Effect of ultrasound-assisted pretreatment on the hygroscopic dimensional stability of Ailanthus altissima wood modified with 1,3-dimethylol-4,5-dihydroxy ethylene urea

Taoyu Han
Anhui Agricultural University
Jingjing Gao
Beijing Forestry University
Manman Lu
Anhui Agricultural University
Stavros Avramidis
University of British Columbia
Shengquan Liu
Anhui Agricultural University
Zhengbin He
Beijing Forestry University
Jing Qian (bjfu130534110@163.com)
Anhui Agricultural University

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Taoyu Han[a], Jingjing Gao[b], Manman Lu[a], Stavros Avramidis[c], Shengquan Liu[a], Zhengbin He[b], Jing Qian[a,*]

[a] Key Lab of State Forest and Grassland Administration on Wood Quality Improvement & High Efficient Utilization, School of Forestry & Landscape architecture, Anhui Agricultural University, Hefei 230036, Anhui, China

[b] Beijing Key Laboratory of Wood Science and Engineering, College of Material Science and Technology, Beijing Forestry University, No. 35 Tsing hua East Road Haidian District, Beijing, China

[c] Department of Wood Science, University of British Columbia, Vancouver, BC, Canada

*Corresponding authors.

E-mail addresses: bjfu130534110@163.com (J. Qian)

Abstract

Fast-growing wood is particularly favored as the lightweight material and has potential used in construction and furniture. However, dimensional instability, one of fast-growing wood's inherent weaknesses, limits its utilization as solid wood products. In this study, fast-growing *Ailanthus altissima* wood was modified with 1,3-dimethylol-4,5-dihydroxy ethylene urea (DMDHEU) after ultrasound-assisted pretreatment to improve its hygroscopic dimensional stability. Ultrasound was first used in combination with DMDHEU for wood impregnation modification. The weight percentage gain (WPG), absolute dry density, tangential/radial swelling rates, resin distribution and functional groups of chemical components were investigated. The results indicated that the WPG and absolute dry density of DMDHEU-ultrasonic samples increased compared to DMDHEU-untreated samples. The hygroscopic dimensional stability of DMDHEU-ultrasonic samples improved to varying degrees compared to DMDHEU-untreated samples. In particular, the tangential/radial swelling rates of DMDHEU-ultrasonic-4% NaOH samples decreased from 2.01%/1.22% for untreated samples to 0.55%/0.38%. On the one hand, ultrasound-assisted pretreatment affected the distribution of resin inside vessel. Raised-membranous resin appeared along the vessel of DMDHEU-ultrasonic-4% NaOH samples, while only sporadic resin deposition was observed for the DMDHEU-untreated samples. On the other hand, ultrasound-assisted pretreatment promoted better penetration of the DMDHEU resin into the wood cell wall, and the hydroxyl groups in the hydrophilic part were converted into hydrophobic ester bonds and ether bonds. In conclusion, ultrasound-assisted pretreatment had a positive effect on the wood DMDHEU impregnation. And these findings shed light on promising pretreatment methods for wood dimensional stability modification.

Key words: Wood modification; Ultrasound-assisted pretreatment; DMDHEU; Hygroscopic

dimensional stability

1 Introduction

Lignocellulosic materials have green and sustainable characteristics and are considered as a superior substitute for petroleum-based material. Among these materials, wood and wood-based products are particularly favored as carbon-intensive lightweight materials in construction, furniture and decoration due to their natural composition, mechanical strength, and cost-effectiveness (Berglund and Burgert 2018; Favero et al. 2020). Nowadays, in the absence of high-quality hardwood timber resources, the development and utilization of fast-growing wood has attracted wide attention. However, dimensional instability, one of fast-growing wood's inherent weaknesses, limits its utilization as solid wood products since it affects the wood processing, and the service life and sophistication of wood products (Dong et al. 2023). *Ailanthus altissima*, commonly known as tree-of-heaven, is a fast-growing hardwood species primarily found in the northern and central parts of mainland China. With a lifespan of approximately 50 years, it can reach a height of 15 meters in just 25 years. It is also considered as an invasive alien species due to its aggressive growth outside of China. The *Ailanthus altissima* wood exhibits advantageous shaving properties, and its long fibers are highly suitable for paper-making applications (Ferreira et al. 2013; Merhar et al. 2020). Nevertheless, *Ailanthus altissima* wood possesses poor permeability and dimensional stability (Li et al. 2012; You and Li 2000). Therefore, appropriate modification of *Ailanthus altissima* wood is necessary to enhance its dimensional stability before practical applications.

Physical and chemical methods, as well as a combination of both, are usually applied in wood modification, including heat treatment, densification, impregnation etc. Wood impregnation modification typically involves the impregnation of wood with chemically, biologically, or physically modified agents. These agents react with hydroxyl groups in the cell wall, occupying or sealing the micropores to enhance desired performance (Hill 2007). One such agent is 1,3-dimethylol-4,5-dihydroxy ethylene urea (DMDHEU), a water-soluble glyoxal resin initially used as a crosslinking finishing agent for cellulose and fiber fabrics. When applied to cotton fabric, it cross-links covalently with the hydroxyl groups in the cellulose molecules, providing long-lasting wrinkle resistance and dimensional stability (Schindler and Hauser 2004). DMDHEU has also been utilized in wood modification. Since 2000, extensive feasibility studies for DMDHEU modification were conducted at the University of Gottingen, and Schaffert had developed a process for Scottish pine in 2006 with support from BASF (Ludwigshafen, Germany) (Bollmus 2011; Emmerich et al. 2019; Krause 2006; Schaffert 2006; Wepner 2006). The action mechanism of DMDHEU can be divided into two aspects. On the one hand, DMDHEU has a small effective size of molecules (10 A˚) and can enter into the cell wall, then react with hydroxyl groups in the cell wall to form ether bonds. On

the other hand, it can condense and deposit itself in the lumen and cell wall micropores (Emmerich et al. 2019; Militz 1993; Pfeffer et al. 2011). The DMDHEU-modified wood exhibits ideal properties for dimensional stability, anti-fungal efficacy, biological durability, bending strength (Emmerich et al. 2020; Militz 1993). However, it is important to note that the modification effects of DMDHEU can vary significantly among tree species (Emmerich et al. 2019). The radius and number of pit membranes, as well as the ultra-micropores that connect internal wood pores, influence the impregnation effectiveness (Lallart et al. 2017; Wang et al. 2018). Thus, enhancing impregnation efficacy, reducing extractives and pit occlusion to improve wood's liquid permeability is an advisable approach.

