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Improvement of wood properties by impregnation with TiO₂ via ultrasonic-assisted sol-gel process

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Abstract:

Wood with improved thermal and mechanical properties as well as dimensional stability, was successfully prepared by modified with TiO₂. In this paper, we report an innovative and simple method, namely, ultrasonic-assisted sol-gel method, to prepare TiO₂-modified wood. The formation mechanism of TiO₂-modified wood is also presented. After sonication under mild conditions, weight percent gains (WPGs) of wood samples in the range of 18%–30% were obtained. The WPGs increased with increasing ultrasonic irradiation time of up to 120 min, after which the WPGs increased slightly then hardly changed. The functional groups and morphology of the synthesized modified wood were examined by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) with built-in energy-dispersive X-ray analysis. SEM investigations showed that majority of TiO₂ particles deposited in lumen by adhesion to cell walls in the form of aggregating. The thermal and mechanical performances as well as moisture absorption behavior of the generated modified wood materials were also evaluated.

Keywords: Ultrasonic sol–gel, Wood, TiO₂, Microstructure, Properties

1. Introduction

Wood is popular in many applications, such as building, construction, and furniture, because of its excellent material properties. However, given its hygroscopic and organic nature, wood is sensitive to humidity changes and fire, which lead to dimensional and thermal instability. Therefore, wood modification has attracted much interest in terms of coating, heat treatment, and impregnation with organic compounds.^{1,2} Each of these treatments may have separate advantages and limitations in terms of peeling, altered morphology, and easy combustion. As of this writing, increasing demand for high quality products and environmental awareness of societies have made inorganic modification of wood popular in this field.³⁻⁵ Sol-gel method can convert precursor monomers into polymer chains,^{6,7} which establish covalent bonds by addressing functional hydroxyl groups of natural polymers (lignin, cellulose, and hemicellulose) to retain the inorganic substance in wood.^{8,9} Sol-gel method also confers good leaching resistance and eco-friendly properties, while retaining all the natural properties of the wood matrix.

Sol-gel processes combined with vacuum impregnation method have been conventionally used to fabricate inorganically modified wood.¹⁰⁻¹² However, the vacuum impregnation process frequently requires a long processing time.¹³

Herein, a new synthetic method was introduced, namely, ultrasonic-assisted sol-gel technology, in which generated polymeric TiO₂ particles can efficiently infiltrate into the wood matrix. Compared with vacuum impregnation which has persistent pressure acted on the mixture, ultrasound oscillation propagating in the medium can induce acoustic cavitation that strongly enhances the diffusion of particles and mass transfer in the mixture.¹⁴⁻¹⁸ With large kinetic energies and speeds accelerated by shock waves and macro streaming of ultrasonic irradiation, the interactions between the precursor solution and wood will therefore be enhanced, leading to the accelerating deposition of TiO₂ particles in wood matrix.

In this study, TiO₂ sol-modified wood was prepared via ultrasonic-assisted sol-gel method under mild conditions (*i.e.*, relatively low sonication intensity and low temperature) for a short period of time. The thermal, mechanical performances and moisture absorption behavior of the wood were subsequently evaluated. We chose fir as a model species because it is one of the most important fast-growing trees in China. We found that our protocol can be extended to other species.

2. Experimental

2.1. Wood specimens

Wood blocks of 20 (R) × 20 (T) × 5 (L)/mm were obtained from the sapwood sections of fir wood from Jiangsu province of China. They were kiln-dried (18 h, 103 °C) before ultrasonic sol-gel impregnation treatment for obtaining a defined reference of weight (W_0).

2.2. Preparation of the TiO_2 -modified wood

The precursor solutions were prepared by the hydrolysis of tetrabutyl titanate (TBT, Sinopharm Chemical Reagent, ≥98%) in the presence of ethanol as solvent and acetic acid as catalyst ($H_2O/TBT/ethanol/acetic\ acid=1:1:6:0.01$ in mole ratio). The solution was transparent, yellow or light brown. A pH value within the range of 2 to 3 was adjusted by addition of concentrated hydrochloric acid (HCl) with the help of a pH meter. The wood blocks were then impregnated in the precursor solutions. Subsequently the mixture were put in a flask subjected to sonication in an ultrasonic bath (80 kHz/50 W, KQ-100TDE, Kunshan Co. LTD, China) continuously at different ultrasonic irradiation time (5, 15, 30, and 60-240 min). After the treatment, specimens were placed in the open air for 3-5 days and then cured up by heat treatment at 103 °C for 20 h, so that sols were aged and the modified fir wood was prepared. Then, the oven-dried weights (W_1) of the modified wood were measured.

