Improving Dimensional and Thermal Stability of Poplar Wood *via* Aluminum-based Sol-Gel and Furfurylation Combination Treatment

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Wood modification is an efficient method to improve wood performance and expand the applications of wood material. In this study, a combination modification method of aluminum sol-gel and furfurylation was developed to improve the performance of poplar wood. Wood samples were characterized by Fourier transform infrared spectroscopy and field emission scanning electron microscopy. The properties of the treated wood, including thermal stability, water uptake, dimensional stability, and dynamic wettability were also evaluated. The thermogravimetric analysis results indicated that the incorporation of an aluminum-based gel could prevent furfurylated wood from thermal degradation by converting the gel into nano-Al_2O_3. The aluminum-based sol-gel apparently hindered furfuryl alcohol polymerization and reduced the weight percent gain of the samples; the anti-swelling efficiency of the treated wood was over 57% (with little decrease) due to crosslinking between the wood and aluminum-based gel. The water uptake and hydrophobicity of the modified samples were improved significantly in comparison to the control samples.

Keywords: Poplar wood; Furfurylation; Aluminum sol-gel; Dimensional stability; Thermal stability

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INTRODUCTION

Wood, a natural and highly molecular material, has numerous distinctive and potentially very advantageous properties such as porous character, a high strength-to-weight ratio, anisotropy, processability, and an aesthetically pleasing appearance. Its drawbacks include hygroscopicity, interior dimensional instability, poor strength, and other factors (which are especially pronounced in fast-growing wood) that strictly limit its practical applications. Various wood treatments such as acetylation (Li *et al*. 2009), glyoxal crosslinking (Yan *et al*. 2014), grafting polystyrene or polyethylene glycol dicrylate onto wood cell walls (Dong *et al*. 2016a; Wang *et al*. 2016), *in situ* polymerization of furfuryl alcohol in wood cell walls (Lande *et al*. 2008), and heat treatment (Esteves and Pereira 2009) are currently the most popular modifications for improving the dimensional stability, durability, mechanical properties, and other properties of wood material. Wood furfurylation, which involves impregnating pristine wood with furfuryl alcohol (FA) followed by *in situ* polymerization, has been investigated extensively in recent decades (Xie *et al*. 2013).

Furfurylated wood is commonly applied in construction, furniture, and flooring products due to its excellent physical and mechanical properties (Lande *et al*. 2004a; b). Due to the thermal degradation of poly (furfuryl alcohol) (PFA), however, the weight of furfurylated wood decreases considerably from 200 °C to 300 °C compared with untreated wood (Dong *et al*. 2014).

The incorporation of inorganic compounds can endow wood with various properties such as weather resistance, thermal stability, and UV resistance (Hazarika and Maji 2014). Inorganic and organic hybrid modifications, which provide the advantages of both wood and inorganic compounds, have attracted considerable attention in recent years as well (Merk *et al*. 2015; Dong *et al*. 2016b). Many mineral phases have been utilized to prepare wood-inorganic composites via the sol-gel technique (Mahr *et al*. 2012; Qin and Zhang 2012), impregnation (Ghorbani Kookandeh *et al*. 2014), or chemical reactions (Merk *et al*. 2015). Among these methods, the sol-gel process is most commonly used for material synthesis, preparation, and fabrication by virtue of several distinct advantages (Ko 2008). A typical sol-gel process involves roughly three steps: (1) sol preparation, (2) wood impregnation with the sol, and (3) the formation of gel from sol (Mai and Militz 2004). Wood properties such as dimensional stability, flame retardancy, water repellency, antimicrobial properties, and antileaching efficacy can be significantly enhanced after sol-gel treatment (Mahltig *et al*. 2008; Mahr *et al*. 2013).

Aluminum-based sol (which can be aluminum hydroxide, aluminum hydrous oxide, or related compositions) is a commonly used precursor for fabricating coatings, films, phase change materials, and alumina nanostructures; it has considerable potential in terms of preparing treated wood with very favorable performance (Farrell *et al*. 2006; Figueira *et al*. 2015; Ji *et al*. 2015). The word “aluminum sol” will be used in the present article to refer to a wide range of aluminum hydroxide or hydrous oxide species that might be present. Combined treatments have been effectively used to improve wood properties while avoiding extensive side effects. For instance, wood polymer nanocomposites, coupling the advantages of both polymers and nanoparticles, exhibit excellent comprehensive performance (Devi and Maji 2013; Dong *et al*. 2014, 2016c).

