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Alumina nanoparticle modified phenol-formaldehyde resin as a wood adhesive

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ABSTRACT

Phenol-formaldehyde resin was synthesized and modified by alumina nanoparticles (ANPs). The crystal form of the ANPs was characterized by X-ray diffraction (XRD), and differential scanning calorimetry (DSC) was used for thermal analysis of the resin. In addition, the resin was applied in plywood manufacture, and the curing time as well as the bonding strength was measured. The results showed, with an appropriate doping amount of ANPs, both the curing rate and the bonding strength increased significantly. The modified resin showed extensive application prospects in the wood construction industry.

1. Introduction

Adhesives have played an important role in the wood construction industry during many decades. Among the various types of adhesives employed, phenol-formaldehyde (PF) resins have been widely used in plywood, oriented strandboard and particleboard panel manufacture due to the advantages of strong resistance to moisture, low initial viscosity and excellent temperature stability [1,2]. The most common PF resin used in the plywood industry is the “resol-type”, which can be stabilized in solution by incorporating excess alkali and which can finally be changed to branched and cross-linked three-dimensional networks after hot-press treatment [3–5]. The energy consumption during the hot-press process is high and the curing efficiency needs to be improved, especially for large-size components [6,7]. So accelerating and optimizing the curing process is vital to cost reduction and quality improvement in plywood manufacture [8].

Recently, a considerable amount of research has focused on the curing process of the PF resin and some progress has been made. Fan et al. studied the cure properties of phenol-urea-formaldehyde and found that sodium carbonate, zinc oxide and magnesium oxide could increase the curing rate as a catalyst [9]. Other inorganic salts or inorganic oxides were also found to have an effect on the cure reactions of a PF resin, such as barium carbonate [10], silicon dioxide [11], magnesium oxide [12] and titanium dioxide [13]. Most of these inorganic salts or inorganic oxides have low solubility or dispersity in aqueous PF resin solutions, so the utilization ratio of the additives is relatively low. Researchers have also considered nanosize materials in an attempt to obtain a better reinforcement result and product performance [14,15]. Gao and Du studied the curing kinetics of a nano cupric oxide modified PF resin. Results showed that the addition of nano cupric oxide could effectively improve the shear strength of plywood [16]. In sisal fiber/PF resin composites, the incorporation of nano-silica was shown to improve the thermal stability of the composites and presented better wear resistance at different temperatures [17]. Lei and Pizzi et al. studied the influence of montmorillonite (MMT) nanoclay on PF and PUF resins for use as wood adhesives. Both dry and after boiling tensile strengths improved when the MMT with larger interlayer distance was introduced at a concentration of 5 wt% [18].

Alumina nanoparticles (ANPs) have been used as a reinforcement filler in polymer composites for many purposes [19], for example, dental resin composites [20] and epoxy electrical insulators [21,22]. With very small concentrations of ANPs, usually below 5 wt%, mechanical strength, abrasion resistance, thermal conductivity and electrical resistivity could be improved [23]. However, little research has been conducted on ANP reinforced PF resins as wood adhesives. Kumar et al. reported that ANPs could enhance the heat transfer rate of medium density fiberboard during hot-pressing, and could therefore improve mechanical properties [15]. ANPs have also been used to enhance the properties of PVA (polyvinyl acetate) polymers when used as wood adhesives. The bonding strength of PVAs under wet conditions and at elevated temperatures were increased by the addition of ANPs [24]. Recently, Dabbagh and Shahraki prepared mesoporous nanorod-like γ-alumina with a narrow pore size distribution using PF resin as a template [25]. Results showed there were strong interactions between ANPs and PF resins. Here, γ-ANPs were used to reinforce a PF resin for use as a potential wood adhesive with an attempt made to study the influence of ANPs on the curing process of a PF resin. Through mechanical tests and thermal analysis, reinforcement of a PF resin at

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different ANP contents revealed the existence of an acceleration effect on the curing process thus providing a good example of energy consumption control in plywood production.

2. Experimental

2.1. Materials and synthesis

Phenol (AR), formaldehyde (AR) and sodium hydroxide (AR) were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd., China. Alumina nanoparticals (γ phase, 20 nm) were obtained from Suzhou Huaweite Powder Tech. Co., Ltd., China.

The aqueous PF resin (resol type) was synthesized via a common route: phenol and the first part of formaldehyde and sodium hydroxide aqueous solution were mixed at 40 °C in a three neck flask with a mechanical stirring bar and the mixture was slowly heated to 95 °C over a period of 1 h. After stirring at 95 °C for 30 min, the mixture was cooled to 75 °C, the second part of formaldehyde and, sodium hydroxide aqueous solution were added. Then the mixture was heated to 85 °C and the viscosity was continuously monitored. When the viscosity reached 500 mPa s, the mixture was quickly cooled to room temperature. The total molar ratio of formaldehyde to phenol was 1.76:1. The concentration of sodium hydroxide aqueous solution was 30 wt%. The mass ratio of the first and second parts of the formaldehyde and sodium hydroxide aqueous solution was 7:1 and 3:2 respectively. The viscosity of the final product was between 500 mPa s to 1000 mPa s, and the pH was about 11.