2.3. Characterization of the TiO_2 -modified wood

The relative mass changes were calculated from the difference of the sample mass after and before sonication sol-gel impregnating treatment divided by the initial sample mass and expressed as weight percent gain (WPG). As the different density of the natural grown wood, the WPG values are averages over 6–8 samples.

The chemical compositions of the modified wood were examined by the Fourier transform infrared spectroscopy (FTIR, Nicolet 5700). For FTIR analysis, thin sample disks were made by grinding small portion of the titania wood composites and pressing them with potassium bromide. To obtain information about the surface morphology and the dispersion of titania in wood matrix, electron microscopic investigations were carried out using an environmental scanning electron microscope (ESEM, FEI Netherlands, XL30) and a SEM (zeiss, supra55) combined with an energy dispersive X-ray (EDX) analysis system.

The thermal performances of the titania modified wood were examined using a thermal

analyzer (TGA, SDT Q600) in the temperature range from room temperature up to 800 °C at a heating rate of 10 °C/min in an open air.

For mechanical characterization, wood specimens of 20 (R) × 20 (T) × 30 (L)/mm were used, and their deformation behavior under compression in the longitudinal direction was recorded using a universal testing machine (Instron 1185) at a crosshead speed of 10 mm/min.

The moisture absorption behavior was evaluated by exposing the wood samples to humid atmosphere (95% relative humidity, 20-23 °C) obtained by KNO₃ saturated salt solutions for some months to reach equilibrium moisture content. Then the weights of the wood samples were determined using a precision balance (0.001 g resolution BS124S).

The relative gain of mass during such storage was calculated for time t according to

$$\Delta m = \frac{m(t) - m(t=0)}{m(t=0)} \cdot 100\%$$

where $m(t=0)$ is the mass of the sonication sol-gel treated cured sample at the beginning of the storage and $m(t)$ is the mass at time t .

The relative gain of volume was determined by

$$\Delta v = \frac{v(t) - v(t=0)}{v(t=0)} \cdot 100\%$$

where $v(t=0)$ is the initial volume of the cured sample and $v(t)$ is the volume at time t .

3. Results and Discussion

3.1. Incorporation mechanism of TiO₂ into wood matrix by ultrasonic sol-gel treatment

It is known that lots of micropores exist in the wood, which provides a good tunnel structure for penetration of TBT-derived precursor solutions into the 3D network of the wood matrix, while the wood block is immersed in the TBT precursor mixed solutions which with the solid content of 12%, as shown in Fig. 1. Wood also features numerous hydroxyl groups that confer the hydrophilic nature of the cell wall. The hydrophilic nature makes the polymeric -Ti-OH trapped inside the wood samples by interaction with the fir wood hydroxyl.^{8,19}

An ultrasonic-assisted sol-gel method was used to accelerate dispersion and decrease particle size.²⁰ During sonication, acoustic streaming leads to enhance the medium mixing and in addition the particle size of TiO₂ present in the medium reduces into either micrometer or nanometer

scale²¹⁻²⁴ within a certain period of time, during the time titania sols could penetrate into the micro pores of wood samples easily. Ultrasonic treatment favors the chemical reactions between liquid and solid phases.^{25,26} To this effect, with the energy provided by ultrasonic treatment, the penetrated solution is converted to polymeric TiO₂ inside the wood matrix. As each Ti is coordinated with four oxygen atoms, therefore the development of -Ti-O-Ti- chains results in three-dimensional polymeric skeletons with closed packing. Finally, the modified wood samples were dried and maintain the original porous structure of the wood sample.

In summary, TiO₂ modified wood was obtained under ultrasonic irradiation which is an innovative, simple, and time-saving technology.

3.2 Structural characterization and morphology of the TiO₂-modified wood

The infiltration amounts of TiO₂ into wood block at different ultrasonic irradiation time were studied by the measured WPG values. With increasing the ultrasonic irradiation time to 120 min, their WPG values improves (Fig. 2), after then turns to be a steady increased level, then hardly changed. The wood samples displayed a mass increase of 18%–30% from 5 min to 120 min, indicating that more TiO₂ infiltrated with increasing the irradiation time.