In an effort to improve the performance of poplar wood, this study developed a modification process that includes FA polymerization combined with an aluminum-based gel. Wood treated with this combined method showed enhanced performance compared with the control, reflecting a synergistic effect between the PFA and aluminum gel in the wood structure. The aluminum sol was first prepared from aluminum isopropoxide hydrolysis and then mixed with the FA solution at the appropriate level. Poplar wood samples were impregnated with the solution, followed by *in situ* polymerization. The properties of the treated wood samples, *e.g.*, thermal stability, water uptake, dimensional stability, and dynamic wettability, were characterized.

EXPERIMENTAL

Materials

Furfuryl alcohol (chemically pure, 98.0%), aluminum isopropoxide (chemically pure), and formic acid were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Other reagents were obtained from Beijing Chemical Works (China).

Wood samples were prepared from sound fast-growing poplar sapwood (*Populus* spp.) with dimensions of 20 × 20 × 20 mm^3. The manufactured samples were extracted through a toluene/ethanol/acetone (4:1:1 v/v) mixture solvent in a Soxhlet apparatus, oven-dried to a constant weight at 105 °C for 12 h, and stored in a desiccator until use.

Methods

Aluminum sol preparation

Aluminum isopropoxide and water with a mole ratio of 1:100 were added to a flask and stirred constantly at 85 °C for 6 h. When the mixture became a slurry, the pH was adjusted to 4 with formic acid and stirred for another 6 h until it became transparent. The transparent aluminum sol was cooled to ambient temperature. About 10 g of this sol (A) was oven-dried at 100 °C until it reached a constant weight (B). The solid content was calculated according to Eq. 1,

$$\text{Solid content (\%)} = B / A \times 100 \tag{1}$$

Three replicates were conducted for each sample, and the averaged values were reported as the final results.

Furfurylation

The combination wood modifiers were prepared by mixing FA with different amounts of aluminum sol. The percentage of FA solutions was fixed to 50%, and the aluminum sol percentage was fixed to 0%, 25%, or 50%. The pH of the resultant solutions was adjusted to 4 with formic acid. Pristine wood samples were treated with distilled water as a control. The samples were impregnated with the obtained mixed solutions under a vacuum (*ca*. 0.095 MPa) for 40 min and then held at atmospheric pressure for another 2 h. The samples were then wrapped in aluminum foil and oven-cured at 100 °C for 20 h. After the aluminum foil was removed, the samples were oven-dried uncovered at 105 °C until a constant weight was reached.

The weight percentage gain (WPG) and bulking efficiency (*BE*) of the samples were calculated according to Eq. 2 and Eq. 3,

$$WPG\ (\%) = (W_2 - W_1)/W_1 \times 100 \tag{2}$$

$$BE\ (\%) = (V_2 - V_1)/V_1 \times 100 \tag{3}$$

where W_1 and W_2 are the oven-dried weight of the wood sample before and after treatment, respectively (g), and V_1 and V_2 are the volume of the wood sample before and after treatment, respectively (mm^3).

Physical and mechanical analysis

Volumetric swelling (S) for the control and treated wood samples after 24 h of immersion in deionized water at room temperature were calculated as follows,

$$S\ (\%) = (V_3 - V_2)/V_2 \times 100 \tag{4}$$

where V_3 is the volume of samples after immersion in deionized water (mm^3).

The next variable calculated was the dimensional stability in terms of anti-swelling efficiency (ASE) based on the swelling difference between the control and treated samples as follows,

$$ASE\ (\%) = (S_u - S_t)/S_t \times 100 \tag{5}$$

where S_u and S_t are the volumetric swelling of the control and treated wood samples, respectively.

The water uptake (WU) after 24, 48, 72, 96, and 120 h of immersion in deionized water at room temperature was calculated as follows,

$$WU\ (\%) = (W_3 - W_2)/W_2 \times 100 \qquad (6)$$

where W_3 is the weight of the sample after immersion in deionized water (g).

Morphologies of the control and treated wood

The morphologies of the control and treated wood samples were observed under a field emission scanning electron microscope (FE-SEM). The interior portions of the tangential and cross planes were removed with a surgical blade, mounted on conductive adhesives, gold-sputter-coated, and observed under a Hitachi SU8010 instrument (Tokyo, Japan) at a voltage of 5 kV with a magnification of 1.0 k.

