Modification of Chinese Fir with Alkyl Ketene Dimer (AKD): Processing and Characterization

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A process for the chemical modification of Chinese fir with alkyl ketene dimer (AKD) was studied. The hydrophobicity of the resulting products was evaluated by characterization of the equilibrium moisture content, water-surface contact angle, water absorption coefficient, and anti-swelling efficiency. The results indicated that when 5% AKD solution was used, the modified wood generally showed good hydrophobicity and improved dimensional stability. The result of boiling water and hexane extraction tests showed that the modified fir possessed very stable hydrophobicity.

Keywords: Wood modification; Chinese fir; Alkyl ketene dimer; Hydrophobic character

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INTRODUCTION

To prolong the service life of wood-based materials, chemical modification of wood has been widely studied. Such treatments also may improve wood's dimensional stability. The chemicals used have mainly included various derivatives of anhydride, epoxide, chlorosilane, alkyl chloride, aldehyde, *etc*. (Rowell 2005). Generally, such modification has worked by replacement of the hydrophilic hydroxyls in lignocelluloses with hydrophobic organics, rendering the wood materials water-repellent; consequently the dimensional stability can be greatly improved. For example, acetylated wood has been found to have a low equilibrated moisture content (EMC) of 2 to 5% and a high anti-swelling efficiency (ASE) of around 70%, depending on the wood species and treatment conditions (Rowell 2005, 2006). Another feasible strategy is to fill wood with polymerizable monomers followed by a polymerization process, or by directly filling wood with polymers. The monomers used in the latter method included acrylics (Kowalski and Kyziol 2002), polyethylene glycol (Makoto 2002), and furfural-urea (Schneider and Phillips 2009a,b). The two methods mentioned above are promising approaches to producing wood-based materials with good dimensional stability.

Recently, alkyl ketene dimer (AKD) has been studied as a hydrophobic reagent for wood modification, where it is assumed that the AKD molecules can directly react with hydroxyl groups of cellulose to form β-ketoester linkages by esterification (Song *et al*. 2012; Yoshida *et al*. 2007, 2012). AKD has been widely used as a sizing agent in papermaking (Chen and Biermann 1995; Asakura *et al*. 2006; Lindstrom and Larsson 2008). For wood modification, most previous studies have focused on the hydrophobization of wood surfaces using emulsified AKD mixture (Antti-Korpela 2009; Kukkonen *et al*. 2010), treatment of thermally modified wood with AKD solution (Laitinen *et al*. 2005), or making particleboard from AKD-modified chips (Hundhausen

et al. 2009). Compared with anhydride, epoxide, chlorosilane, alkyl chloride, or aldehyde, AKD is a very mild chemical, and the involved solvents are recyclable. Theoretically, no toxic chemicals are produced. In addition, there is no special requirement for equipment. However, there are few reports about the inner hydrophobicity and dimensional stability of AKD-modified solid wood. The objective of this research is to optimize the process of modifying Chinese fir with AKD by characterizing the inner hydrophobicity and the dimensional stability of the modified wood.

EXPERIMENTAL PROCEDURE

Materials and Instruments

Chinese fir was purchased from the lumber market of Shaoxing, Zhejiang Province, China, and used without further pretreatment.

The n-Hexane (pure) and Alkyl Ketene Dimer (AKD) wax (R, R'=C14－C16) (pure) were purchased from Tian Yi Chemical Company, Zhenjiang, Jiangsu Province, China.

The water-contact angle was measured with a CA-W automatic contact angle meter (Kyowa Interface Science) equipped with an AD-31 auto-dispenser. FTIR spectra were collected using a Nicolet impact 410 FTIR spectrometer.

Methods

First, 10 Chinese fir samples were randomly selected and cut into small specimens with dimensions of 2 x 2 x 30 cm (radial x tangential x longitudinal). Following the cutting, the mass was recorded, and all the specimens were labeled with Arabic numerals. Respectively, they were used as follows: one as control, one for moisture content determination, six for the modification process under different conditions, and the extra two were kept in reserve. Finally, the wood samples were treated with a high-pressure impregnation process. The typical pressure process was as follows: 1) the AKD wax was dissolved in n-hexane solvent at 2% and 5% (w/w) concentration; 2) 10 specimens were placed in the reaction tank and AKD solution was then infused; 3) and high pressure was applied and the samples were impregnated with the solution for a certain time at 1.0 MPa. Two concentrations (2% and 5%) and three durations (0.5 h, 1 h, and 2 h) were tested; 4) the resultant samples were put in a ventilating cabinet where the hexane was allowed to evaporate overnight. Then the samples were heated at 105 to 110 ^{o}C for 5 h to allow the reaction of the AKD with the wood to proceed. Finally, the samples were cooled to room temperature and kept in desiccators for testing.