To investigate the functional group composition of the wood samples, FTIR measurements were performed before and after the ultrasonic sol-gel treatment (Fig. 3). It also can provide semiquantitative analysis of the incorporated TiO₂ at different irradiation time of 30 min and 120 min.

For modified samples, the bands below 1000 cm⁻¹ were attributed to Ti-O stretching vibrations that are characteristic of TiO₂.²⁷ Therefore, at 120 min there are more TiO₂ existed in the wood than 30 min. For untreated control, the peaks at 3380 cm⁻¹ correspond to stretching vibrations of hydroxyl groups,^{28,29} which shifted to lower wavenumbers (3350 cm⁻¹) in the modified wood samples.³⁰ The bands at 2820–2980 cm⁻¹ correspond to asymmetric -CH₃ and symmetric -CH₂. The peaks at 1160 cm⁻¹ and 1120 cm⁻¹ correspond to Ti-O-C stretch vibrations in the modified wood.³¹ We assumed that, it is generated from the reaction of Ti-OH and wood-OH.^{8,19}

The morphology and titanium element distribution of the as-prepared TiO₂ incorporated wood block at irradiation time of 120 min were investigated by SEM and EDX. Fig. 4 shows SEM images and EDX mappings of the cross-sectional morphology of wood samples at a magnification

of 1,000 \times (a, b) and 1500 \times (c, d), as well as radial-sectional morphology of wood samples at a magnification of 500 \times (e, f), respectively. For the cross-section morphology, titanium element was presented in the cell walls of EDX mapping of the modified wood samples. At the radial-section, most of the titania gels generated a thin film coating on the cell walls. The SEM/EDX mapping revealed that titanium element existed in the whole wood body in the form of depositing in lumen by adhesion to cell walls.

By sonication, the precursors can diffuse into the wood matrix by concentration gradient during immersion of wood block in precursor solutions. The wood hydroxyl was hypothesized to act as a nucleating site for the formation of TiO₂ gels. The hydrophilic nature of wood provides good tunnels for Ti-OH adsorption. The formation and distribution of TiO₂ inside the wood matrix is confirmed by the FTIR above and SEM-EDX.

3.3 Thermal, mechanical properties and dimensional stability of the TiO₂-modified wood

Thermal analyses were performed to examine the thermal stability of the prepared modified wood samples. Curves representing thermal degradation (TG and DTG) for tested wood specimens are displayed in Fig. 5(a). For untreated wood three steps of thermal degradation were observed, which is a typical TG profile for wooden materials. In Fig. 5(a) for the TG curves, the initial small mass loss from room temperature to 100 °C is mainly attributed to the evaporation of adsorbed water. An abrupt weight loss was observed between 250 °C and 370 °C. Another remarkable weight loss was found between 420 °C and 500 °C. All these distinct weight losses are due to oxidation and pyrolysis of wood components.³² As opposed to the untreated control, the modified wood samples displayed similar TG/DTG curves up to 250 °C, after which a lower rate of weight loss was observed and eventually a higher amount of residues remained with increased WPGs.

For the DTG curves in Fig. 5(a), two obvious peaks were found between 250 °C and 500 °C. Compared to that of non-modified control, the peak of the modified wood weakened and shifted to higher temperatures, especially for the sample sonicated at 120 min. It can be assumed that the wood combustion reaction is delayed compared to untreated samples.

To understand the thermal behavior of the modified samples furthermore, a differential thermal analysis (DTA) was conducted (Fig. 5b). In the DTA curves two obvious characteristic exothermic peaks were observed. In all cases a first exothermic peak occurs at 330 °C followed by a second

one in the range of 420-500 °C. The second exothermic peak was weakened and shifted to higher temperatures with increasing titania content. These results indicate an improved thermal stability of the modified wood compared to untreated control. Similar results were obtained by Miyafuji.³³ Owing to the TiO₂ infiltrated in wood, the cell wall components are likely to be shielded by the fire-retardant inorganic gels which organized with the inorganic coating. So the cell wall components are hampered from being accessible to oxygen and the complete combustion is delayed, thus enhancing the thermal stability of wood.