Fourier transform infrared (FTIR) spectroscopy analysis for the control and treated wood samples was conducted on a Nicolet 6700 infrared spectrophotometer (Thermo Scientific, Waltham, MA, USA) with a scan range of 4000 to 400 cm^{-1} at the 4 cm^{-1} resolution for a total of 32 scans.

Contact angle analysis

The surface contact angles parallel to the grain were measured as follows. Sessile droplets of deionized water (3 μL, measured with a microsyringe) were placed on the wood surface, and the right and left angles of the drops on the surface were collected at 0.1 s intervals for 120 s. Six replicates were conducted for each sample, and the average values were calculated to evaluate the dynamic wettability.

Thermogravimetric analysis (TGA)

The thermal stabilities of the control and modified samples were investigated with a Q50 TG analyzer (TA Instruments, New Castle, DE, USA) at a 10 °C/min constant heating rate under a flowing nitrogen atmosphere from room temperature to 600 °C.

RESULTS AND DISCUSSION

Morphology Analysis

The average solids content of the aluminum-based sol was 3.38%. As shown in Fig. 1, the mixed modification solutions were uniform and stable. The appearance of the modified poplar wood samples was dark brown. The average WPG and BE of the control and aluminum sol-treated wood samples are listed in Table 1.

Table 1. WPG and BE of Control and Treated Wood Samples

Sample*	WPG (%)	BE (%)
Control	--	--
0	90.03 ± 6.17	8.54 ± 0.57
25%	55.97 ± 4.92	7.50 ± 0.58
50%	49.44 ± 5.24	5.27 ± 0.55
* Percentage of aluminum-based sol		

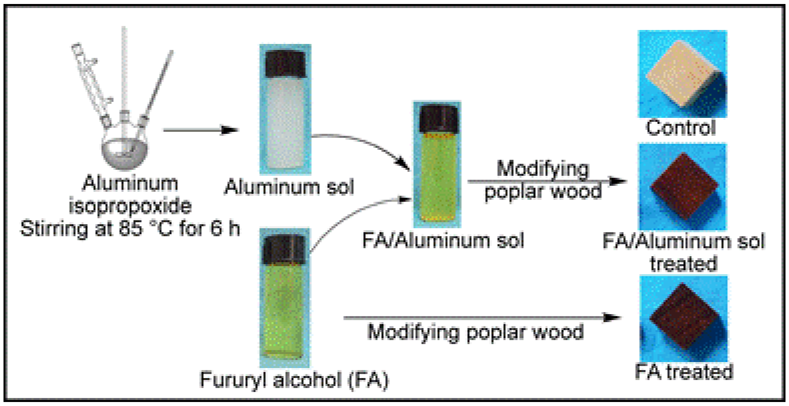

Fig. 1. Schemes of the preparation of aluminum sol and wood composites

As the proportion of the aluminum sols to FA increased, both WPG and BE markedly declined; this was likely a result of an increased quantity of the pseudoboehmite phase (AlOOH) in the aluminum sol having formed during the prolonged heating polymerization time (Aguado *et al.* 2005). The generated AlOOH partially neutralized the acid catalyst and impeded FA polymerization. The BE of the treated wood decreased from 8.54% to 5.27% when the aluminum isopropoxide/FA was 50%. This could have occurred due to a low PFA loading in the wood structure, or possibly due to the crosslinking between aluminum gel and wood having shrunk the wood structure.

FE-SEM photographs of the cross and tangential wood samples are shown in Fig. 2. Compared with the pristine wood, there were many more substances in the furfurylated wood, with or without aluminum sol observable in the cross photographs (Figs. 2b to 2d). Furfurylated wood cell lumens were partially filled with PFA (black arrows), but the cell lumens of aluminum sol-treated wood were not filled (Figs. 2c and 2d). Instead, the cell walls of aluminum sol-treated wood were substantially thickened, suggesting that PFA mainly adhered to cell lumen walls and in the cell walls; furthermore, FA polymerization in wood cell lumens was impeded by the aluminum sol. In the tangential photographs, the polymers that precipitated on cell lumen walls in furfurylated wood with or without aluminum sol were remarkable (and consistent with the cross observations).

