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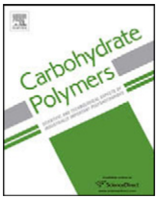

Study of dextrin-derived curing agent for waterborne epoxy adhesive

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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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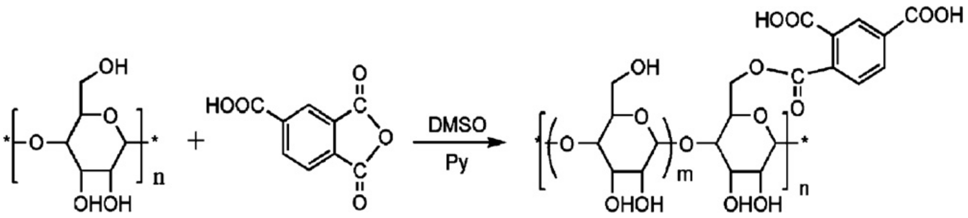

Scheme 1. Synthesis of dextrin-based curing agent (DCA).

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.

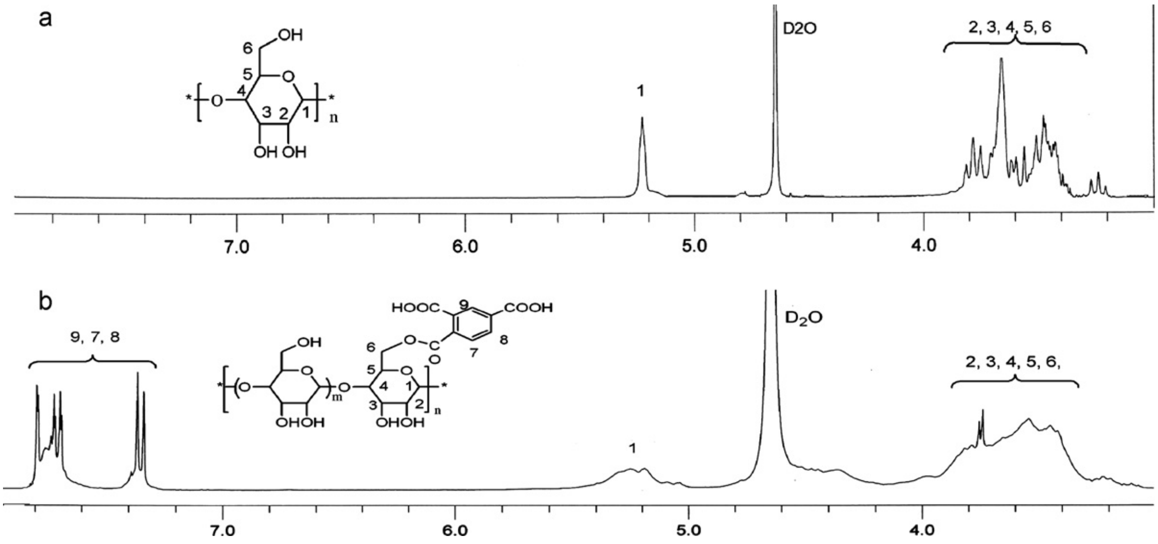

Fig. 1. ^{1}H NMR spectrum of (a) starch and (b) DCA.

3. Results and discussion

3.1. Synthesis and characterization

The chemical structure of DCA was confirmed by FT-IR and ^{1}H NMR. Fig. 1 shows the chemical shifts of dextrin (a) and DCA (b). The peaks at 7.35–7.99 ppm in Fig. 1b were attributed to the characteristic chemical shifts of aromatic protons in the trimellitic anhydride group. The degree of substitution (DS) of hydroxyl groups on dextrin was determined by comparing the peak intensity attributed to aromatic protons to that attributed proton at C-1. The DS was found to be 0.57 and the acid value calculated based on the DS equaled 242 g/mol, which was in a good agreement with the acid value determined by titration (260 g/mol).

3.2. Dry and wet block shear strength

Fig. 2 gives the comparison of block shear strength of DCA cured epoxy and PF bonded maple samples prior to and after water soaking, respectively. The average dry shear strength of DCA cured epoxy bonded maple (25.2 MPa) was slightly lower than that of PF (27.7 MPa). However, if the low coefficients of variation (COV) for PF and DCA (both are 8%) are considered, the difference in dry strength is of little or no practical significance. In other words, DCA cured waterborne epoxy would result in a comparable dry bonding strength to that of commercial PF resin when used for wood composites.