There are various methods currently employed to enhance the permeability of wood, including physical methods such as steam treatment and microwave treatment, chemical methods like alkali treatment, and biological methods such as fungi and bacterial treatment (Guo et al. 2014; Jacobs-Young et al. 1998; Mascarenhas et al. 2021; Todd et al. 2000; Zhen et al. 2013). In recent years, ultrasound technology, considered as a green technology, involves cavitation, mechanical, and thermal effects has been increasingly utilized to accelerate drying process (Pandiselvam et al. 2023; Rashid et al. 2023). In essence, the drying rate of the material is increased by increasing the permeability under ultrasound-assisted treatment. Studies have shown that ultrasonic treatment can reduce the content of wood extractives and create water channels, such as pit membranes (Sivakumar et al. 2017; Tang et al. 2020). Our previous research applied ultrasound at 25 kHz and 320 W in combination with water and alkali solutions (NaOH at concentrations of 1, 4, and 8 wt%). Significant differences were observed in the distribution of extractives and chemical components, particularly hemicellulose and lignin, within the wood cell walls. Additionally, the ultrasonic-alkali treatment resulted in a uniformly self-shrinking wood substrate with relatively high oven-dried density and bulk density. Although it exhibited lower porosity, the distribution of pores shifted toward larger diameters compared to the water-immersion samples (Qian et al. 2021; Qian et al. 2021; Qian et al. 2022). However, it remains unclear whether these aforementioned alterations positively influence the progress of DMDHEU modification. Limited information is available regarding the properties of *Ailanthus altissima* treated with ultrasonic water/alkali pretreatment in combination with DMDHEU impregnation. Furthermore, the underlying mechanism by which ultrasonic water/alkali pretreatment contributes to the hygroscopic dimensional stability of *Ailanthus altissima* wood modified with DMDHEU remains unknown.

This study explored the feasibility of improving the dimensional stability of *Ailanthus altissima* wood by impregnating DMDHEU after ultrasound-assisted pretreatment. The impregnation degree was evaluated based on the weight gain rate and absolute dry density, while hygroscopic dimensional stability served as the index for assessment. The deposition of DMDHEU within the

wood interior was visually examined using scanning electron microscopy (SEM), and the bond between DMDHEU and the cell wall was analyzed through IR spectroscopy analysis (ATR-FTIR) and X-ray photoelectron spectroscopy analysis (XPS).

2 Material and methods

2.1 Materials

Ailanthus altissima disks were collected from a 20-year-old tree located in the plot of Hedong Village, Duqu Town, Linying County, Luohe City, Henan Province (Coordinates: Lat. 33.81° N, Long 113.88° E). The test block measuring 2 cm (longitudinal) × 2 cm (radial) × 2 cm (tangential) was obtained from the sapwood of the disk, as shown in Fig. 1. The cubes were placed in the air for six months before experiments. Before conducting experiments, the cubes were exposed to air for a period of six months. The chemicals used in the study were as follows: NaOH (Meryer, 96% purity, Shanghai, China), lithium chloride (Beijing Chemical Works, China), and distilled water (Beijing Jialejie Technology Co., LTD, China), magnesium chloride hexahydrate (Tianjin Guangfu Technology Co., LTD, China). Additionally, DMDHEU (1,3-dimethylol-4,5-dihydroxy ethylene urea) with a solid content of 55% was obtained from Zhongshan Lanxiang Resin Co., LTD. (China). All reagents were used directly without further purification.

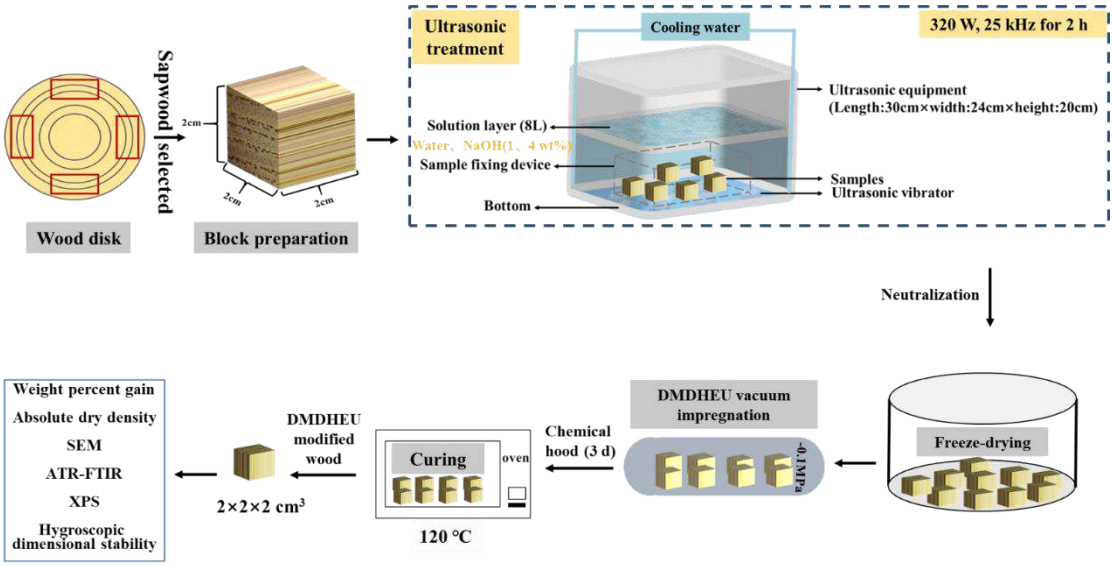

Fig. 1. Experimental procedure flowchart

2.2 Preparation of treated samples

2.2.1 Ultrasonic-water and ultrasonic-NaOH pretreatment

The pretreated substrates included ultrasonic-water treated samples and ultrasonic-NaOH treated samples, as presented in Fig. 1. The ultrasonic treatment was conducted at a power of 25 kHz, 320 W, and a duration of 2 hours. The ultrasonic-water treated samples (designated as A_1) were obtained by immersing the samples in water for 48 hours at a temperature of 20±2 ℃, followed by 2 hours of ultrasonic treatment. Prior to DMDHEU impregnation, the ultrasonic-water treated samples were freeze-dried using a BILON-FD50AE freeze dryer (Shanghai Bilon Instrument Manufacturing Co., LTD, China). For each NaOH concentration solution (1 wt% and 4 wt%), the samples were suspended for 48 hours at a temperature of 20±2 ℃, followed by 2 hours of ultrasonic treatment. The samples were then freeze-dried after neutralization. The neutralization process involved two steps: first, the samples were impregnated in distilled water containing 1% acetic acid for 6 hours; next, they were thoroughly rinsed with distilled water for 48 hours. The mass of the freeze-dried samples was denoted as M_0. Subsequently, the freeze-dried samples were subjected to DMDHEU modification.