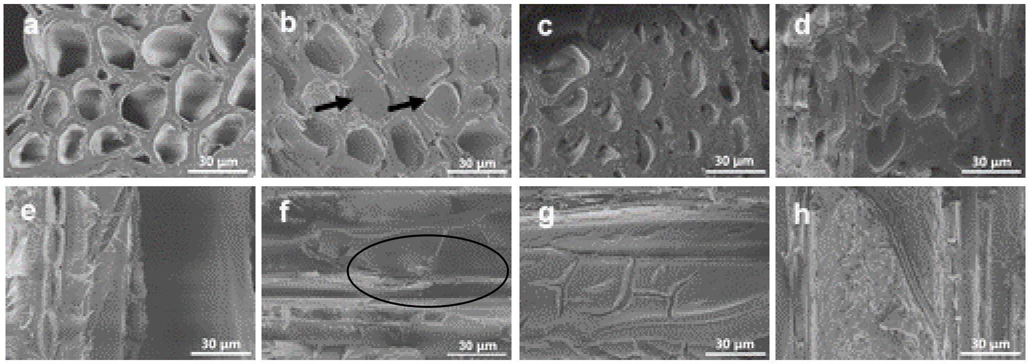

Fig. 2. Cross section (a-d) and tangential section (e-h) FE-SEM photographs of the control wood (a, e) and 0% (b, f), 25% (c, g), and 50% (d, h) aluminum sol combined with furfurylated wood

The polymers in the furfurylated wood (Fig. 2f, black ellipse) showed sharp and distinct edges, while those in the aluminum sol-treated wood showed rough edges (Figs. 2g and 2h).

Thermal Stability

TGA and differential TG (DTG) curves of the various wood samples are shown in Fig. 3. The weight loss curve of the control is divisible into three different stages: moisture evaporation (from room temperature to 100 °C), hemicellulose and cellulose degradation (from 220 °C to 370 °C), and lignin degradation (above 400 °C). Interestingly, an additional degradation region appeared in the furfurylated wood samples (from 100 °C to 220 °C), which was attributed to the thermal degradation of PFA (Guigo *et al*. 2009). The moisture content of the treated wood was also considerably lower than that of the control, indicating that the hydrophobic characteristics of the wood were enhanced by the modification, *i.e.*, that the treated wood had a lower water content (Dong *et al*. 2014). The lower degradation of treated samples compared to control from 250 to 350 °C could be due to the partly hydrolysis of hemicellulose in the process. As the proportion of aluminum sols increased, the mass loss at temperatures from 100 °C to 220 °C gradually decreased compared with the individual furfurylated wood due to enhanced thermal stability.

