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Preparation and characterizations of a chitosan-based medium-density fiberboard adhesive with high bonding strength and water resistance

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ABSTRACT

An efficient method was developed for preparing medium-density fiberboard (MDF) adhesives with high performance, using chitosan as the main component and glutaraldehyde as a crosslinking agent. The effects of glutaraldehyde content on the bonding strength and water resistance were investigated. The results indicated that the optimum internal bonding strength (IB, 1.22 MPa), modulus of elasticity (MOE, 3162.69 MPa), modulus of rupture (MOR, 29.10 MPa), water absorption (WA, 22.23%) and thickness swell (TS, 26.17%) of the MDF complied with the requirement of the Chinese national standard for MDF. The chitosan-based adhesive was characterized by Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and X-ray diffractometry (XRD). The thermal stability and water holding capacity of the chitosan-based adhesives were influenced by the extent of crosslinking. The excellent properties were attributed to the network structure of the chitosan-based adhesives, formed by crosslinking of chitosan with self-polymerized glutaraldehyde or glutaraldehyde monomers through C=N bonds.

1. Introduction

Medium-density fiberboard (MDF) is a traditional composite which is used for a variety of applications, e.g., the fabrication of laminated floors, paneling, cabinet doors and underlays of carpet floors and the furniture industry (Hu & Guo, 2015). In recent years, the use of formaldehyde in MDF adhesives has caused widespread concerns, e.g., the release of free formaldehyde which is harmful to human and the environment and the non-renewable and depleting petroleum resource for producing formaldehyde. In order to address these concerns, research on formaldehyde-free adhesives made from natural resources, such as lignin (Mansouri, Pizzi, & Salvado, 2007), soy protein (Kumar, Choudhary, Mishra, Varma, & Mattiason, 2002), wheat protein (Nikvash, Kharazipour, & Euring, 2013) and starch (Imam, Gordon, Mao, & Chen, 2001), has been extensively carried out. However, high costs of these materials and their relatively complicated manufacturing processes along with their poor bonding strengths and water resistances have limited their industrial applications. Hence, it has become very essential and important to develop a simple and facile process to prepare environmentally friendly and low-cost MDF adhesives with high bonding strength and water resistance.

Chitosan has received world-wide attention as a renewable and biodegradable material. It is a carbohydrate polymer obtained by deacetylation of chitin, one of the most abundant natural polysaccharides, next to only cellulose (Liu & Li, 2007; No et al., 2007). Chitin occurs as a component of crustacean shells, insect exoskeletons, fungal cell walls, microfauna and plankton. Chitosan is a copolymer, consisting of β-(1,4)-linked 2-acetamido-2-deoxy-D-glucopyranoses and 2-amino-2-deoxy-D-glucopyranoses. Similar to traditional amino resin adhesives (e.g., urea-formaldehyde resins and melamine resins), chitosan has free amino groups in its framework and hence can provide strong adhesion between surfaces (Arima & Iwata, 2007; Benhabbour, Sheardown, & Adronov, 2008; Hopper et al., 2014). Besides, incorporation of chitosan into hydrophilic materials, such as starch, has been regarded as an alternative to reduce water affinity and improve its mechanical properties, due to the formation of intermolecular hydrogen bonds between the amino and hydroxyl groups of chitosan and the hydroxyl groups of starch (Xu, Kim, Hanna, & Nag, 2005). Moreover, it has been reported that chitosan acts as an environmentally friendly preservative, by effectively protecting wood against water and fungus (Kobayashi & Furukawa, 1995; Lee et al., 1993). Hence, chitosan shows great potential as a multifunctional MDF adhesive.

However, in contrast to conventional amino resin adhesives, which are polymeric networks, chitosan is a basic linear polysaccharide. Hence, certain short-comings, such as easy deformation due to external stress and poor durability seriously restrict the applications of chitosan

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in MDF industry.

The chemical cross-linking technique using glutaraldehyde (Montazer & Afjeh, 2007) converts chitosan into a network structure and improves its performance. Therefore, the objective of this paper was to prepare and characterize a chitosan-based MDF adhesive with high bonding strength and water resistance by crosslinking it with glutaraldehyde.

2. Materials and methods

2.1. Materials

Wood fibers, consisting of a blend of soft wood and hardwood fibers from different species, were procured from the Greater Khingan Range Hengyou Furniture Co. Ltd. The wood fibers were produced through the fiber hot grinding process and contained cellulose (46.70 wt%), hemicellulose (29.17 wt%), and lignin (22.39 wt%). The original moisture content of fibers was approximately 18%. However, the fibers were dried in an oven at 80 °C to reduce the moisture content to approximately 6%. Chitosan (CAS No. 9012-76-4) was purchased from Sun Chemical Technology (Shanghai) Co. (China). It had a deacetylation degree of more than 95% and molecular weight from 100,000 to 150,000 Da. Acetic acid (CH_3COOH, CAS No. 64-19-7, AR) was supplied by Harbin Kaimeisi Technology Co. (China). Glutaraldehyde ($CHO(CH_2)_3CHO$, 50%, CAS No. 111-30-8, AR) was provided by Tianjin Ruijinte Chemicals Co. (China). Water distilled in our laboratory was used. All chemicals were used as received without any further purification.