To further understand the structure-property relationship of the TiO₂-modified wood materials, their mechanical behavior under compression in the longitudinal direction was characterized (Fig. 6). The modified wood showed a deformation behavior generally similar to that of untreated control. However, a higher Young's modulus and an elevated stress threshold were observed for the modified wood with increasing the WPGs, which sonicated at 30 min, 60 min and 120 min, respectively. This indicates that the wood stiffness and yield strength in compression were improved with increased WPGs.¹⁰

The results of the hygroscopicity and dimensional stability studies of selected modified wood samples are presented in Fig. 7. In Fig.7a, the moisture uptake of the samples sonicated at 30 min, 60 min and 120 min was reduced significantly compared with the non-modified control. For non-modified wood, the moisture sorption saturation value is 22%. While, samples sonicated at 30 min, 60 min and 120 min displayed a 16%, 12%-14% and 10%-12% mass gain, respectively.

In Fig.7b, the gains in volume during storage in humid air of fir sapwood control are contrasted with three modified wood. Storage in humid atmosphere results in saturation values of bulking between about 12-13% of non-modified control. While, samples sonicated at 30 min, 60 min and 120 min displayed a 7-8%, 5% and 3-4% volume gains, respectively.

This indicated that longer irradiation time with higher WPG values lead to lower water uptake and less volume bulking. Hence, better dimensional stability was achieved by modified with TiO₂ compared to the non-modified wood sample. We attribute this to the blocking effect of the impregnated TiO₂, as well as the possible formation of hydrogen bonds between TiO₂ gels and wood-OH.¹⁰ Similar results are found for the moisture absorption behavior of wood samples that has been impregnated or coated with inorganic nanosols.³³⁻³⁶

Due to our study is similar as the paper published in Bioresources¹⁰ in terms of measured

properties, so we compared our results to their study which used the preparation method of vacuum soak. The differences are listed in Table 1 and elaborated as follows: (The presented differences in Table 1 are the best results of each work)

The shorter preparation time used by sonication compared to vacuum soak is caused by the accelerating deposition of TiO₂ particles in wood matrix via sonication. Ultrasound oscillation propagating in the medium can induce acoustic cavitation that strongly enhances the diffusion of particles and mass transfer in the mixture. Also the hygroscopicity and dimensional stability are better by sonication. We attribute this to the blocking effect of the impregnated TiO₂. With large kinetic energies and speeds accelerated by shock waves and macro streaming of ultrasonic irradiation, the interactions between the precursor solution and wood therefore be enhanced. To this effect, the penetrated solution is converted to polymeric TiO₂ inside the wood matrix. The mechanical behavior of the composites is strengthened by sonication. It may be caused by the deposition of TiO₂ in wood with the form of depositing in lumen by adhesion to cell walls which assisted by sonication.

Table 1. Comparison of measured properties gained from the results of vacuum soak¹⁰ and sonication.

Methods	WPG values ^a	Relative weight gain (%)	Relative volume gain (%)	Maximum compressive stress (MPa) ^b
Vacuum soak	29% (20 h)	13-14%	7-8%	45-50 (5.5%)
Sonication	30% (2 h)	10-12%	3-4%	45-50 (12%)

^a The time showed in the brackets are the operation hours of vacuum soak and sonication that apart from the oven-dried time.

^b The figures showed in the brackets represent the strain of the stress beginning to decrease in the stress-strain curves of the modified composites.

4. Conclusions

In this study, polymeric TiO₂ gels were incorporated into the 3D network of the wood matrix, and the modified wood was successfully prepared by ultrasonic-assisted sol-gel synthesis. Ultrasonic treatment provided the formation of TiO₂-modified wood material with a good distribution of TiO₂ throughout the wood matrix, in which these gels were deposited in lumen by adhesion to cell walls. The modified wood also possessed improved thermal, mechanical

properties and dimensional stability with increasing loads of inorganic TiO₂ gels (*i.e.*, prolonging the ultrasonic irradiation time). The current method has potential for preparing other inorganically modified wood materials.

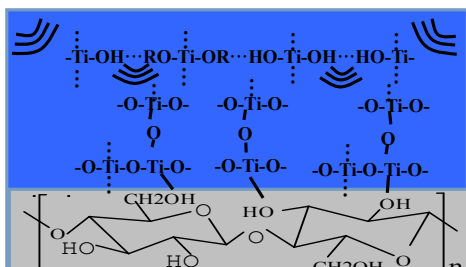
Acknowledgments

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Wood with improved properties was successfully prepared by impregnation with TiO₂ via ultrasonic-assisted sol-gel method which is an innovative, simple, and time-saving technology.