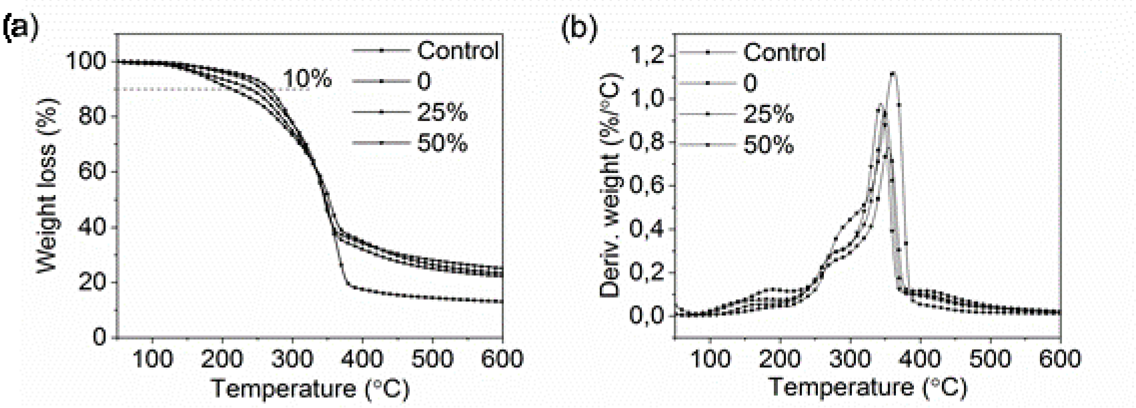

Fig. 3. (a) TGA and (b) DTG curves of control and treated wood

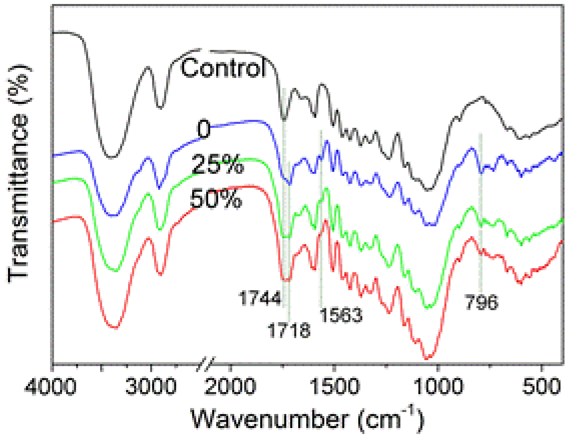

Fig. 4. FTIR spectra of control and treated wood samples

Specifically, the 10% weight loss temperature for treated samples with 0, 25% and 50% additions were 213, 240 and 257 °C, respectively. The aluminum gels were likely converted into nano Al_2O_3 under heat and thus inhibited heat transfer (Hull *et al*. 2011). The char yields of the treated wood samples were much higher than the control, possibly due to the combination of PFA and aluminum gels. The extra-incorporated aluminum sols did not cause any further increase in residual weight in the treated wood samples.

FTIR Analysis

The FTIR spectra of control and treated samples within the range from 400 cm^{-1} to 4000 cm^{-1} are shown in Fig. 4. The absorption bands at around 3350 cm^{-1} of all the curves were attributed to O–H stretching. The peaks at 2910 cm^{-1} were assigned to C–H stretching, and the peak at 1744 cm^{-1}corresponded to C=O stretching vibration. The absorption peaks at 1592 cm^{-1} and 1508 cm^{-1} were ascribed to the aromatic skeletal vibration of lignin (Pandey 1999). Three new absorptions peaks at 1718, 1563, and 796 cm^{-1} in the treated woods were attributed to the C=O stretching vibration of diketonic structures, which resulted from the hydrolytic opening reaction of furan rings in the PFA, conjugated C=C descriptions, and skeletal vibrations of 2,5-disubstituted furan rings, respectively (Chuang *et al*. 1984; Pranger and Tannenbaum 2008; Dong *et al*. 2015). The weak peak located at 733 cm^{-1} in the treated wood samples was related to the furan rings of PFA (Oishi *et al*. 2013). Taken together, these results indicate that FA was indeed successfully incorporated into the treated woods. In addition, the peak at 1594 cm^{-1} in the curves of the aluminum sol-treated woods was significantly enhanced compared with the control corresponding to the Al-OH group (Zaki *et al*. 2001).

Dimensional Stability and Water Uptake Capability

The ASE values of the samples after three water immersion cycles are shown in Fig. 5.

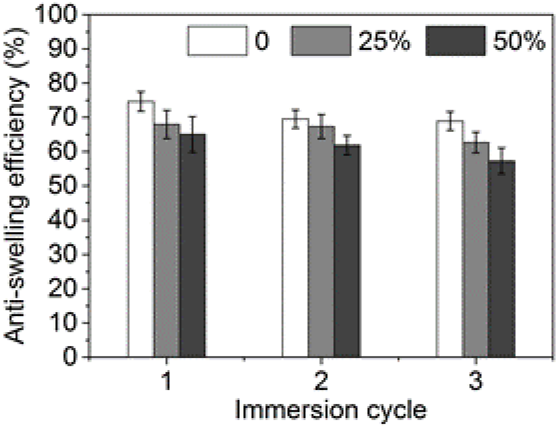

Fig. 5. ASE of treated wood with different amounts of aluminum sol

For the single furfurylated wood, the ASE value reached 69% after three cycles. The ASE values slightly decreased after incorporating aluminum sol, but the minimum ASE values after three cycles were still greater than 57%. In effect, the hydrophilic aluminum sol had no significant influence on the ASE of the treated wood. As expected, although the WPG values of aluminum sol/FA-treated wood decreased 50% compared with single furfurylated wood, the ASE values decreased slightly. This indicated that crosslinking between aluminum gel and wood components had occurred and also reduced the BE value (Wang *et al*. 2014). The decreased WPG was mainly a result of the reduced bulking in wood lumens, while the bulking in wood cell walls was not reduced (Figs. 2b and 2c) and thus did not decrease the ASE (Hill 2006).

