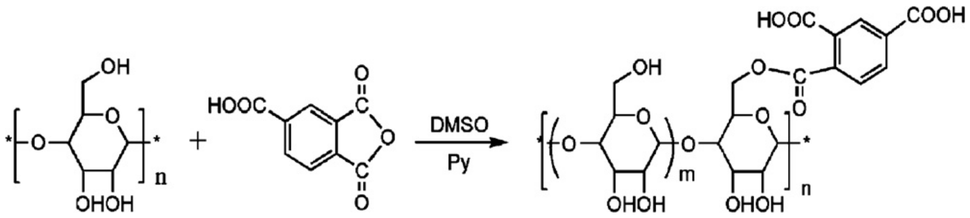

Scheme 1. Synthesis of dextrin-based curing agent (DCA).

knowledge, starch-based adhesives with high performance, comparable to those of PF or UF in wood composites, have not been reported in the literature. In this study, the hydroxyl groups of dextrin were substituted by trimellitic anhydride (Scheme 1) and the resulting dextrin derivative containing carboxyl groups was used as a curing agent for waterborne epoxy. The main objective of this work is to explore the feasibility of utilizing starch as feedstock for the synthesis of an environment-friendly and economical adhesive system comparable to PF as well as its application in wood composites.

2. Method

2.1. Materials

Dextrin (M_n = 900) was provided by Grain Processing Corporation (Iowa, USA). Waterborne Epoxy ANCAREZ AR555 (55% solid content, intrinsic viscosity of 200 cPs at 25 °C and epoxy value of 1300 g/mol) was provided by Air Products and Chemicals, Inc. (PA, USA). PF resin (55.7% solid content; intrinsic viscosity of 290 cPs at 25 °C) was a common commercial product. Other chemicals and solvents, such as pyridine (99%), dimethylsulfide oxide (anhydrous), ester acetate, trimellitic anhydride (97%) and aqueous toluidine blue dye (1%) were purchased from Sigma–Aldrich. Hard maple (*Acer sacharum*) for block shear test with a specific gravity of 0.68 was provided by Woodcraft (Spokane, USA).

2.2. Synthesis of dextrin-based curing agent (DCA)

A single-necked round flask equipped with mechanical stirrer was charged with 1.76 g of dextrin (ca. 0.01 mol anhydroglucose units), 3.44 g (0.02 mol) of trimellitic anhydride, 1.58 g (0.02 mol) of pyridine and 10 mL of dimethylsulfide oxide. After the mixture was stirred at room temperature for 24 h, it was poured into 30 mL of ester acetate. The precipitate was collected by filtration and washed with ester acetate for several times before it was dried in the vacuum oven at 60 °C for 12 h. The received product was white powder weighing 2.26 g (yield 85%) and was ready for the following curing reaction. ^{1}H NMR [D_2O, δ ppm]: 7.99 (s, 1H), 7.69–7.72 (d, 1H), 7.38–7.35 (d, 1H), 5.1–5.4 (s, 1H), 3.94–3.31 (m, 5H). FT-IR (cm^{-1}): 3500–3100, 2934, 1725, 1640, 1450, 925, 890, 720. Acid value: 260 g/mol.

2.3. Preparation of waterborne epoxy adhesive and bonded wood samples

4.0 g of above received DCA was dissolved in 6.0 mL de-ionized water at 50 °C to get the solution with acid value of 650 g/mol. 20 g of waterborne epoxy ANCAREZ AR555 with the epoxy value of 1300 g/mol was added dropwise to above solution (1:1 epoxy group/acid group mole ratio). The resulting mixture was stirred for 2 min by hand and used for bonding wood immediately.

A test joint assembly was prepared by bonding two pieces of conditioned wood with the dimension of 305 mm × 50.8 mm × 19 mm. After the predetermined amount of DCA/E mixture was applied on one surface (305 mm × 50.8 mm) of the bonding wood by brush with a spread rate of 50 g/m^2 (solid content). Two pieces of coated wood surfaces were stacked together and compressed at 1 MPa by four clamps before they were put into a preheated oven to cure at 150 °C for 4 h. The pressure was then removed and the joints were conditioned at 23 °C and 50% RH for seven days. Before block shear testing, each of the assembly joint was cut into 5 specimens with the bonding area of 50.8 mm × 38.1 mm. In order to get the accurate shear stress of the adhesive, 20 specimens were prepared by this method for each adhesive formulation. For the preparation of sample bonded with PF, the same procedure and spread rate was followed.

2.4. Shear strength of wood composites

Block shear strength before water-soaking (defined as Dry-Stress) was conducted according to ASTM standard D 905-08 using an Instron 4400 R series universal testing machine. The crosshead speed was 5 mm/min. Bond strength was reported as the maximum shear stress at breakage between two pieces of wood.

A water-soaking-and-drying test (defined as WSD-Strss) was employed to evaluate the water resistance of wood composites. More specifically, the block shear specimens were soaked in water, and vacuumed at 508 mm Hg for 30 min. Upon the removal of vacuum, a pressure of 0.52 MPa was applied and held for 2 h. The specimens were then dried at 71 °C for 10 h before the shear stress was measured following the same procedure that used in determining the dry-stress.

2.5. Effective penetration of DCA and PF into wood microstructure

A 305 mm × 50.8 mm × 10 mm block was cut from the middle part of each assembly joint for strength test to quantify the adhesive penetration. This characterization was conducted on confocal laser scanning microscopy (Zeiss LSM 510 META). Before observation, each specimen was stained with 1% toluidine blue aqueous solution for 20 min to suppress the autofluorescence of the maple (Johnson & Fakamke, 1992). The equipment condition was set to be Diode laser-405 nm, HFT 405/488, LP 475 nm in the whole process and the detection wavelength was narrowed in the range of 475–600 nm. For each assembly joint, 6 images were taken along the width of bondline and totally 48 images were acquired for the determination of penetration of DCA and PF.

2.6. Characterization of the chemical structure

^{1}H NMR spectra were recorded with a Bruker 300 MHz spectrometer at room temperature using deuterium oxide (D_2O) as the solvent. Fourier transform infrared (FT-IR) spectra were recorded with NEXUS 670 FT-IR from 4000 to 600 cm^{-1}. Titration method was used to determine the acid value of DCA and DCA indicating by phenolphthalein.