2.2. Synthesis of chitosan-based MDF adhesive

The chitosan-based wood adhesive was prepared as follows: chitosan powder (1 g) and distilled water (24.5 mL) were taken in a four-necked round-bottom flask and stirred at room temperature until the chitosan powder was uniformly dispersed in distilled water. A solution containing acetic acid (0.67 g) and distilled water (24.5 mL) was then added to the flask and the reaction mixture was stirred at room temperature until an even and stable chitosan solution was formed. The chitosan solution served as the main component of the adhesive. Thereafter, glutaraldehyde was diluted with additional distilled water (24.5 mL), which served as the curing and crosslinking agent for the adhesive.

2.3. MDF preparation

MDF was prepared using a traditional hot-pressing process. Prior to MDF preparation, the glutaraldehyde solution was poured into the chitosan solution and stirred immediately until the mixture was evenly blended. The stoichiometric amounts of glutaraldehyde added are shown in Table 1. Thereafter, the wood fibers and the adhesive mixture just prepared were immediately mixed together in a chitosan to wood fibers mass ratio of 1.22:100. The mixture was then rotated in a high-speed mixer at 750 r/min for 5 min. The blended fibers were collected and hand-filled into a 250 mm × 250 mm forming box for pre-pressing to form a mat by applying a pressure of 1.0 MPa. The box was gently removed after the mat forming process, and the mat was placed between the parallel flat plates (400 mm × 400 mm) of a mechanically controlled oil-heated press for the final pressing process. The fiber mat was pressed at 170 °C for 480 s, according to a pre-programmed hot-pressing schedule (Fig. 1). In this process, a 5 mm thick steel gage was used to control the thickness of the board. Finally, the edges were trimmed off by 30 mm, resulting in final MDF dimensions of 220 mm × 220 mm × 5 mm, with a target density of 0.8 ± 0.02 g/cm^3. The MDFs were stored in a room having constant relative humidity of approximately 40%, at room temperature for 2 days, prior to the tests described in the subsequent sections. The control samples (CS) of MDF were prepared by the same process, but without the addition of chitosan-based adhesives.

Table 1
Stoichiometries of chitosan and glutaraldehyde used for the synthesis of the adhesives.

Adhesive code	Mass of glutaraldehyde solution[a] (g)	Mass of chitosan (g)	Mass ratio of glutaraldehyde and chitosan
GC 0.125	0.25	1	0.125
GC 0.25	0.5	1	0.25
GC 0.75	1.5	1	0.75
GC 1.25	2.5	1	1.25

[a] Mass concentration of glutaraldehyde solution is 50% (w/v).

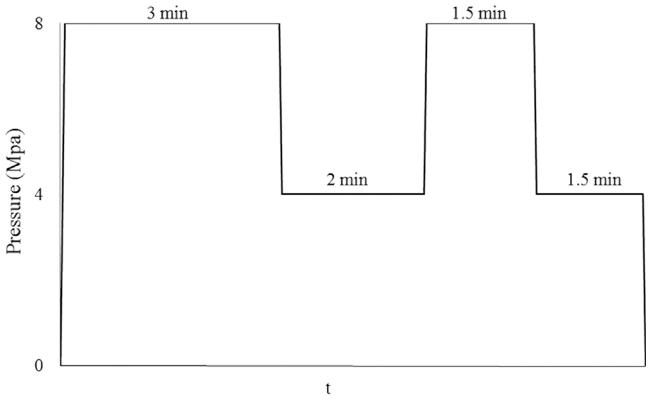

Fig. 1. Program schedule for hot-pressing process.

2.4. Bonding strength test

The bonding strength of the adhesives could be evaluated from the mechanical properties of the MDFs, which were determined in accordance with the Chinese national standard, GB/T 17657-2013, using a universal mechanical testing machine (CMT5504, Shenzhen XinSanSi Co. Ltd., China). The modulus of rupture (MOR) of a specimen refers to the ratio of the bending moment and bending modulus under maximum load, while the modulus of elasticity (MOE) refers to the ratio of the stress and strain of the load within the range of the elastic limit. The internal bonding strength (IB) refers to the ratio of maximum damage tension, perpendicular to the surface of the specimen and the specimen surface area. The MOR and the MOE of the MDFs were measured by conducting three-point static bending tests on specimens with dimensions of 200 mm × 50 mm at a crosshead speed of 5 mm/min. The IB was measured by pulling the specimen (50 mm × 50 mm) apart in a perpendicular direction. The specimens were sanded to improve the surface finish and to remove the low-density surface area. Thereafter, steel fixtures were bonded on each side of the specimen using hot melt glue. A tensile load with a crosshead speed of 0.5 mm/min was applied to each steel fixture until failure occurred in the specimen. The MOR and the MOE tests were repeated 12 times and the IB measurements were repeated 8 times.

2.5. Water resistance test

The thickness swell (TS) and water absorption (WA) were also measured according to the Chinese national standard, GB/T17657-2013. The TS and WA are defined as the percentage increase in the thickness and weight of a specimen, after immersing in water for 24 h at room temperature. The thickness and weight of the specimens having dimensions of 50 mm × 50 mm were measured, before and immediately after the 24 h soaking process. Measurements were performed on 8 specimens for each MDF.