2.2.2 DMDHEU modification

The DMDHEU modified reagent consisted of DMDHEU resin, distilled water, and catalyst. The DMDHEU resin was dissolved in distilled water to create a stock solution with an active ingredient concentration of 30% ($W_{DMDHEU}/W_{stock\ solution}$). A 3% magnesium chloride solution ($W_{catalyst}/W_{DMDHEU}$) was used as a catalyst for the DMDHEU reaction. Following preparation, ten samples each of ultrasonic-water pretreated samples, ultrasonic-alkali pretreated samples, and untreated samples were randomly selected. These samples were fully impregnated in a vacuum of -0.1 Mpa for 0.5 hours and then immersed in the DMDHEU modification reagent for 6 hours at normal pressure, as depicted in Figure 1. Subsequently, all the DMDHEU modified samples were pre-dried in a chemical hood at room temperature for 48 hours prior to curing at 120 ℃ for 24 hours. Finally, all the DMDHEU-modified samples were oven-dried at 103±2 ℃ until completely dry, following the guidelines in GB/T 1931-2009 (China). The mass, tangential dimension, radial dimension, and longitudinal dimension of the oven-dried samples were denoted as M_1, T_1, R_1, and L_1, respectively.

2.3 Weight percent gain and absolute dry density

The weight percentage gain (WPG) was calculated by comparing the dry mass before and after DMDHEU modification, as per Equation 1.

$$WPG = \frac{(M_1 - M_0)}{M_0} \times 100\% \quad (1)$$

Where M_0 represents the initial mass of freeze-dried samples before DMDHEU modification is the initial mass of freeze-dried samples before DMDHEU modification (g), while M_1 refers to the oven-dried mass of the DMDHEU-modified samples (g).

The absolute dry density (D) of the DMDHEU-modified wood was determined using Equation 2.

$$D = \frac{M_1}{T_1 \times R_1 \times L_1} \times 100\% \quad (2)$$

Where M_1, T_1, R_1 and L_1 are the mass (g), tangential dimension (cm), radial dimension (cm) and longitudinal dimension (cm) of oven-dried DMDHEU-modified samples, respectively.

2.4 Scanning electron microscope (SEM) observation

The morphology of the DMDHEU-modified samples was examined using a scanning electron microscope (GEMINISEM 500, Germany). Specimens measuring 1 cm (tangential) × 1 cm (longitudinal)× 1 mm (radial) were obtained from the surface of each sample using a sliding microtome (Leica Microsystems, Wetzlar, Germany). Each specimen was then affixed to a metal bracket with double-sided conductive adhesive and coated with gold-palladium using an Emitech sputter coater. Subsequently, the specimen was placed into the sample chamber of the scanning electron microscope to observe the microstructure and resin distribution inside the wood, with an accelerating voltage of 15 kV.

2.5 IR spectroscopy analysis (ATR-FTIR)

In order to observe the influence of ultrasonic-water and ultrasonic-alkali treatment on the chemical groups in DMDHEU-modified samples. The DMDHEU-modified samples obtained under different treatment conditions were oven-dried and milled to collect 100~120 mesh wood powder. IR spectra were collected directly from the wood powder by using an attenuated total reflection Fourier transform infrared spectrometer (iD7, thermo scientific, USA). All spectra were taken at the step length of 0.482 cm^{-1} in the range of 4000~500 cm^{-1}, and the number of scans was 32 times.

2.6 X-ray photoelectron spectroscopy (XPS) analysis

The tested samples were selected in accordance with the ATR-FTIR experiment. 100~120 mesh

wood powder was selected and placed in the vacuum chamber of the XPS apparatus (ESCALAB 250 Xi, Thermo Fisher, Germany). Samples were guaranteed to be free from contaminants caused by the cutter blade and bare hands. The XPS analyses were carried out under the pressure between 10^{-9}~10^{-8} mbar with a Sigma probe (Thermo VG Scientific, Britain). Survey spectra were recorded in 1.0 eV steps and 100 eV analyzer pass energy. The detailed spectra of C1s, O1s, N1s and Na1s were recorded with 0.05 eV steps and 30 eV pass energy. The mathematical resolution enhancement of C1s signal was fitted by Gaussian curve.

2.7 Hygroscopic dimensional stability

Five samples were randomly selected from each group: DMDHEU-modified and untreated. These samples were then placed in an environment with a relative humidity of 11.3%, which was simulated using LiCl saturated salt solution at a temperature of 25 °C. During the process of wood moisture absorption, three samples were used to measure the change in tangential dimension every 6 hours until the difference between the two measurements was less than 0.2 mm. The mass (M_2), tangential dimension (T_2) and radial dimension (R_2) of samples after reaching hygroscopic equilibrium were recorded. The moisture content (MC), tangential dimension change rate (T) and radial dimension change rate (R) of samples at hygroscopic equilibrium were calculated according to equations 3, 4 and 5, respectively.

$$MC(\%) = \frac{M_2 - M_1}{M_1} \times 100\% \quad (3)$$

Where M_1 and M_2 represent the mass of samples before and after reaching hygroscopic equilibrium, respectively (g).

$$T(\%) = \frac{T_2 - T_1}{T_1} \times 100\% \quad (4)$$

Where T_1 represents the tangential dimension of the oven-dried sample before moisture absorption, and T_2 represents the tangential dimension of the sample at hygroscopic equilibrium (mm).

$$R(\%) = \frac{R_2 - R_1}{R_1} \times 100\% \quad (5)$$

Where R_1 represents the radial dimension of the oven-dried sample before moisture absorption, and R_2 represents the radial dimension of the sample at hygroscopic equilibrium (mm).

3 Results and discussion

3.1 Weight percent gain and absolute dry density

The weight percent gain (WPG) and absolute dry density of DMDHEU-modified samples were shown in Fig. 2, providing direct insights into the resin content within the wood. The WPG of DMDHEU-modified untreated samples (A_0-D) and DMDHEU-modified ultrasonic-water treated samples (A_1-D) were about 16.22 % and 23.13 %, respectively. The WPG of A_1-D was 6.91 % higher than that of A_0-D, indicating that the ultrasonic-water pretreatment facilitated extractives migration and increased internal pores in *Ailanthus altissima*. Moreover, the WPG of DMEHEU-modified ultrasonic-1% NaOH treated samples (B_1-D) and DMEHEU-modified ultrasonic-4% NaOH treated samples (C_1-D) were around 14.33% and 13.74% higher than A_0-D, respectively, revealing the positive influence of ultrasonic-alkali pretreatment on DMDHEU impregnation. Furthermore, compared with A_0-D, the absolute dry density for A_1-D, B_1-D and C_1-D increased due to DMDHEU deposition within the wood and/or shrinkage of the ultrasonic-alkali treated substrate. The absolute dry density values for A_0-D, A_1-D, B_1-D, and C_1-D were approximately 0.60 g/cm^3, 0.62 g/cm^3, 0.90 g/cm^3, and 0.99 g/cm^3, respectively.