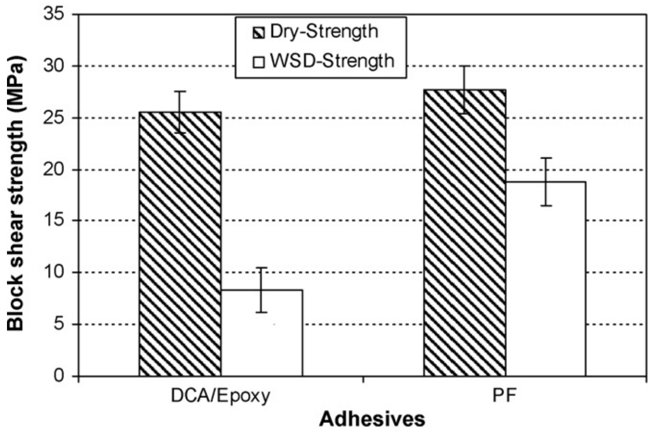

Fig. 2. Dry and wet block shear strengths of DCA cured epoxy and PF bonded maples.

On the other hand, the water resistance of wood composites, which is usually determined by water-soaking-and-drying test, is a crucial parameter to evaluate an adhesive application performance. The wet shear strength of DCA cured epoxy and PF bonded maple after water-soaking was also presented in Fig. 2. Both adhesives demonstrated significant strength reduction after water-soaking. The value reduced to 8.3 MPa (decreased 68%) for the DCA cured epoxy and 18.7 MPa (decreased 32%) for the PF adhesive, respectively. Compared with the wood bonded with PF, the specimens bonded with DCA cured epoxy suffered a much larger strength reduction, but it was still strong enough for interior application (Zhong, Sun, Wang, & Ratto, 2003). The lower water resistance of DCA cured epoxy is due to the hydrophilicity of the residual hydroxyls and glycosidic bonds in dextrin.

3.3. Effective penetration

Wood is a hygroscopic material, thus moisture absorption is one of the biggest weakness of wood materials in many applications. One of the advantages of waterborne adhesives for forest products is that the adhesive monomers carried by water can easily penetrate into the microstructure of wood and their further polymerization under heat will result in a more stable dimension and stronger moisture resistance of composites. However, an excessive penetration may lead to a starved bondline with insufficient adhesive remaining at the interface (Marraa, 1992). So far, the optimum penetration of adhesive into wood microstructure is an open question.

Fig. 3 is the image for penetration of DCA/epoxy and PF (bright spots represent the adhesive particles) into the microstructure of wood. Their effective penetrations were determined by the following equation: (Sernek, Resnik, & Kamke, 1999; Zheng, Fox, & Frazier, 2004).

$$\text{Effective penetration (EP)} = \frac{\text{Total area of penetrated adhesive particle in the field of view}}{\text{Bonding length in the field of view}}$$

Effective penetrations for DCA/epoxy and PF were 74.8 (±21.7) and 96.8 (±24.2) μm, respectively. Apparently, the effective penetration of DCA/epoxy was satisfactory and comparable to that of PF, which displayed excellent penetration into wood microstructure.

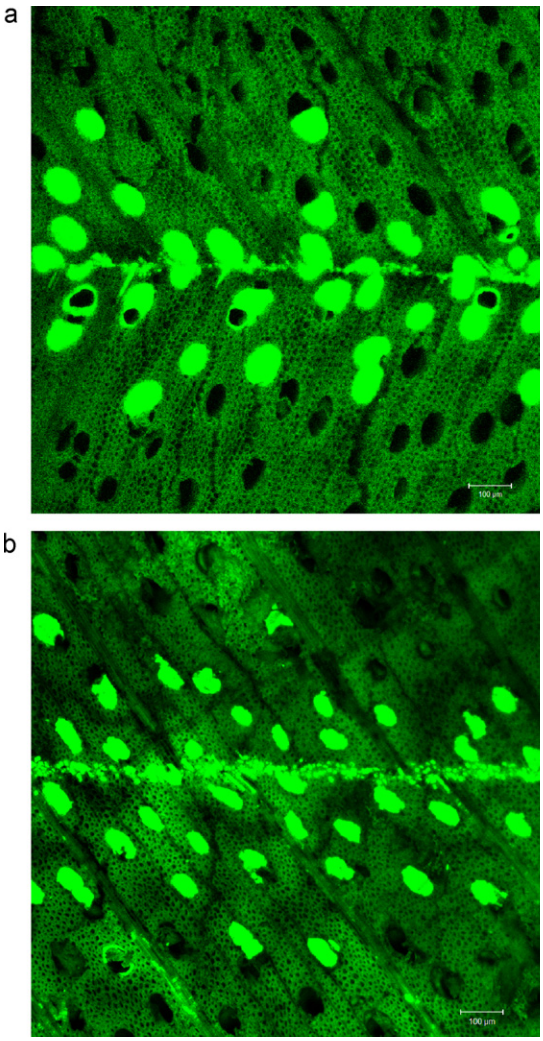

Fig. 3. Images for the penetrated particles of PF (a) and DCA/epoxy (b) into wood microstructure.

It is understood that viscosity or solid content of adhesive, process conditions and other wood related-factors can all influence adhesive penetration. Detailed investigation of the effective penetration will be further pursued in the future.