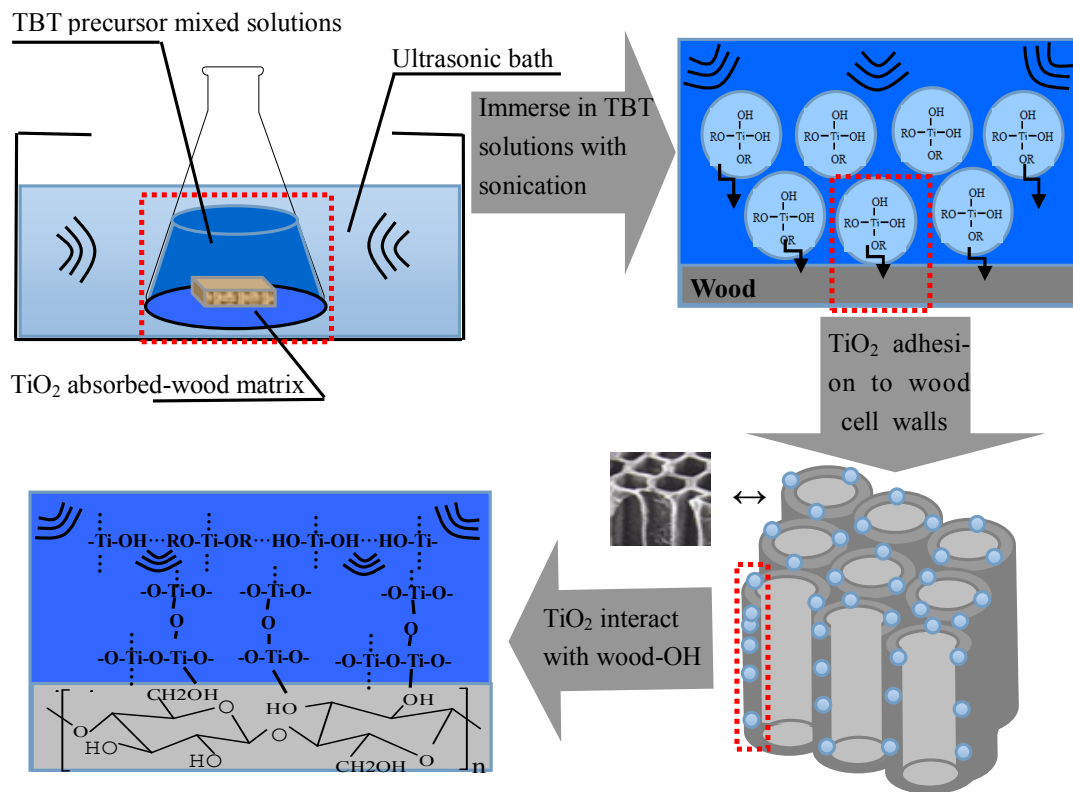


Fig. 1 Schematic of experimental set-up for preparing TiO₂-modified wood by ultrasonic-assisted sol-gel method.

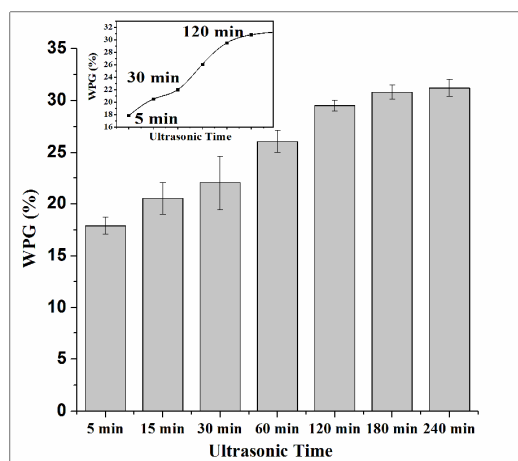


Fig. 2 Comparison of the WPG values at different ultrasonic irradiation time.