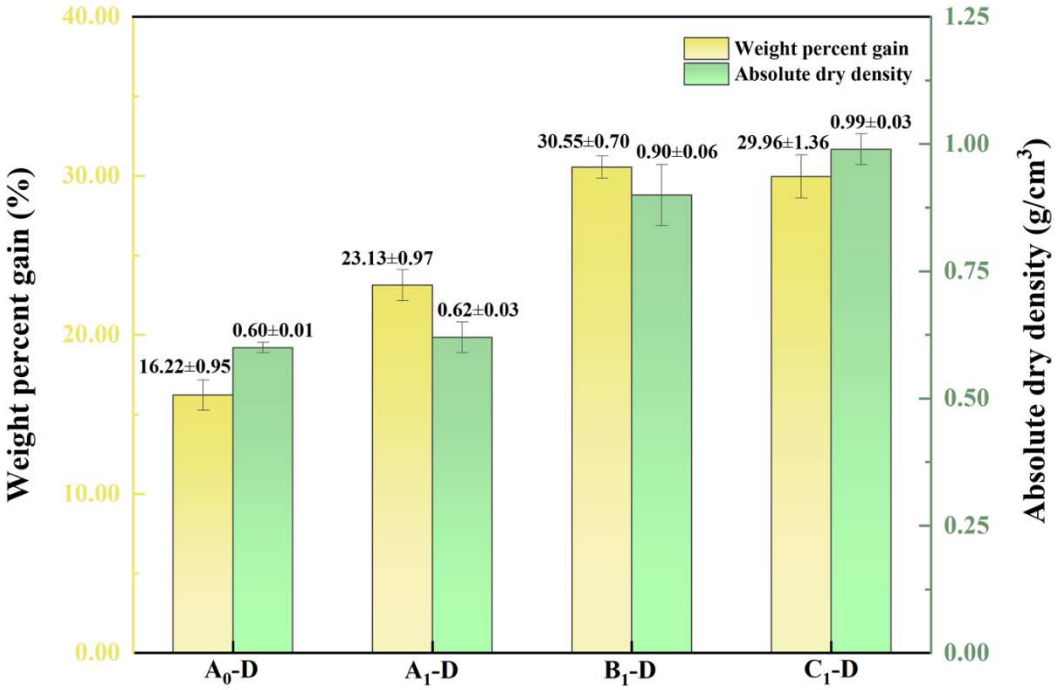

Fig. 2. Weight percent gain and absolute dry density of DMDHEU-modified samples: (A_0-D) DMDHEU-modified untreated samples, (A_1-D) DMDHEU-modified ultrasonic-water treated samples, (B_1-D) DMDHEU-modified ultrasonic-1% NaOH treated samples, (C_1-D) DMDHEU-modified ultrasonic-4% NaOH treated samples

3.2 SEM observation

As illustrated in Figure 3, the deposition of DMDHEU within the wood was directly observed through SEM analysis. Based on our previous studies, untreated *Ailanthus altissima* samples (A_0) are rich in extractives, and ultrasonic-water pretreatment has been found to facilitate the removal of these extractives from the wood's interior (Qian et al. 2022). Upon examining A_0-D, it was observed that the extractives had vanished, resulting in localized areas with uneven resin filling. This could be attributed to the vacuum-assisted DMDHEU impregnation process, which promoted the migration of extractives, and the heat-curing process of acidic DMDHEU could lead to hydrolysis of the extractives. A_1-D exhibited a dense and smooth resin film, indicating the formation of a DMDHEU resin film along the vessel's interior, which suggested that ultrasonic-water pretreatment enhances DMDHEU resin impregnation. However, it was worth noting that the majority of pits on the vessel were still visible.

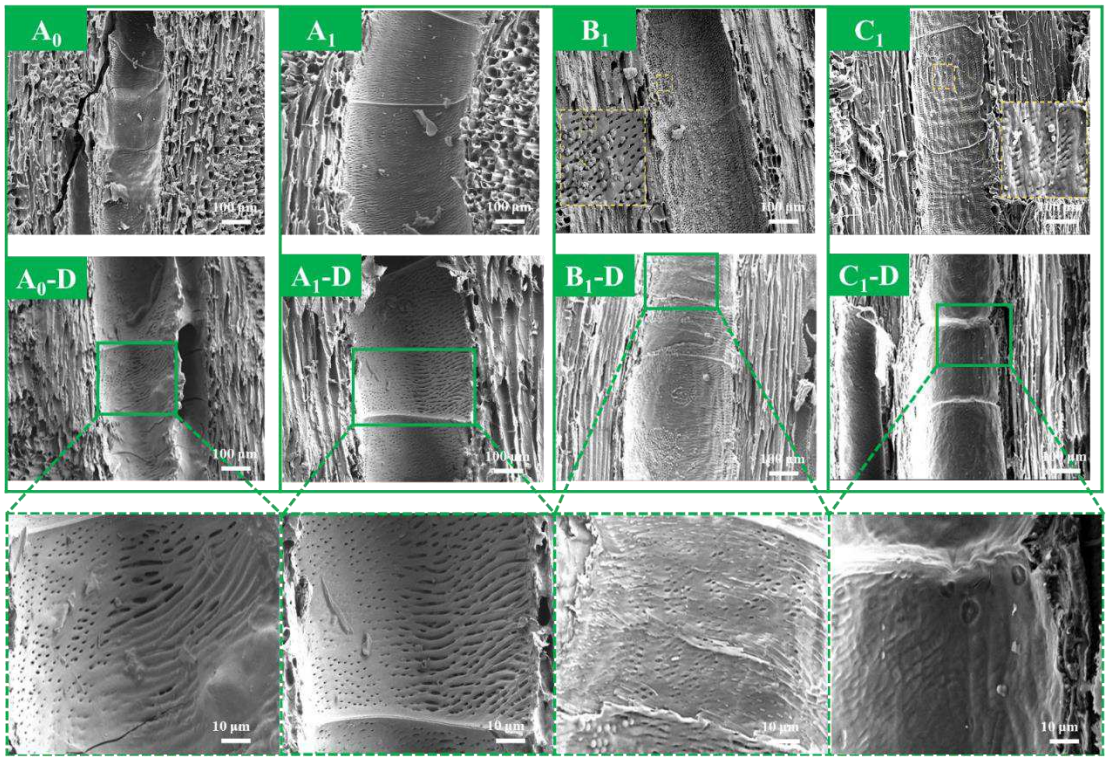

Fig. 3. SEM images of untreated and treated samples: (A_0) the untreated sample, (A_0-D) the DMDHEU-modified untreated sample, (A_1) the ultrasonic-water treated sample, (A_1-D) the DMDHEU-modified ultrasonic-water treated sample, (B_1) the ultrasonic-1% NaOH treated sample, (B_1-D) the DMDHEU-modified ultrasonic-1% NaOH treated sample, (C_1) the ultrasonic-4% NaOH treated sample, (C_1-D) the DMDHEU-modified ultrasonic-4% NaOH treated sample