Characterization

FTIR spectra

Each sample for FTIR testing was prepared as follows: First, the sample was sawn at the middle longitudinally then one of the new cross-sections was sanded to obtain wood powder. The FTIR spectra were collected by scanning a potassium bromide (KBr) pellet with about 2% wood powder inside.

Weight gain

Weight gain (W_g) was calculated with the following formula,

$$W_g = (\frac{W_2 - W_1}{W_1}) \times 100\% \quad (1)$$

where W_1 is the mass of oven-dried wood sample before modification, and W_2 is the mass of oven-dried wood sample after modification.

Water contact angle

Samples for characterization of the water contact angle (WCA) were prepared as follows: The modified samples were sawn at the middle in the longitudinal direction, and the resulting cross section was then sanded to get a smooth surface. The value of WCA was an average of the numbers collected from five spots, including four from four corner areas and one from the center of the cross section, on the resultant smooth surface. The WCA was recorded every 20 seconds; a total of 100 seconds were evaluated.

Equilibrium moisture content

The equilibrium moisture content (EMC) is the moisture content (MC) of wood when it is in equilibrium with the temperature and humidity (Siau 1984) in its environment. The EMC was obtained by calculating the difference between the samples' weights at equilibrium moisture and when oven-dried. The conditions tested were the following. First, the modified and control specimens were oven-dried; they were then placed into the equilibrium environment. The environment's temperature was 25 ^{o}C, and the humidity was 50%. After the MC was constant (30 days for equilibrium here), the resulting MCs were recorded as EMCs.

Dimensional stability

The dimensional stability of the resultant wood was evaluated by its anti-swelling efficiency (ASE). The procedure used here was the modified water-soaking method described by Rowell and Ellis (1978). First, the weight and size of specimens were recorded (precision was 1 mg for weight and 1 μm for size), which was followed by immersing the samples in water at room temperature. The weight and size of the samples were recorded carefully after a certain period. Five replications were performed under each condition.

Based on the results, the ASE was calculated according to the following equations,

$$S = [(V_{wet} - V_{dry}) / V_{dry}] \text{ x } 100\% \quad (2)$$

where S is the volumetric swelling coefficient, V_{wet} is the wood volume after wetting with water, and V_{dry} is the wood volume of oven-dried sample before wetting. Then,

$$\text{ASE} = [(S_{unmod} - S_{mod}) / S_{unmod}] \text{ x } 100\% \quad (3)$$

where ASE is the antiswelling efficiency, S_{mod} is the volumetric swelling coefficient of modified wood, and S_{unmod} is the volumetric swelling coefficient of virgin wood. The results are shown in Fig. 4.

Additionally, the water absorption coefficient (WAC) was calculated using the collected data with the following formula,

$$WAC = \frac{W_2 - W_1}{W_1} X100\% \quad (4)$$

where W_1 is the weight of sample before wetting, and W_2 is the weight of sample after wetting. The WAC results for the 5%-AKD-modified wood are shown in Fig. 5.

Durability

To evaluate the durability of the modified wood, the following two extraction experiments were performed:

1) Hot hexane extraction: One of the 5%-AKD modified samples was cut into 20 small pieces with a thickness of 1 cm (details can be found in Fig. 1). Then the labeled samples were put into excess n-hexane, and refluxed at 70 to 75°C, and then four pieces were randomly taken out after a certain time (0, 6, 12, 18, and 24 h, respectively). The resulting samples were oven-dried, and the corresponding weight gains were calculated by Formula 1;

2) Boiling water extraction: One of the samples was cut as shown in Fig. 1. Then the labeled samples were put into a cage and sunk into boiling water, and then two pieces were randomly taken out after a certain time (0, 0.5, 1, 1.5, 2, 3, 4, 6, 8, and 10 h, respectively). Then the extracted samples were oven-dried. The durability of hydrophobicity was evaluated by measuring the WCA of the resultant samples using the method described above.