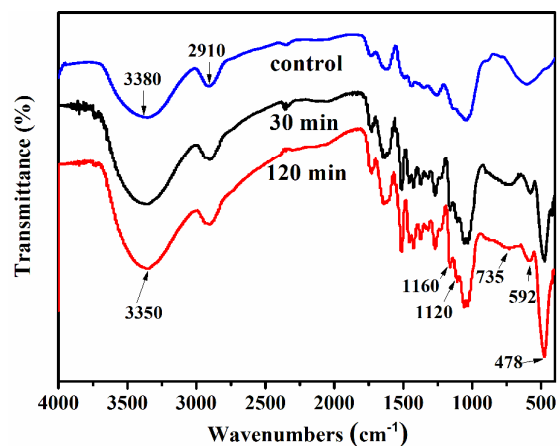


Fig. 3 FTIR spectra of wood particles before and after ultrasonic sol-gel treatment.

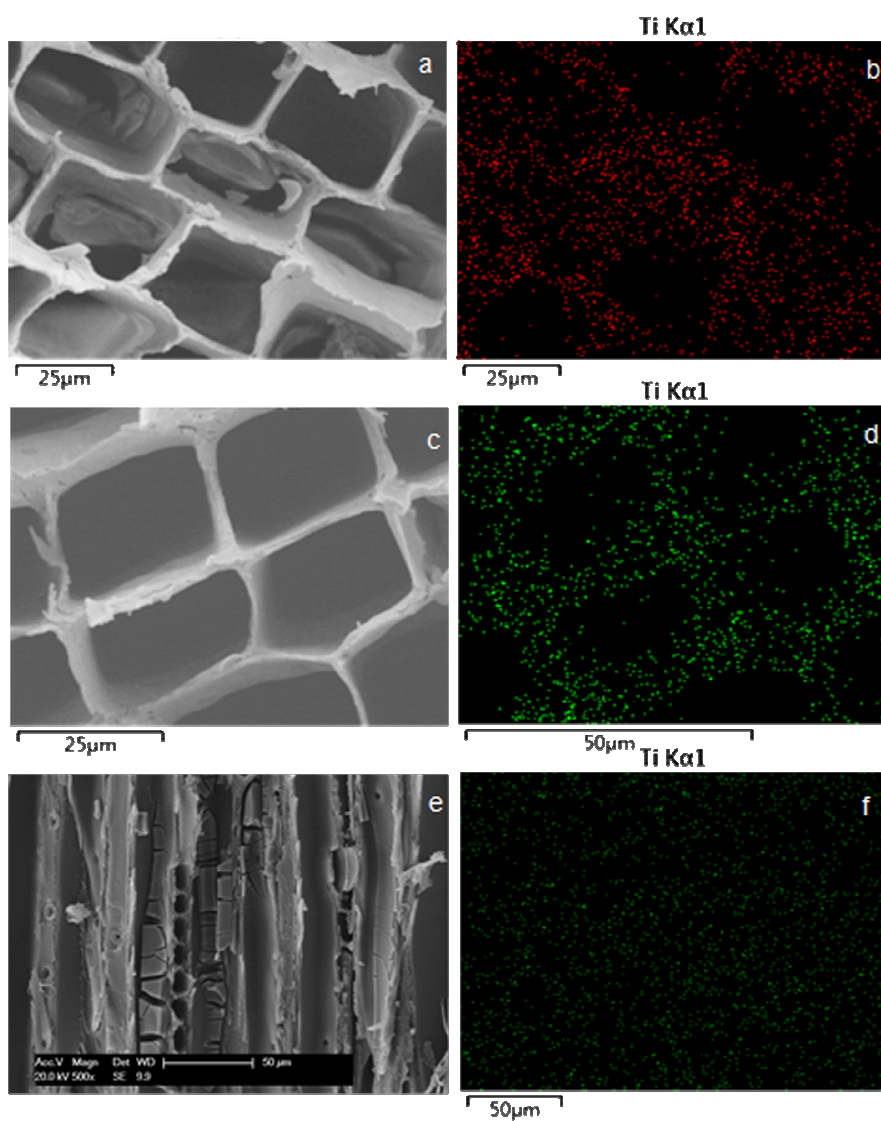


Fig. 4 SEM images (left) and X-ray dot mapping images of titanium element (right) in the modified wood at a magnification of 1,000 \times (a,b) , 1500 \times (c,d) of cross-section and 500 \times (e, f) of radial-section, respectively.

