THERMAL, MECHANICAL, AND MOISTURE ABSORPTION PROPERTIES OF WOOD-TiO_2 COMPOSITES PREPARED BY A SOL-GEL PROCESS

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Wood-TiO_2 (titania) composites were prepared by a sol-gel process, in which wood was impregnated with the precursor solutions prepared from tetrabutyl titanate (TBT), followed by a curing step. The surface morphology and moisture absorption behavior of the wood composites, as well as their thermal and mechanical performances, were examined. Environmental scanning electron microscopy (ESEM) analysis revealed that TiO_2 gels were deposited principally in the cell lumens and partly in the cell walls, as confirmed by the energy dispersive X-ray (EDX) analysis. By this inorganic modification, the hygroscopicity of wood was significantly reduced and its dimensional stability was improved consequently. Greater amounts of TiO_2 gel deposited in the cell lumens were not helpful in enhancing the hygroscopicity of wood. Thermal analysis (TG-DTA) showed that the incorporation of TiO_2 gel retarded the thermal decomposition of wood matrix and improved the thermal stability of wood. The incorporated inorganic gel seemed to stiffen the wood cell walls, as indicated by the increased resistance of the wood composites to deformation and collapse in compression.

Keywords: Dimensional stability; Moisture absorption; Sol-gel; Thermal analysis; TiO_2

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INTRODUCTION

Wood has been widely used for many applications owing to its excellent material properties and desirable environmental characteristics. However, as a natural biological material wood also suffers from many inherent disadvantages such as dimensional instability due to moisture changes, susceptibility to biodegradation, weathering, and combustion, without protective treatments. To overcome these drawbacks, many wood modification attempts have been made, including acetylation, heat treatment, oil treatment, furfurylation, resin impregnation, and treatments involving silicones and silanes (Hon 1996; Mai and Militz 2004; Hill 2006). Each of these treatments may have its own advantages and limitations in terms of effectiveness, costs, and environmental impacts.

Inorganic modification of wood to form hybrid wood-inorganic composites by application of nanosols is one of the promising methods for improvement of wood properties. By incorporation of inorganic components into the wood matrix, wood could be functionalized with enhanced properties in terms of fire resistance, water repellence, and biodegradation resistance, while simultaneously retaining the porosity and desirable material properties of wood itself (Mai and Militz 2004; Mahltig et al. 2008). The application of a sol-gel process to produce wood-SiO_2 (silicon dioxide) composites was first reported by Saka et al. (1992). The described process involved an impregnation of wood with the precursor solution of tetramethoxysilane (TEOS) in ethanol with catalytic amounts of acetic acid, followed by a curing step. In this case, the bound water in wood cell walls is utilized to initiate the hydrolysis and subsequent condensation of TEOS so that the silica gel is deposited therein. By tuning the moisture content of wood, the deposition of silica gel within wood body could be manipulated, and thereby the efficiency of the modification could be governed, depending particularly on whether the silica gel is located in the cell wall or in the lumen. On the basis of this approach, other processes involving the use of TEOS in combination with other reagents to form P_2O_5-B_2O_3-SiO_2, Na_2O-SiO_2 gels or using alternative precursors such as methyltrimethoxysilane (MTMS), methyltriethoxysilane (MTES), and propyltriethoxysilane (PTEO) have also been developed to further enhance the properties of the modified wood (Miyafuji and Saka 1996; Saka and Ueno 1997; Miyafuji et al. 1998; Miyafuji and Saka 2001; Donath et al. 2004).

In a similar way, wood-inorganic composites involving titania have also been prepared by the sol-gel process. However, the property enhancement of the resulting composites is limited, owing to the precipitation of the inorganic gels predominantly in the cell lumens due to a high hydrolysis rate of the used titanium alkoxide precursor (Saka and Yakake 1993). By using titanium alkoxides and titanium chelates having a low rate of hydrolysis, the TiO_2 gels could be deposited within the cell walls, thereby enhancing the wood properties effectively in terms of dimensional stability and fire retardancy (Miyafuji and Saka 1997; Hübert et al. 2010). In contrast to the numerous reports involving SiO_2-based wood-inorganic composites, studies on TiO_2 based wood-inorganic composites are not sufficient, and more attention should be focused on the underlying structure-property relationships of the wood-inorganic composites.