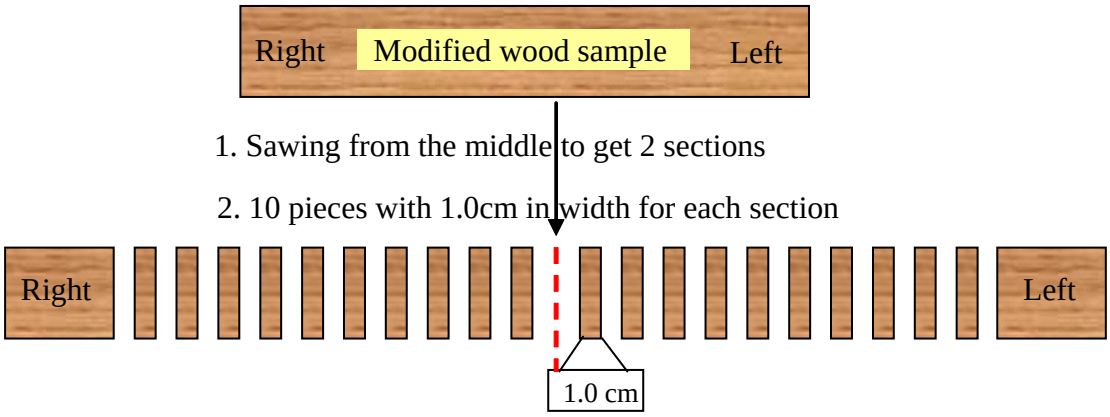

Fig. 1. The illustration for preparation of endurance-test samples

RESULTS AND DISCUSSION

FTIR Spectra

The FTIR spectra are presented in Fig. 2. Compared to the spectrum of the virgin wood, two large peaks occurring at 2844 cm^{-1} and 2917 cm^{-1} were characteristic of the AKD-modified wood. These two peaks were the result of the stretching vibration of C-H in methylene and methyl from AKD. Also, the reaction between the hydroxyls in the wood and AKD will result in an ester group, but the peak for the ester group was

overlapped by a peak from the wood around 1740 cm^{-1}, so it is difficult to identify it from the FTIR spectrum. Some researchers have concluded that the AKD molecules can directly react with hydroxyl groups from cellulose to form β-ketoester linkages by esterification (Song *et al*. 2012; Yoshida *et al*. 2007, 2012). Other publications, however, have argued whether AKD is covalently bonded to the cellulose or not (Isogai 1999). Based on the spectra of this research, it was hard to conclude decisively whether the AKD was covalently bonded to the cellulose.