Spherical and square particles, as shown in Figure 3, were found inside the vessel of B_1-D and C_1-D. The square particles might be residual NaOH particles, while the spherical particles might contain lignin or related degradation products derived from lignin and hemicellulose (Chu et al. 2010). For B_1-D and C_1-D, the distribution of DMDHEU resin was found to be spot-like and film-like, respectively. Notably, the impregnation degree of DMDHEU was found to be higher in the ultrasonic-4% NaOH pretreated substrate compared to the ultrasonic-1% NaOH pretreated substrate. Previous studies have demonstrated that ultrasonic-alkali treatment can result in changes in the shape and size of pores in the vessel wall. Specifically, an increase in pore size along with the occurrence of folding at the edges of the vessel wall was observed as the NaOH concentration increased from 1 wt% to 8 wt% (Qian et al. 2021). These changes have also been observed in bamboo treated with alkali (He et al. 2019). The difference in the impregnation effect of DMDHEU between B_1-D and C_1-D might be attributed to the fact that ultrasonic-alkali pretreatment not only dissolves extractives, hemicellulose, and lignin, but also alters the pore structure and promotes fluid penetration in wood (He et al. 2014; Qian et al. 2021). Furthermore, a NaOH solution with a higher concentration has the potential to cause fiber stripping, resulting in the splitting of the liquid penetration path into a series of shorter paths. Ultimately, this could significantly reduce the osmotic pressure during impregnation, thereby increasing the impregnation rate (He et al. 2019; Qian et al. 2022).

3.3 ATR-FTIR analysis

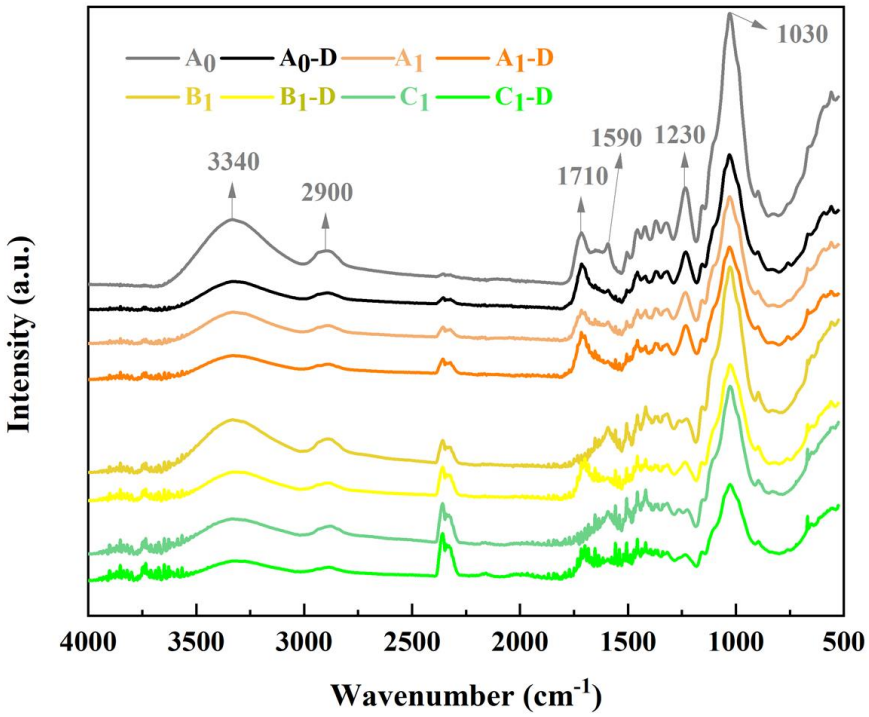

Fig. 4. ATR-FTIR spectrum of untreated and treated samples: (A_0) the untreated sample, (A_0-D) the DMDHEU-modified untreated sample, (A_1) the ultrasonic-water treated sample, (A_1-D) the DMDHEU-modified ultrasonic-water treated sample, (B_1) the ultrasonic-1% NaOH treated sample, (B_1-D) the DMDHEU-modified ultrasonic-1% NaOH treated sample, (C_1) the ultrasonic-4% NaOH treated sample, (C_1-D) the DMDHEU-modified ultrasonic-4% NaOH treated sample

Figure 4 presented the ATR-FTIR spectrum in the range of 4000~500 cm^{-1} for both untreated and treated samples. The attribution of six bands with obvious changes was clarified in Table 1, namely 3340 cm^{-1}, 2900 cm^{-1}, 1710 cm^{-1}, 1590 cm^{-1}, 1230 cm^{-1} and 1030 cm^{-1}. The aforementioned six bands are assigned as follows: 1) 3340 cm^{-1} for -OH stretching and water, 2) 2900 cm^{-1} for C-H stretching vibration in methylene group of polysaccharides, 3) 1710 cm^{-1} for C=O stretching and C=C stretching vibration, 4) 1590 cm^{-1} for aromatic ring stretching vibration, 5) 1230 cm^{-1} for C-N stretching, C-O stretching, and bending -OH antisymmetric stretching, and 6) 1030 cm^{-1} for C-O-C deformation (Pandey 1999).

Table 1. Assignments of bands in the ATR-FTIR spectra of untreated and treated samples

Wavenumber (cm^{-1})	Assignments	The corresponding chemical constituents
3340	-OH stretching vibration	Cellulose, hemicellulose
2900	C-H stretching vibration in methylene group of polysaccharides	Cellulose, hemicellulose
1710	C=O stretching vibration	Hemicellulose, DMDHEU
1590	Aromatic ring skeleton vibration	Lignin
1230	C-N, C-O stretching in xylose	DMDHEU, hemicellulose
1030	C-H bending vibration	Cellulose, hemicellulose

Compared to A_0, the band intensity at 3340 cm^{-1} was weaker in A_0-D, A_1, A_1-D, B_1-D, and C_1-D. However, it became more pronounced after ultrasonic-alkali treatment in B_1 and C_1. This indicated that both ultrasonic-water treatment and DMDHEU-impregnated treatment made a contribution to reducing the hydroxyl content of wood. The band intensity in 2290 cm^{-1} of A_1, B_1, and C_1 was higher than that in A_1-D, B_1-D, and C_1-D, respectively, but lower than that in A_0 for all treated samples.