In the present study we prepared wood-TiO_2 composites by the sol-gel process, in which the hydrolysis of the titanium alkoxides precursor mainly occurs following or during the impregnation step, and subsequently evaluated their moisture absorption behavior as well as the thermal and mechanical performances.

EXPERIMENTAL

Wood Specimens

Wood blocks of 20 mm (R) × 20 mm (T) × 5 mm (L) were obtained from the sapwood sections of Chinese fir (*Cunninghamia lanceolata*), which is one of the most important coniferous tree species in China. The wood specimens were oven-dried (12 h, 105 ^{o}C), and their oven-dry weights were determined. To prepare moisture-conditioned wood specimens with varied moisture contents (7%, 12%, and 22%), they were first oven-dried (12 h, 105 ^{o}C), and then they were placed in conditioning desiccators for several weeks at room temperature, during which time the relative humidity (RH) was controlled by means of selected saturated salt solutions. For comparison, water-saturated wood specimens were also prepared by water immersion with a final moisture content being higher than 70%, in which water was located not only in the cell wall, but also in the lumen.

Preparation of Wood-TiO_2 Composites

The precursor solution was prepared from a mixture of 0.5 mol tetrabutyl titanate (TBT, Sinopharm Chemical Reagent, ⩾98%) in 5 mol ethanol. 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 specimens were impregnated with the prepared solution under a reduced pressure (0.01 to 0.02 MPa) for 20 h at room temperature. The impregnated specimens were then cured up by heat treatment at 105 ^{o}C for 24 h, and their oven-dry weights were measured.

Characterization of Wood-TiO_2 Composites

The weight percentage gain (WPG) of the wood composites was determined on the basis of their oven-dry weights before and after the sol-gel treatment. The surface morphology of the wood composites and the distribution of TiO_2 gels within them were examined by an environmental scanning electron microscope (ESEM, FEI Quanta 200, the Netherlands) combined with an energy dispersive X-ray (EDX) analysis system.

The moisture absorption behavior was evaluated by exposing the wood specimens to ambient atmosphere with varied relative humidity (22% to 98%) for a period of several weeks at room temperature to reach an equilibrium moisture content. The different relative humidity levels were accomplished by using selected saturated salt solutions in conditioning desiccators. After the absorption equilibrium was achieved for each specific relative humidity, the weights of the specimens were determined using a precision balance (0.001g resolution), and the volumes were measured with a micrometer. The relative gains of weight and volume were calculated respectively based on the difference of the weight and volume of the specimens after and before moisture absorption treatment divided by the initial specimen values.

The thermal performances of the wood composites were examined using a thermal analyzer (TG-DTA, SDT Q600 V8.3 Build 101) in the temperature range from room temperature up to 700 ^{o}C at a heating rate of 10 ^{o}C /min.

For mechanical characterization, wood specimens of 20 mm (R) × 20 mm (T) × 30 mm (L) were used, and their deformation behavior under compression in the longitudinal direction was recorded and compared before and after the sol-gel treatment using an universal testing machine (Instron 5582) at a crosshead speed of 2 mm/min, in accordance with the Chinese national standard GB 1927~1943-91 “Testing methods for physical and mechanical properties of wood”.

RESULTS AND DISCUSSION

The initial moisture contents of the moisture-conditioned wood specimens are supposed to affect the hydrolysis of the titanium alkoxides precursor and thus govern the amount of inorganic gels eventually deposited within the wood composites. However, the weight percentage gains (WPGs) of the wood composites prepared from the moisture-conditioned wood varied narrowly in the range 25% to 29%, which shows insensitivity to the variation of the initial moisture contents (7% to 22%). The wood composites prepared from the water-saturated wood showed a WPG value of 16%. Here, we present only the results of the moisture-conditioned (29% WPG) wood samples that were preconditioned at 98% RH (relative humidity) by a saturated salt solution of K_2SO_4 and also the water-saturated wood (16% WPG) for comparison.

The deposition of TiO_2 gels within the wood-inorganic composites is shown in Fig. 1. For the water-saturated specimens, TiO_2 gels were present in the cell lumens, and thin layers of inorganic gels were found to be coated on the lumen surface of cell walls, blocking the aperture of the bordered pits (Fig. 1c,d).