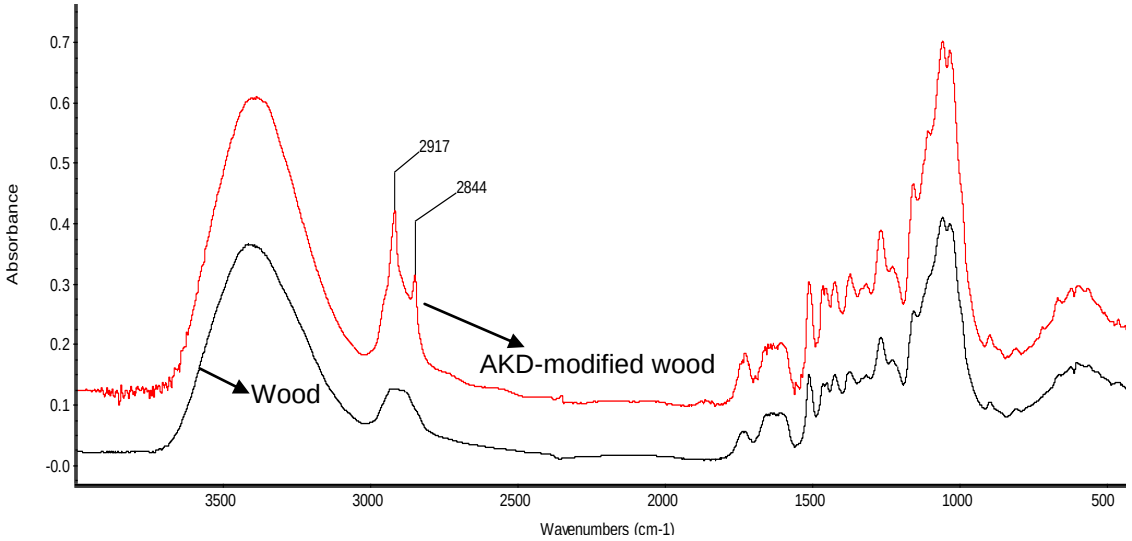

Fig. 2. The FT-IR spectra of hexane-treated wood and AKD-modified wood

Weight Gain

The results for the percentage of weight gain are graphed in Fig. 3. It was found that the samples modified with 2% AKD had a relative lower weight gain than that of the 5%-AKD-modified ones. Generally, the weight gain of the 2%-AKD-modified samples was around 6 to 7%, while it was around 10% for the 5%-AKD-modified samples. The increase of impregnation time did not give a significant increase of weight gain for both 2% and 5%-AKD modified wood in 2 hours.

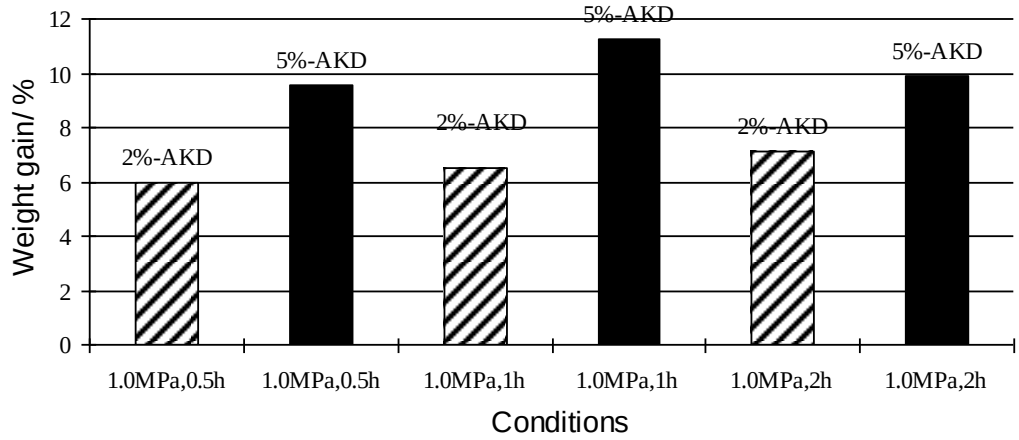

Fig. 3. Weight gain of AKD-modified wood under different conditions

Water Contact Angle

In Fig. 4, the plot of WCAs from samples treated under different conditions indicated that: a) water was soaked up by the virgin wood in seconds; b) the hydrophobicity of wood was greatly improved after it was modified with AKD; c) 2%-AKD-modified wood would not give a high and stable WCA. All the WCAs, especially the 0.5 h-treated and 1.0 h-treated wood specimens, were less than 100° after 40 s of a water droplet being allowed to stay on the cross-section surface; d) For the samples treated with 5% AKD, when the impregnation time was longer than 1 hour, the WCAs of the resultant samples were higher than 110° even when the water droplet stayed on the wood surface for more than 100 s. The sample treated in 5%-AKD for 2 h possessed the highest WCAs in the samples (>120^{o}), followed by the one treated in 5%-AKD for 1 h (>110^{o}). The change of WCAs was less than 10° in 100 s.

The 2%-AKD modified wood samples, based on their initial WCAs, showed a relative decrease, followed by a quick decrease. This indicated that the 2%-AKD solution could not offer sufficient AKD to modify the wood thoroughly. That may be a consequence of the relatively low weight gain of AKD compared to the 5%-AKD treated wood specimens. So the subsequent investigations were just focused on the 5%-AKD modified specimens.