The stretching vibration at about 1710 cm^{-1} typically corresponds to the carbonyl groups of acetoxy groups in xylan. This band decreased in intensity for A_1 compared to A_0, and disappeared altogether for B_1 and C_1. The decrease and absence of this band might be attributed to the breaking of acetyl or acetoxy groups in xylan caused by the ultrasonic-water and ultrasonic-alkali pretreatment. However, the band intensity at 1710 cm^{-1} was stronger in A_0-D, A_1-D, B_1-D, and C_1-D than in A_0, A_1, B_1 and C_1, respectively. Considering the presence of carbonyl groups in the DMDHEU structural formula, this increase in intensity could be attributed to DMDHEU deposition within the wood. The band at 1590 cm^{-1} represents the vibration of lignin aromatic ring skeleton, and the intensity of treated samples was lower than that of A_0. This decrease in intensity could be attributed to the crosslinking reaction between the benzene ring and DMDHEU, as previous studies have demonstrated (Yang et al. 1996). The band around 1230 cm^{-1}, which corresponds to C-N in DMDHEU resin and C-O stretching in xylose (Chen et al. 2010), appeared to decrease during the

ultrasonic-alkali pretreatment but increase after DMDHEU modification. This observation suggested that the deposition of DMDHEU contributes to the increase in intensity of this band. Furthermore, the band intensity at approximately 1030 cm^{-1} decreased after treatment, indicating that the chemical composition of the wood cell wall changed as a result of the treatment.

3.4 XPS spectra analysis

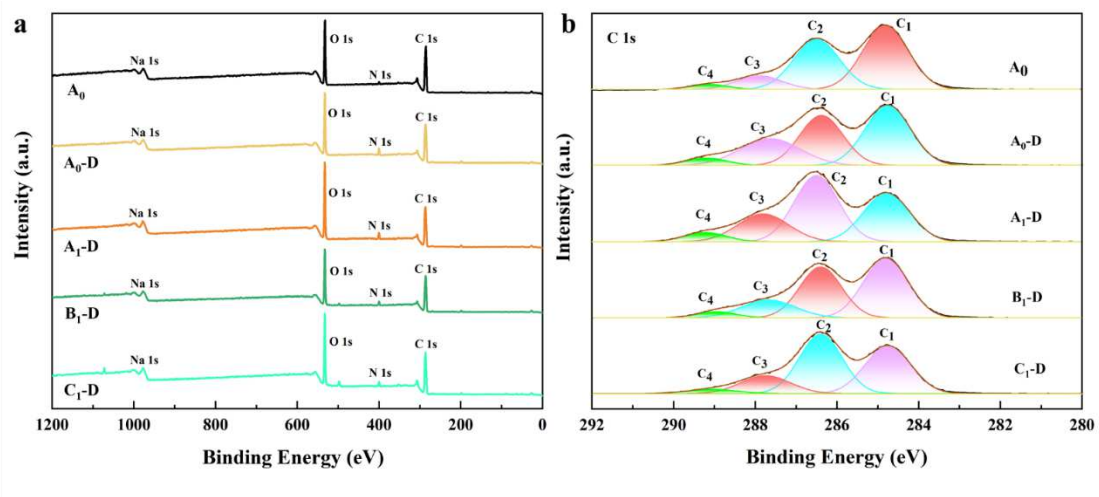

Fig. 5. High-resolution scans of XPS spectra for C 1s of untreated and DMDHEU-modified samples: (A_0) the untreated sample, (A_0-D) the DMDHEU-modified untreated sample, (A_1-D) the DMDHEU-modified ultrasonic-water treated sample, (B_1-D) the DMDHEU-modified ultrasonic-1% NaOH treated sample, (C_1-D) the DMDHEU-modified ultrasonic-4% NaOH treated sample

X-ray Photoelectron Spectroscopy (XPS) technology has been widely employed in the analysis of the surface chemical composition of lignocellulosic materials. In this study, the change of the atomic composition and the bonding mode between the atoms of wood substance was investigated. Figure 5(a) showed the typical peaks in the XPS spectra of untreated and DMDHEU-modified samples, which correspond to C 1s, O 1s, N 1s, and Na 1s. The results obtained from the XPS spectra of the samples under investigation were summarized in Table 2, where the atomic composition (C, O, N, and Na), O/C ratio, and the distribution of C_1, C_2, C_3, and C_4 were calculated.

From the data in Table 2, it could be observed that in the untreated sample, C and O were the main constituent atoms, accounting for 67.94% and 29.84% respectively. In the DMDHEU-modified samples, the introduction of a large number of N and additional O atoms from the

DMDHEU resin resulted in an increase in the relative content of oxygen atoms and a decrease in the relative content of carbon atoms. The O/C ratio for the untreated sample was approximately 0.44%, while it was higher for the treated samples. This increase in the O/C ratio could be attributed to the removal of hemicellulose and extractives during ultrasonic-water and ultrasonic-alkali pretreatment, as well as the deposition of DMDHEU within the wood. A small amount of N atoms (1.98 %) was detected in the untreated sample, possibly corresponding to amino acids/proteins containing a small amount of NH_2 groups in wood. After DMDHEU modification, the nitrogen content increased, with A_0-D, A_1-D, B_1-D, and C_1-D samples showing increases of 2.85%, 2.68%, 1.42%, and 1.41%, respectively. NaOH was used to treat wood, so the relative content of Na atoms (BE around 1071 eV) was also calculated. The proportion of Na atoms in the untreated sample was 0.24%, whereas the content of Na atoms for A_0-D, A_1-D, B_1-D, and C_1-D increased to 0.38 %, 0.36 %, 0.76 %, and 1.51%, respectively. After excluding the possibility of serious contamination of the sample, the study showed that *Ailanthus altissima* wood and DMDHEU resin contained a small amount of Na atomic, ultrasonic-water pretreatment might promote the migration of Na atomic, and ultrasonic-NaOH pretreated samples contained Na atomic.

Table 2. The atomic percentages, O/C ratio, and distribution of C 1s components were determined using XPS spectra for untreated and DMDHEU-modified samples

Samples	Atomic percentages and O/C ratio (%)					C 1s components, area (%)			
	C	O	N	Na	O/C	C_1	C_2	C_3	C_4
						C-C/C-H	C-O/C-OH	O-C-O/C=O	O-C=O
A_0	67.94	29.84	1.98	0.24	0.44	48.10	39.00	8.70	4.20
A_0-D	64.62	30.17	4.83	0.38	0.47	40.30	35.30	19.90	4.50
A_1-D	61.96	33.02	4.66	0.36	0.53	31.50	44.30	16.70	7.50
B_1-D	65.70	30.14	3.40	0.76	0.46	43.90	37.90	12.40	5.80
C_1-D	61.73	33.37	3.39	1.51	0.54	36.80	44.40	8.10	10.70

Wood is mainly constituted of cellulose, hemicellulose, lignin, and a small amount of extract. According to Dorris and Gray (1978), C atoms in wood can be categorized into four types based on the atoms they were bound to: 1) C1, which is only connected with carbon atoms or hydrogen atoms (—C—H, —C—C), originating from lignin phenyl propane and fatty acids, fats and waxes and

other hydrocarbons. 2) C2, which is connected with one non-carbonyl oxygen atom (—C—O—), mainly found in alcohols and ethers existed in cellulose and hemicellulose. 3) C3 presents the carbon atom joints with two non-carbonyl oxygen atoms or with a carbonyl oxygen atom (—O—C —O— or C = O), mainly derived from aldehydes, ketones, acetal, etc. 4) C4 is connected with a carbonyl oxygen atom and a non-carbonyl oxygen atom (—O—C = O), originating from the ester group, the carboxyl group, etc. Theoretically, cellulose contains five C2 and one C3, hemicellulose is mainly composed of glucuronoxylans with one C3, no more than five C2 and less than one C4, and the composition of lignin is complex which contains four types of carbon atoms. In summary, C2 and C3 mainly come from hemicellulose and cellulose while C1 mainly comes from lignin and extractives in wood. The distribution of C1, C2, C3, and C4 is illustrated in Figure 5, and their relative content, as determined by the integral area, is presented in Table 2. It is evident that the contribution of the different carbon types varies significantly between untreated and treated samples. The proportions of C1, C2, C3, and C4 in the untreated sample were 48.1%, 39.0%, 8.7%, and 4.2%, respectively.