3.4. Wood failure

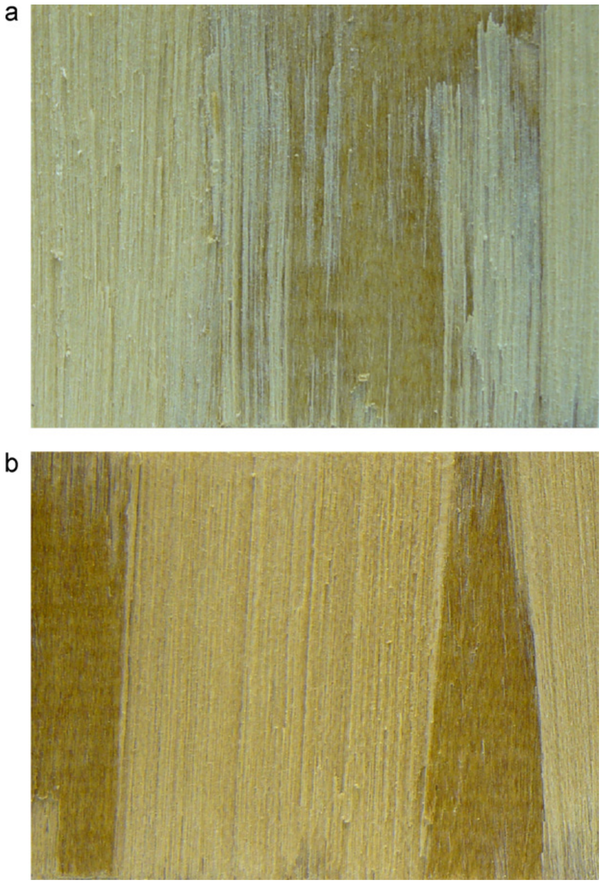

Fig. 4. Representative fracture surfaces of the dry specimens after block shear test. (a: DCA cured epoxy bonded; b: PF bonded).

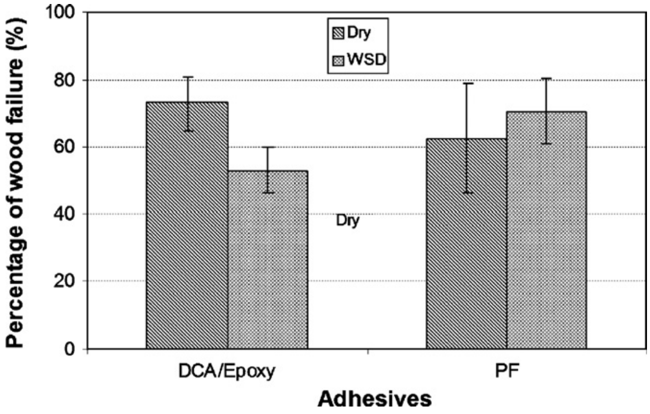

Fig. 5. Comparison of wood failure percentage between DCA cured epoxy and PF bonded maples.

Fig. 4 shows the images of fracture surfaces of bonded maple samples after block shear test and prior to soak treatment. Significant wood failure was noted for both DCA/epoxy and PF bonded maple samples. Cured DCA/epoxy adhesive yielded fairly high shear strength with predominantly wood failure similar to PF resin. This suggests that both DCA/epoxy and PF resin can form fairly good bond with wood, so that most of the shear failure occurred in the wood instead of in the adhesive. These results indicate that DCA/epoxy adhesive most likely had good wetting of the wood substrate and penetration. This similar high performance of DCA/epoxy to PF is not difficult to understand, because both are thermosetting resins. Extensive covalent bonds between adhesive and substrate were likely formed for both adhesive systems. Fig. 5 gives the comparison of wood failure for soaked and non-soaked maples bonded by both DCA/epoxy and PF resins. As we mentioned above, DCA still had many unblocked hydroxyl groups which likely resulted in lower water resistance for cured epoxy. These test results indicate after soaking test the adhesion of DCA/epoxy bonded samples was weakened obviously, while that of PF bonded samples did not change significantly.

4. Conclusions

Dextrin was modified by reacting with trimellitic anhydride under mild reaction conditions. The resulting water-soluble dextrin derivative, which contained free carboxylic acid groups, was used as carboxylic acid type curing agent for the cure of waterborne epoxies. As this epoxy system is aqueous, it can be used like the aqueous PF or UF resin to bond wood substrates, such as in composite manufacturing. Furthermore, the curing conditions and the adhesion properties of this dextrin derivative cured waterborne epoxy were very similar to that of PF resin. On the other hand, the water resistance of epoxies cured with this dextrin derivative was still not as good as that of PF resin. Nevertheless, this drawback might be overcome by blocking some of the remaining hydroxyl group or increasing the degree of substitution by trimellitic anhydride.

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