International Journal of Adhesion & Adhesives 66 (2016) 26–32

Contents lists available at ScienceDirect

International Journal of Adhesion & Adhesives

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

Preparation and characterization of a novel environmentally friendly phenol–formaldehyde adhesive modified with tannin and urea

Cheng Li [a], Jizhi Zhang [a], Zhao Yi [a], Hua Yang [b], Bin Zhao [b], Wei Zhang [a,*], Jianzhang Li [a,*]

[a] MOE Key Laboratory of Wooden Material Science and Application, Beijing Key Laboratory of Wood Science and Engineering, Beijing Forestry University, No. 35 Tsinghua East Road, Beijing 100083, China
[b] Beijing Shoufa Tianren Ecological Landscape Co. Ltd., China

ARTICLE INFO

Article history:
Accepted 8 December 2015
Available online 11 December 2015

Keywords:
Phenol–tannin–urea–formaldehyde (PTUF) resin
Tannin
Plywood
Bonding strength

ABSTRACT

The application of phenol–formaldehyde (PF) resin adhesive has been greatly limited due to its toxicity, non-renewability and high-cost. Tannin, which is mostly extracted from renewable bark, could serve as an environmentally friendly bio-based polyphenol material. In this paper, phenol–tannin–urea–formaldehyde (PTUF) resins were prepared by copolymerization of tannin, urea, phenol and formaldehyde. Plywood bonded with those resins was prepared as well. The properties of PTUF resins were characterized by Fourier transform infrared spectroscopy (FTIR) and thermal gravimetric analysis (TGA). The results showed that the bonding strength of plywood bonded with the optimized PTUF resin could meet the Chinese National Standard (GB/T 17657-2013) for type I plywood. The optimized formula of PTUF resin adhesive was as follows: $T/(P+T)=20\%$, $U/(P+T)=30\%$. The bonding strength of plywood bonded with the optimized PTUF resin was 0.86 MPa, and the formaldehyde emission was 0.13 mg/L which would meet the requirement of E0 class plywood in accordance with Chinese National Standard (GB/T9846.1-9846.8-2004). TGA results showed that the thermal stability of the PTUF resin was better than that of PF resin in the initial thermal degradation. Therefore, the optimized PTUF resin is a promising substitution of PF resin in some aspects of the wood industry.

1. Introduction

Phenol–formaldehyde (PF) resins are generally synthesized from toxic petro-chemicals such as phenol and formaldehyde under alkaline catalysts conditions. They have been extensively used in the wood industry due to their excellent characteristics, including high bonding strength, water resistance, heat resistance and chemical stability [1]. However the rapidly rising cost of petro-chemicals, instability during storage, and toxicity have been the main reasons for the restriction of PF resin adhesives for wood based panel applications [2,3]. However, the use of renewable natural resources has afforded a lot of opportunities for the potential replacement of petro-chemicals [4]. Therefore, many investigations using natural and economical resources as substitutes for preparation of PF resin adhesive were carried out [5]. For example, many attempts involved replacing phenol using urea [6–11], tannin [12–14], bio-oil [15,16], carbohydrate [17,18], soy protein [19–21], and lignin [1,22] for wood adhesive.

Urea as a substitute for phenol has been successfully introduced into PF resins to prepare phenol–urea–formaldehyde (PUF) resins. A well-known modification method is adding urea (U) during or after the resin preparation. In most related studies, the amount of urea is less than 10% by weight because higher substitution of phenol will result in lower hydrolytic stability and higher formaldehyde emissions [23]. According to Scopelitis and Pizzi [24], PUF copolymers were formed at higher curing temperatures than the neat PF resin. Moreover, many investigations indicated that added urea not only contributed to the reduction of economic cost of PF resin but also promoted the curing rate as well as improved strength performance of bonded composites [7,25].

Naturally distributed tannins are oligomeric compounds containing multiple structure units (*i.e.* they have free phenolic groups, and are soluble in water). The molecular weights of tannin oligomers range from 500 to greater than 20,000 [26]. Tannin is similar to phenol in structure but possessed more phenolic hydroxyl groups which make it possible to substitute phenol in the preparation of PF resin [27,28]. Tannin-based adhesives have been studied by many researchers for the past 30 years. However, almost all of the tannin adhesives previously reported had serious disadvantages such as weaker strength of bonded composites, shorter storage life, longer curing time and higher economical cost

* Corresponding authors. Tel./fax: +86 10 62338083.
E-mail addresses: zhangweishe@126.com (W. Zhang), lijianzhang126@126.com (J. Li).

http://dx.doi.org/10.1016/j.ijadhadh.2015.12.004
0143-7496/

than neat PF resin adhesives in application [29]. This is due to the high steric hindrance, the barrier between the hydroxyl groups of tannin macromolecular, resulting in difficulties in the co-polycondensation. However, urea can play a bridge role in connecting the phenolic sections with tannin molecules to improve the bonding strength and shorten the curing time.

In this paper, valonia tannin was used to substitute phenol for synthesizing phenol–tannin–urea–formaldehyde (PTUF) copolymer resins as wood adhesives. The properties of the PTUF resins were characterized by using Fourier transform infrared spectroscopy (FTIR) and thermo gravimetric analyzer (TGA). The effect of the substitution rate on the properties and performance of plywood bonded by PTUF adhesives were investigated.