For A_0-D samples, the proportions of C_1, C_2, C_3 and C_4 were 40.3 %, 35.3 %, 19.9 % and 4.5 %, respectively. It is notable that the relative content of C_3 and C_4 increased by 11.2% and 0.3% respectively. Considering the structural formula of DMDHEU, which contains C = O and C—O chemical bonds, the increase in C_3 suggested that a significant amount of DMDHEU penetrated the wood and experienced etherification. This resulted in the generation of new ester and ether bonds, leading to a significant increase in the relative content of C=O bonds. However, the relative content of C_2 did not increase but instead slightly decreased by 3.7%. This could be attributed to the reduction of free hydroxyl groups in the cell wall due to the etherification process.

For A_1-D samples, the relative contents of C_1, C_2, C_3, and C_4 were 31.5%, 44.3%, 16.7%, and 7.5%, respectively. Compared to A_0-D, the proportion of C_1 and C_3 decreased by 8.8% and 3.2%, respectively, while C_2 and C_4 increased by 9% and 3%. Our previous study revealed that ultrasonic treatment reduces the distribution intensity of lignin in the cell wall and promotes the removal of extractives from wood, which could explain the decrease in C_1 (Qian et al. 2021). Additionally, ultrasonic-water treatment led to an increase in the internal pores of the samples, potentially allowing more DMDHEU resin to penetrate the interior and resulting in an increase in the relative

content of C_2 and C_3 compared to A_0. Furthermore, the ultrasonic-water pre-treatment also affected hemicellulose, leading to a decrease in the relative content of C_3 compared to A_0-D.

For DMDHEU-modified ultrasonic-alkali treated samples, the relative content of C_2 for B_1-D was lower than that of A_0 but C_1-D was higher than A_0. Normally, hemicellulose, extractives and some lignin could be removed by alkali treatment, which could lead to a decrease in the proportion of C_2. Combined with our previous studies, with the increase of NaOH concentration, the hemicellulose content gradually decreased, and the relative content of lignin and cellulose increased. The relative content of hemicellulose and cellulose in ultrasonic-1 % NaOH pretreated samples respectively decreased by about 9 % and 1 %, and the proportion of C_2 and C_3 should be lower than that of untreated wood. In the 4 % NaOH solution environment, the hemicellulose content of C_1-D decreased, but the relative content of cellulose and lignin increased. However, in combination with Fig. 3, it was worth noting that a large amount of DMDHEU entered the interior of the wood, and the resin film could be clearly observed inside the vessel, so the relative content of C_2 increased for C_1-D samples.

3.5 Hygroscopic dimensional stability

The equilibrium moisture contents (EMC), the tangential swelling rate, and the radial swelling rate of DMDHEU-modified samples under a relative humidity of about 11.3 % were exhibited in Figure 6. The EMC for A_0 was about 5.80%, it was observed that the EMC for A_0-D, A_1-D, B_1-D and C_1-D decreased by about 0.42%, 0.75 %, 1.51% and 0.22%, respectively.

The tangential swelling rates of the DMDHEU-modified samples were lower than that of A_0 (about 2.01%), the smallest reduction rate was observed in A_0-D (decreased by 0.02%), while the largest reduction range was observed in C_1-D (decreased by 1.46%). The variation trend of radial swelling rates of DMDHEU-modified samples was similar to that of tangential swelling rates. Notably, a remarkable improvement in the hygroscopic dimensional stability was observed in C_1-D, which was achieved by impregnating DMDHEU based on ultrasonic-alkali pretreated substrates. In contrast, the improvement in A_0, which was directly impregnated with DMDHEU, was not significant. This difference might be attributed to the positive changes in the pore structure, which promotes the entry of DMDHEU after pretreatment (as shown in Fig. 3).

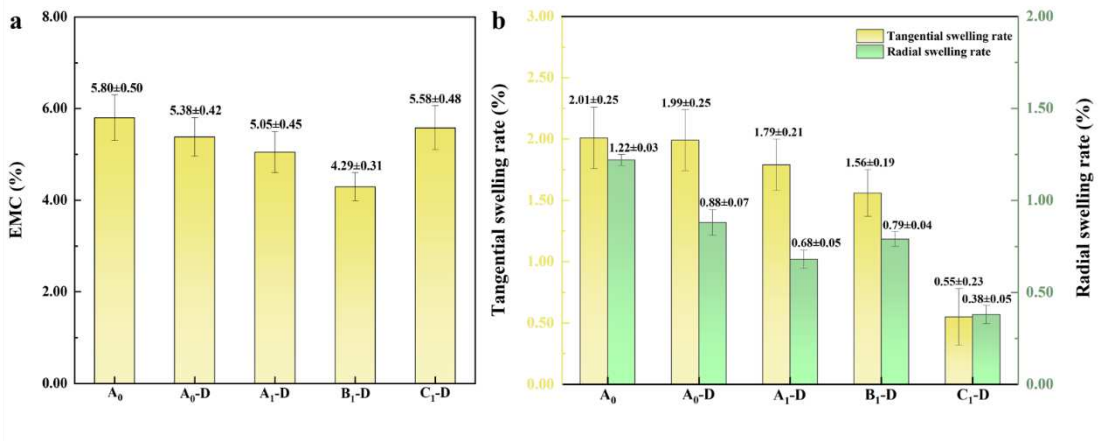

Fig. 6. Influence of DMDHEU impregnation on the EMC, tangential swelling rate and radial swelling rate of untreated and pretreated samples: (A_0) the untreated sample, (A_0-D) the DMDHEU-modified untreated sample, (A_1-D) the DMDHEU-modified ultrasonic-water treated sample, (B_1-D) the DMDHEU-modified ultrasonic-1% NaOH treated sample, (C_1-D) the DMDHEU-modified ultrasonic-4% NaOH treated sample