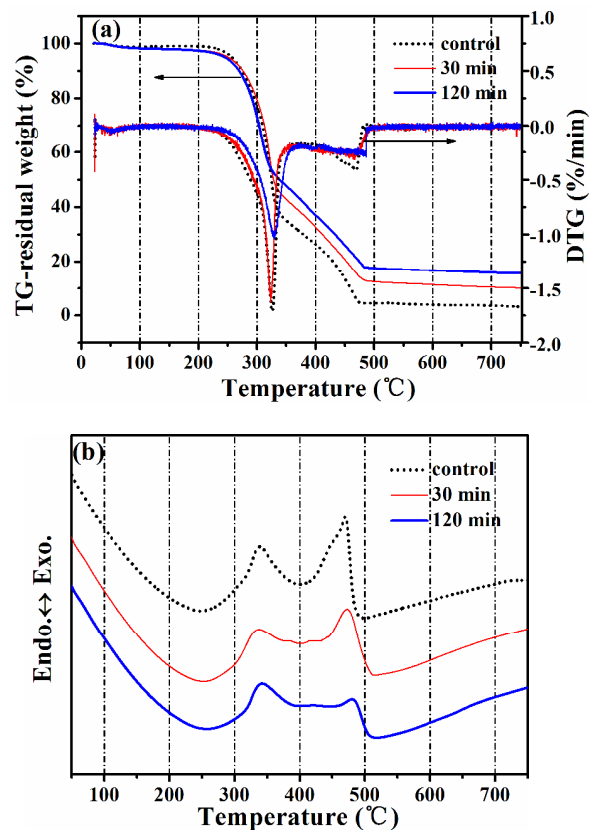


Fig. 5 Thermal behaviors (a, TG and DTG curves; b, DTA curves) of the TiO₂-modified wood samples with different WPGs at different sonication time (control, black line; 30 min, red line; 120 min, blue line).

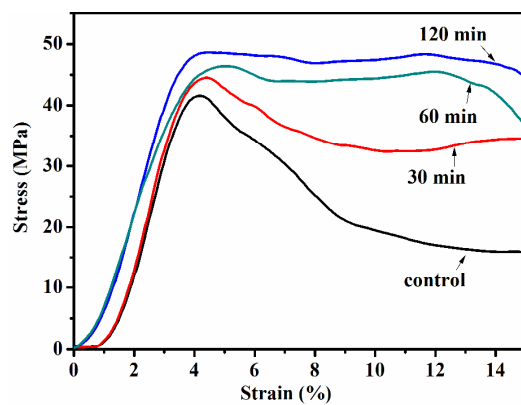


Fig. 6 Stress-strain curves of the TiO₂-modified wood at different irradiation time compared with untreated control under compression in the longitudinal direction.

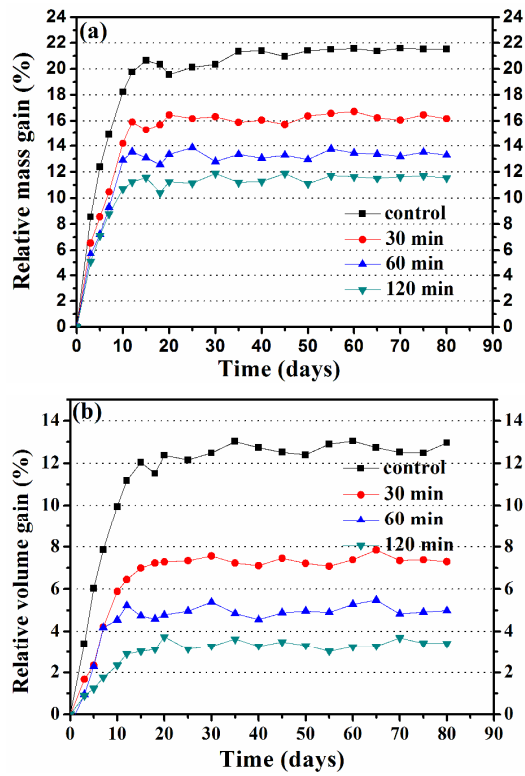


Fig. 7 Mass (7a) and volume (7b) changes of conditioned wood samples during storage in humid atmosphere (95% r.h.) at room temperature (20-23 °C).