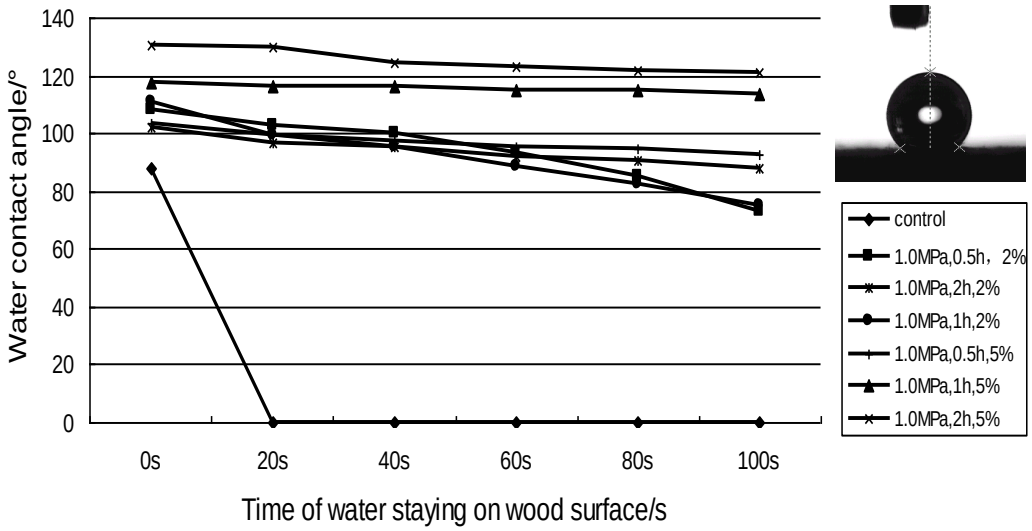

Fig. 4. Water contact angles of AKD-modified wood in different conditions, a typical digital picture was shown at top right corner

Dimensional Stability

The results of the water contact angle test indicated that the hydrophobicity of the 2%-AKD-modified samples was not as stable as that of the 5%-AKD-modified ones, so only the ASE of the 5%-AKD-modified wood was tested. The results are graphed in Fig. 5. Also, the WACs of the 5%-AKD-modified wood are shown in Fig. 6.

From Fig. 5, it can be seen that the AKD-modified wood had very high ASE values at the first 4 h (generally over 55%) in the water-soaking test. However, they decreased quickly to 20% at 24 h, and 10% at 48 h. Figure 6 shows that the WACs of virgin wood were much higher than those of the modified ones. The WACs of most

modified samples were around 10% at 4 h, but they increased to 25% at 24 h and 35% at 48 h. For virgin Chinese fir, the WACs were more than 90% in 4 h and 110% in 48 h.

This indicated that when the WAC is more than 20%, the ASE of AKD-modified wood will decrease very quickly, and the dimensional stability will become relatively poor for Chinese fir. That is probably because the raw material, Chinese fir, has relatively high porosity.

Other research by the authors (Yang *et al.* 2013) has shown that after treatment with AKD (5% concentration) for 2 hours the longitudinal modulus of the S2 layer of cell wall measured by nanoindentation was decreased by about 15.2%. This supports the finding that AKD did penetrate into the cell wall and reacted with the hydroxyl groups in the cellulose, hemicellulose, or lignin. Hydroxyl groups in the cell walls absorb moisture through hydrogen bonds. The wood dimensional stability can be improved either by chemical reaction with the hydroxyl groups in the cell walls with a chemical such as acetic anhydride (Rowell 2005; Van Houts *et al.* 2003) or by decreasing carbohydrate content of wood itself (Hosseinaei *et al.* 2011a,b). The weight gain of a fully acetylated wood could reach 25% (Youngquist *et al.* 1986). In this research the weight gain was just 10% for the 5%-AKD-modified samples, which indicates that a part of hydroxyls reacted with AKD.