3.6 Dimensional stability mechanism of DMDHEU-modified wood

Based on the aforementioned findings, the contribution mechanism of improving the hygroscopic dimensional stability of *Ailanthus altissima* wood treated with DMDHEU impregnation following ultrasonic water/alkali pretreatment was illustrated in Figure 7. The reduction of free hydroxyl group content and the blocking of water channels were two key factors in enhancing the dimensional stability of wood. SEM, ATR-FTIR, and XPS analyses confirmed that the DMDHEU resin not only physically deposited within the wood but also chemically bonded to the wood cell wall. Specifically, for A_0-D, the presence of resin deposition areas and a decrease in the relative content of free hydroxyl groups resulted in a slight improvement in hygroscopic dimensional stability compared to A_0. In the case of A_1-D, a dense and smooth resin film formed, physically isolating water to a certain extent, and the relative content of free hydroxyl groups was further reduced. Although the cell wall morphology of the ultrasonic-NaOH treated substrate changed significantly during the drying process due to cellulose and hemicellulose conversion or degradation, it retained characteristics such as high density and a large proportion of large pores. These characteristics were favorable for DMDHEU resin to bind to more free hydroxyl groups in the cell wall, leading to a decrease in the overall content of free hydroxyl groups. Additionally, there was a protruding distribution of resin inside the vessel pit of DMDHEU-impregnated-ultrasonic-treated wood, resulting in a dense resin film structure, thus achieving the greatest improvement in

the hygroscopic dimensional stability of the wood.

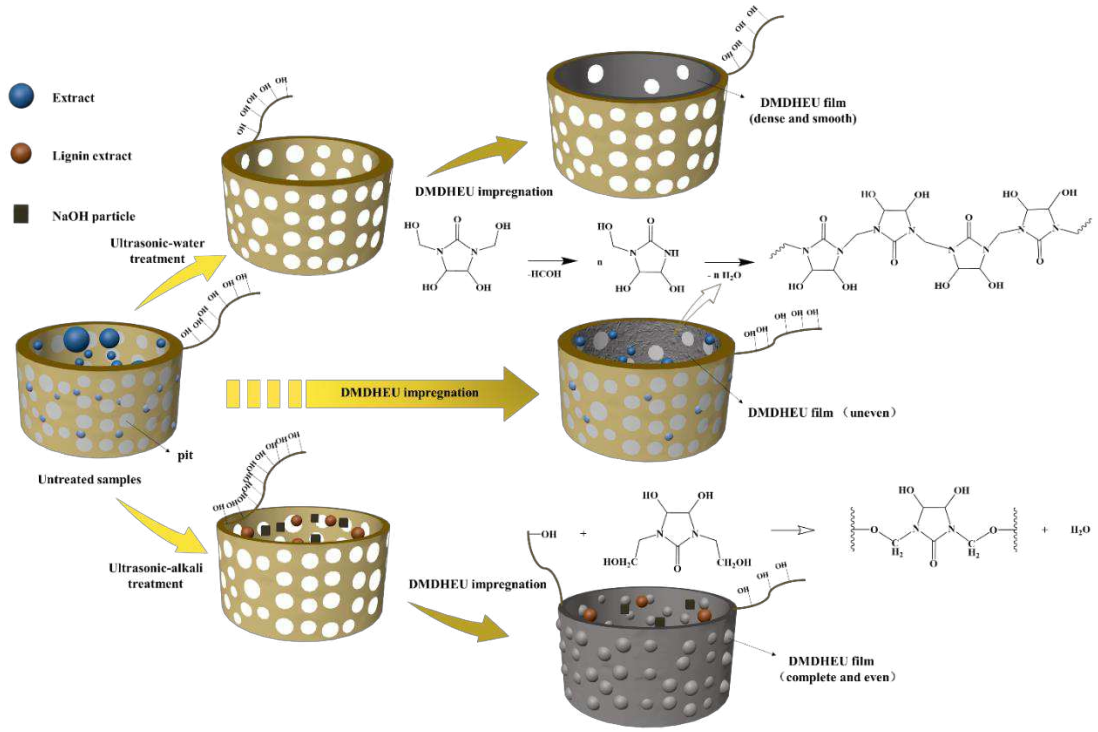

Fig. 7. Mechanism for improving the hygroscopic dimensional stability of *Ailanthus altissima* through DMDHEU impregnation pretreatment

4 Conclusion

In this work, DMDHEU reagent with an active ingredient concentration of 30 % was used to impregnate untreated samples as well as samples subjected to ultrasonic-water pretreatment and ultrasonic-alkali pretreatment using 1 wt% and 4 wt% NaOH. The weight percentage gain (WPG) and the absolute dry density for DMDHEU-ultrasonic-pretreated samples increased compared with DMDHEU-untreated samples, which indicated that the ultrasonic pretreatment had a positive effect on the DMDHEU impregnation process. The distribution of DMDHEU resin in different pretreatment samples was directly observed through SEM analysis. Notably, distinct resin distributions were observed in the various pretreatment samples. The DMDHEU-ultrasonic-water samples exhibited a dense and smooth resin film, spot-like resin was found distributed inside the vessel pores in the DMDHEU-ultrasonic-1% NaOH samples, and raised-membranous resin appeared in the DMDHEU-ultrasonic-4% NaOH samples. The hygroscopic dimensional stability of the DMDHEU-ultrasonic samples showed improvement to varying degrees compared to the DMDHEU-untreated samples. Particularly, the DMDHEU-ultrasonic-4% NaOH samples

demonstrated the highest improvement, the radial/tangential swelling rate showed a decrease from 2.01%/1.22% in untreated samples to 0.55%/0.38%. This improvement in hygroscopic dimensional stability was attributed not only to the deposition of resin inside the vessel but also to the chemical bonding between the resin and the cell wall. ATR-FTIR and XPS results indicated that both ultrasonic-water pretreatment and ultrasonic-alkali pretreatment contributed to a reduction in the hydroxyl content of the samples. The valence state of C in the DMDHEU-impregnated samples also underwent changes, converting the hydroxyl groups in the hydrophilic portion into hydrophobic ester bonds and ether bonds.

Overall, the experimental results revealed that the ultrasonic pretreated substrate exhibited a favorable pore structure, providing an excellent pathway for resin impregnation. Additionally, the ultrasonic alkali treatment facilitated the bonding between DMDHEU resin and a larger number of free hydroxyl groups within the cell wall. These findings shed light on promising pretreatment methods for wood dimensional stability modification.

CRediT authorship contribution statement

TH contributed to investigation, data curation, writing-original draft. JG contributed to methodology and investigation. ML contributed to investigation. SA contributed to methodology and project administration. SL contributed to methodology and project administration. ZH contributed to validation, funding acquisition, writing - review & editing. JQ contributed to conceptualization, software, validation, formal analysis, writing - review & editing , project administration, supervision, funding acquisition.

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