The water uptake of the control and treated samples as a function of time at room temperature is shown in Fig. 6. Wood is innately hydrophilic; the samples' water absorption grew higher over time as water filled into the capillaries and void spaces. The treated wood absorbed much less water than the control wood. Furfurylation effectively decreased the wood equilibrium moisture content, as the PFA filled vacant spaces in the material and thus reduced its water absorption (Esteves *et al*. 2011). The water absorption capability gradually increased after the incorporation of aluminum sols, possibly due to the low WPG values.

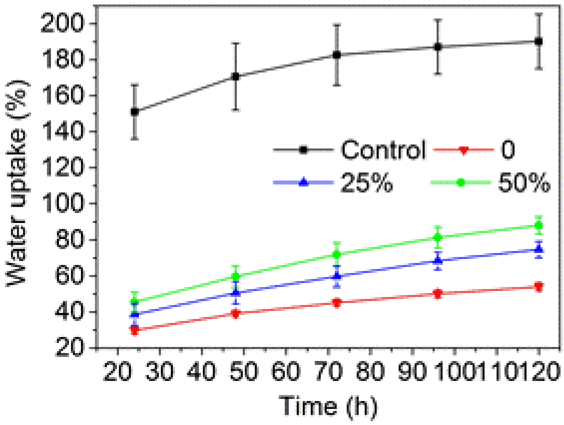

Fig. 6. Water uptake of control and treated wood samples as a function of time

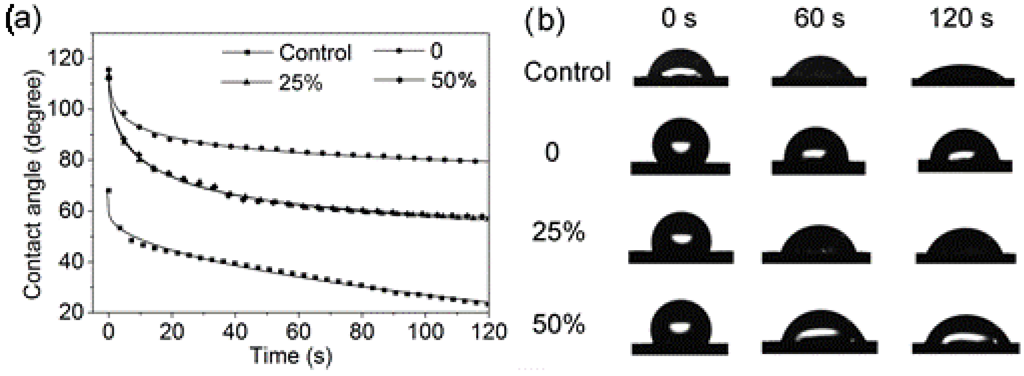

Fig. 7. Contact angles of control and treated wood samples: (a) as a function of time; (b) at different times (0 s, 60 s, 120 s)

Dynamic Wettability Analysis

The model fit lines of contact angles as a function of time for both the control and treated wood are summarized in Fig. 7a. The surface contact angles at different times (0 s, 60 s, and 120 s) are shown in Fig. 7b. The contact angle of all samples decreased sharply within the first 10 s for all the samples and then ultimately reached a relative equilibrium state at 120 s. Both the initial and final contact angles of the control were much lower than those of the treated samples as a result of the filling effect of hydrophobic PFA. The hydrophobicity of the combination-treated wood decreased compared to that of furfurylated wood due to the incorporation of hydrophilic aluminum sols. However, the decrease was restricted when the percentage of aluminum sol was 50%. This phenomenon could be due to the crosslinking of aluminum sol and wood component, which reduced the hydrophilic groups.

CONCLUSIONS

1. A combination of aluminum sol-gel and furfurylation was used to enhance the performance of poplar wood samples in this study. FE-SEM observations indicated that the formation of PFA and aluminum gel appeared in the wood structures and that FA polymerization in wood cell lumens was impeded by aluminum sol.
2. The addition of aluminum sol altered the distribution and structure of PFA, which reduced the weight percent gain; the ASE of the treated wood stayed above 57% due to crosslinking between the wood and aluminum gel. Thermogravimetric analysis indicated that the incorporation of aluminum gel improved the thermal stability of the furfurylated wood by converting it into nano-Al_2O_3 under heat and by inhibiting heat transfer.
3. In addition, the water uptake and hydrophobicity of the modified samples were improved significantly compared to the control.

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