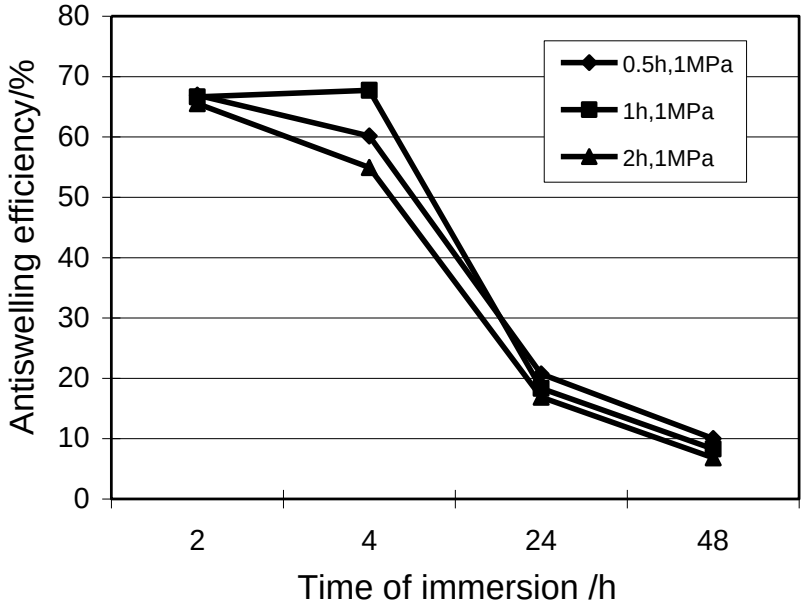

Fig. 5. The antiswelling efficiency of 5%-AKD modified wood in different immersion period

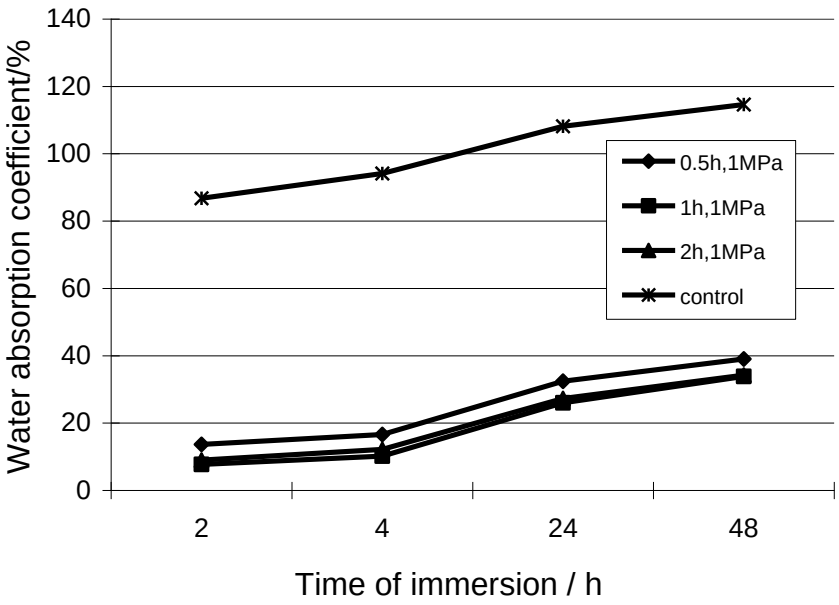

Fig. 6. The water absorption coefficient of 5%-AKD modified wood in different immersion period

In summary, the modification mechanism in our system involves a synergism of chemical reaction inside cell walls and the cell lumen surface covered with a monolayer of AKD. The chemically grafted AKD layer just plays a role to retard the water penetration into cell wall. Therefore, the water can penetrate into the wood cell wall after long-time immersion. So, the ASE of modified wood is high at the beginning of testing, but as the water absorption increases, the grafted AKD layer cannot completely prevent the water penetration into cell wall, so the ASE decreases gradually.

Equilibrium Moisture Content

For the 5%-AKD modified Chinese fir, the statistical results of the EMC measurements were 7.19% for the virgin wood; 2.05% for the 0.5 h-treated sample; 2.49% for the 1 h-treated sample; and 2.18% for the 2 h-treated sample. This indicated that all the AKD-modified wood possessed very low moisture content compared to that of the virgin wood. The EMC measurements also demonstrated that the AKD was a good hydrophobic reagent for improving the hydrophobicity of the interior of wood.

Durability

Because the hexane is a very good solvent for AKD, here it was employed as eluent to perform the extraction of potentially free AKD (Fig. 7).