The ANPs were introduced into the PF resin with loading levels of from 0% to 4% (weight ratio to the PF resin solution). The samples were labeled as PF0, PF1, PF2, PF3 and PF4, according to the loading level of alumina. To prepare the samples, the nanoparticles were added into the resin with a precise amount, and then the mixture was stirred vigorously under ultrasonic conditions at room temperature for 1 h. For XRD and DSC characterization, the resin samples were vacuum freeze-dried for 72 h, and the residues were ground into a powder at room temperature.

2.2. Morphology characterization

The morphology of the ANPs was characterized by transmission electron microscopy (TEM, Tecnai G2 F20 U-TWIN, FEI Co., USA). The diameter of the nanoparticles was about 20 nm.

2.3. X-ray diffraction

The X-ray diffraction data of the powdered samples were collected using a Philips X'pert (PW3040/60) diffractometer with Cu Kα radiation of wavelength 1.5406 Å operated at a voltage of 40 kV, a current of 40 mA and a scanning rate of 10°/min (2θ range 30–90°), where θ is the diffraction angle.

2.4. Differential scanning calorimetry

The DSC measurements of the powdered resin samples were performed on DSC-Q100 from TA Instruments under a nitrogen atmosphere. The sample weight varied from 4 mg to 6 mg and the heating rate was 10 °C/min at a scanning temperature range from 40 to 200 °C.

2.5. Viscosity and curing time

According to Chinese national standard (GB/T 17657-2013), the viscosities of the PF resin with different amount of ANPs were measured using a Brookfield rotary viscometer at 25 ± 2 °C. The curing time of the resin was measured separately at 120 and 140 °C with no addition of other curing agent. Both the viscosity and the curing time were tested three times and the average result of each sample was recorded.

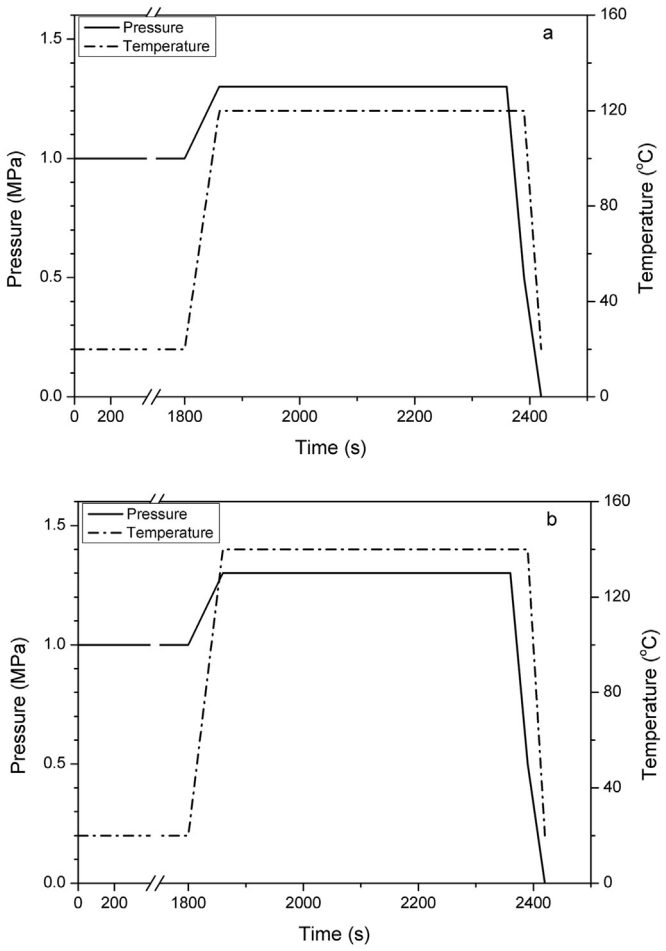

Fig. 1. Pressing condition of plywood production (a. 120 °C; b. 140 °C).

2.6. Bonding strength

Three-layer plywood panels were prepared for bonding strength tests. Each veneer with dimensions of 400 (Width) × 400 (Length) × 1.5 (Thickness) mm was prepared from Chinese white poplar (*Populus tomentosa*), and purchased from a local factory (Shandong Province) and dried to 8%-12% moisture content. Before glue spreading, 20% wheat flour was added to each adhesive sample by weight. The spreading amount was 300 to 360 g/m^2 double glue line. Then, the panel assembly was cold pressed for 30 min under 1 MPa at room temperature, as shown in Fig. 1. In this work, the hot press temperature was set at 120 and 140 °C, with a pressure of 1.3 MPa. After that, the pressure was released and the panel was cooled to room temperature in 60 s.

According to Chinese national standard (GB/T 17657-2013), the plywood panels were cut to dimensions of 100 mm × 25 mm and the bonding strength (wet shear strength) with twelve repetitions was tested using a rapid detection method: the specimens were soaked in boiling water for 3 h, and then cooled quickly to room temperature. Then the shear strength was tested in a wet state. According to the standard, a wet shear strength of more than 0.78 MPa is required for type I plywood [26]. Here, the shear strength was measured with an Instron 101 Universal Testing Machine under a crosshead speed of 5 mm/min.

3. Results and discussion

The viscosity and curing time of the PF resin samples varied with ANP content, as shown in Fig. 2. A TEM image of ANPs is shown in