2. Materials and methods

2.1. Materials

In the following experiments formaldehyde aqueous solution (37%), solid phenol, calcium oxide (CaO) and sodium hydroxide (NaOH), which were AR grade reagents, were purchased from Beijing Chemical Reagents Co. Ltd. (Beijing, China). Industrial grade solid urea was purchased from Zhong'an Chemical Industries (Beijing, China). Commercial tannin, which was purchased from Tian'guan Biotech Company Limited in Henan province of China, was used in the polymerization experiments as received. Poplar veneer with a moisture content of 8.0% was obtained from Wen'an, Hebei, China.

2.2. The commercial tannin composition analysis and determination

The moisture content of tannin was determined by drying samples at 105 °C to constant weight following JIS Standard P8002-1996. The ash content of the residue was obtained following treatment in a muffle furnace for 4 h at 575 °C following TAPPI Standard T211om-1993. The content of tannin in the raw tannin material was determined in accordance with GB/T15686-2008. With ultraviolet-visible spectrophotometer at 280 nm wavelength, the tannin content of raw powder was determined utilizing standard curve.

2.3. Preparation of PF resin adhesive

A PF resin adhesive with a phenol/formaldehyde molar ratio of 1:2.2 was synthesized by batch copolymerization. The addition of 50% NaOH water solution was 40% based on the mass of phenol. In the first step, phenol with one third formaldehyde and NaOH solution were mixed in a flask, and then an appropriate amount of distilled water was added to the reactor whilst maintaining temperature of 85 °C. In the second step, another one third of the formaldehyde and NaOH were added into the flask for 1 h at 85 °C. In the third step, the rest of the formaldehyde and NaOH were added into the flask for 1 h at 85 °C. When the viscosity (measured at 20 °C) of the resin reached 100–300 mPa s and pH was about 10–12 the reaction mixture was rapidly cooled to 40 °C to yield PF resin. The resin's color was reddish brown, and other properties of the PF resin are shown in Table 2.

2.4. Preparation of PTUF, PUF and PTF resin adhesives

The PTUF resin adhesives were prepared by batch polymerization, the substitution rate of phenol by tannin or urea was in range of 10–40% by weight. In the first step, phenol, tannin, urea one third formaldehyde and NaOH were mixed in a flask. The mixture was heated for 1 h at 85 °C. The rest of the synthesis process was similar to the synthesis of PF resin. When the viscosity was 100–350 mPa s and pH about 10–12, the reaction mixture was rapidly cooled to 40 °C to obtain PTUF adhesives. PUF resin adhesive was synthesized without tannin; analogously, during the PTF resin adhesive preparation urea was not used. PTF and PTUF resins were of a dark color because of tannin's color, while PUF resin was of a lighter color than PF resin. The other properties of these resins are shown in Table 2.

2.5. Preparation of plywood

Three-layer plywood (400 mm × 400 mm × 6 mm) was prepared with single poplar veneer in the middle and two veneers on top and bottom by the method of floor substrate wood which adopted industry parameters. The dosage of adhesive was maintained at approximately 250–300 g/m^2 on both sides. First, plywood was cold-pressed under 0.8 MPa for 0.5 h and then hot-pressed at 135 °C under 1.1 MPa for 6 min.

2.6. Characterization of the PF, PUF, PTF and PTUF resins

The pH values of the resins were measured at 25 °C. Gel time was measured by charging 1 g of resin into a 16 mm diameter test tube and heating the test tube in an oil bath at 150 ± 1 °C. Gel time was defined as the time period from the immersion of the test tube into the oil bath to the beginning of resin gelation (resin forming a string when a glass rod was lifted from the resin). An average value of three replicate measurements was reported. The non-volatile (solid) contents of the resins were determined in accordance with ASTM standard D4426-01. Free formaldehyde was determined by the hydroxylamine hydrochloride method in accordance with DIN EN ISO 9397-1997. The viscosity of the resins was measured at 25 °C by a Brookfield LVDV-II+P viscometer at 25 °C, according to the standard ASTM 1084-97 (Standard test methods for viscosity of adhesives, test method B employing a Brookfield viscometer with a suitable spindle) [2].

2.7. Characterization of the plywood

The shear strength was measured in accordance with the procedure described in Chinese National Standard (GB/T 17657-2013) for interior and exterior plywood. Formaldehyde emissions were measured by the desiccator method [30]. For this test 10 specimens with the dimension of 15 cm × 5 cm were placed into a desiccator of 10 L capacity containing 300 mL distilled water. After 24 h at 20 ± 2 °C, the concentration of formaldehyde absorbed in the distilled water was determined by the acetylacetone method with an ultraviolet spectroscope (UV) at 412 nm.

2.8. Thermal gravimetric analysis (TGA) of the cured resins

The PF, PUF, PTF and PTUF resins were cured in an oven at 120 °C for 2 h. The cured resins were powdered to 200-mesh particle size. About 5 mg of each cured resin sample was added to a platinum pan and heated from room temperature to 700 °C at a rate of 20 °C/min under a N_2 atmosphere using a thermal gravimetric analyzer (TGA-Q50, TA Instruments, USA).

2.9. FTIR analysis of PF, PUF, PTF and PTUF resins

Resin samples were freeze-dried at −70 °C for 24 h. Then, the uncured resins were milled to 200 mesh meal, and embedded in potassium bromide (KBr) pellets at a ratio of 1:100 in weight. The FTIR spectra of uncured PF, PUF, PTF and PTUF resins were recorded on a Nicolet 6700 spectrometer (Nicolet Instrument