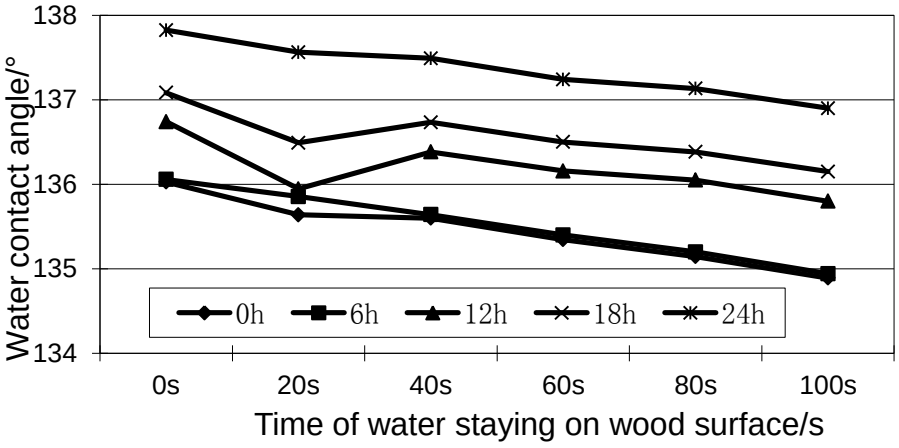

Fig. 7. Water contact angles of hexane-extracted modified wood with extraction time. The modification conditions for the present sample is: 5%-AKD concentration and 1.0 MPa for 2 h.

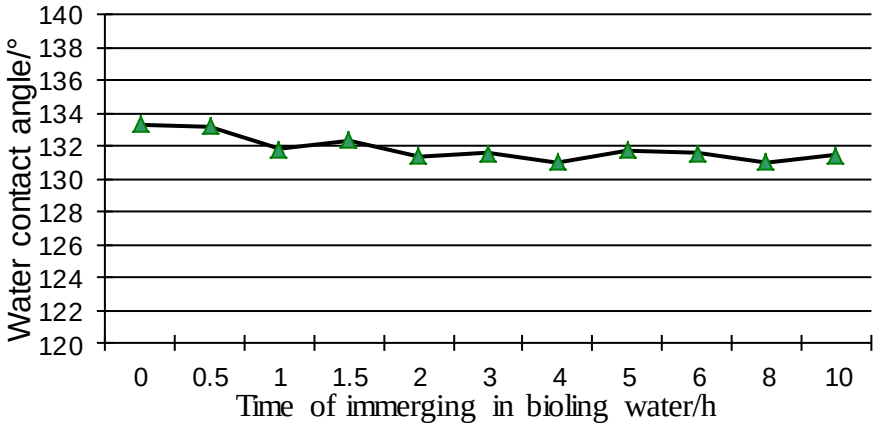

Fig. 8. Water contact angles of boiling-water-treated 5%-AKD modified wood

The WCAs given in Fig. 7 showed that: 1) For one specimen, its WCAs exhibited a decrease of 1 to 2° in 100 s; 2) As extraction was prolonged, all the WCAs were slightly increased; the longer the extraction, the higher the WCA. The extraction process likely teases out the hydrophobic AKD molecules which were anchored on the surface of wood cell wall, and make them more exposed to air.

Also the weight loss was 2.28% for 6 h extraction, 2.84% for 12 h, and 2.90% for 24 h. That indicated the free AKD may be removed by the extraction, while the covalently grafted AKD survived well during the hot hexane extraction.

In order to estimate the treated material's durability for exposure to water, a boiling water test was also conducted. The resultant WCAs of boiling-water-treated samples are given in Fig. 8. There was very little decrease in the WCA after treatment with boiling water, and the value had decreased by about 2° after 10 h of treatment. That also evidently showed that the AKD-modified Chinese fir possesses very good resistance to boiling water. That could be very helpful if it will be used outdoor, because the prevention of chemicals from wash-out is an important feature for industrial products.

CONCLUSIONS

This study provided a detailed investigation into the modification of Chinese fir with alkylketene dimer (AKD). The hydrophobic properties associated with different processing conditions were characterized. The following can be concluded:

1) The weight gain results indicate that the high-pressure impregnation can efficiently introduce AKD into the interior of wood. When 5% AKD in hexane was used as solution, a higher weight gain was observed.

2) The results from ASE and WCA demonstrated that the unitary hydrophobicity and dimensional stability of modified wood were greatly improved by modification of wood with AKD.

3) The durability tests by extraction with hot hexane and boiling water revealed that the AKD was covalently reacted with the hydroxyl groups from wood rather than being physically absorbed.

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