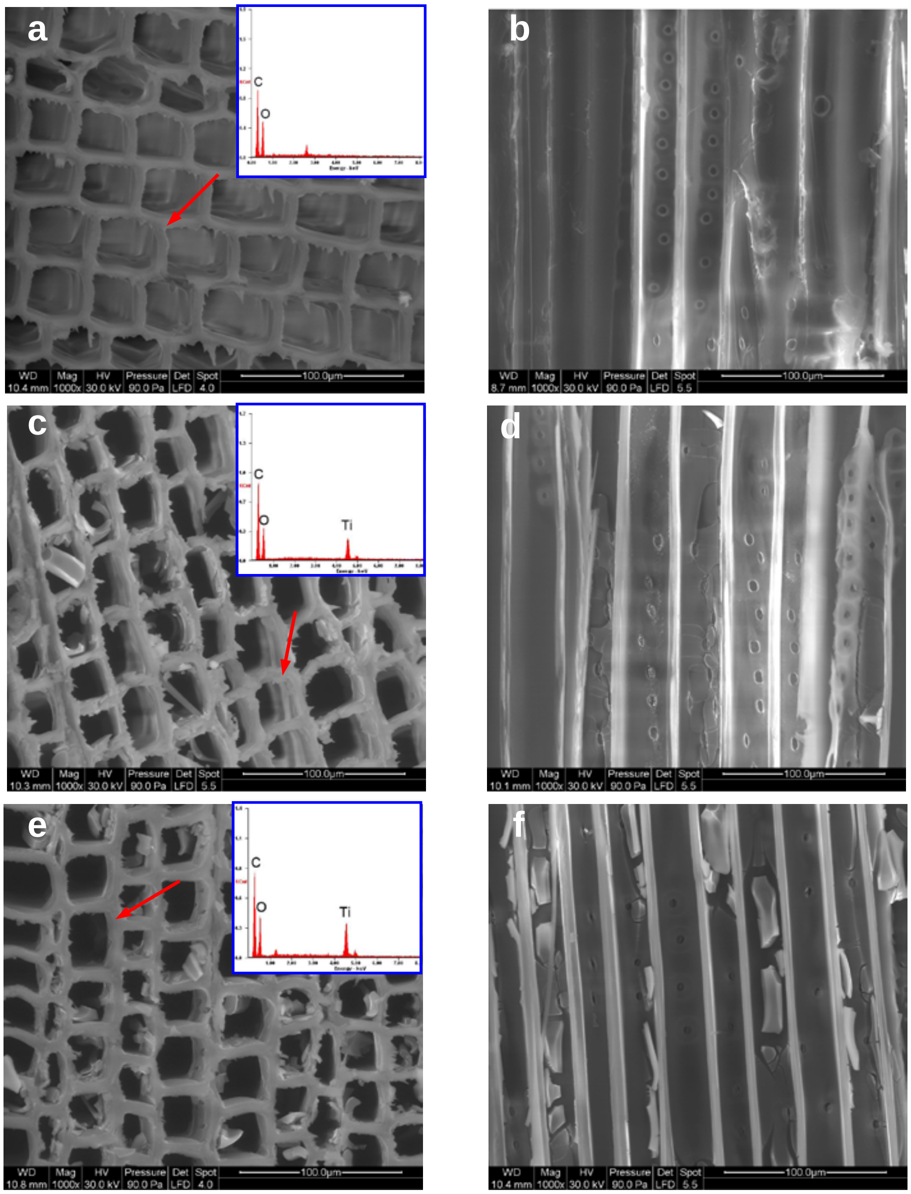

Fig. 1. ESEM images of wood-TiO_2 composites with weight percentage gain (WPG) of 16% (c, d) and 29% (e, f) in comparison with the untreated control (a, b). Cross section (a, c, e), radial section (b, d, f). The inserted pictures are the corresponding EDAX spectra of cell walls.

For the moisture-conditioned specimens, a much higher value of WPG (29%) of the wood composites was achieved, and thus more TiO_2 gels were found to be present in the cell lumens. This effect is clearly displayed on the radial section of the specimens with thick-layered inorganic gels being formed and agglomerated in the cell lumens (Fig. 1e,f).

Generally for effective modification of wood, the modifying agent is expected to be incorporated into the cell wall. For further characterization, the EDAX method was used. The EDAX spectra clearly revealed that carbon and oxygen were the only elements present at detectable levels in the cell walls of untreated reference specimens (Fig. 1a). However, an additional strong signal of titanium element was present in the spectra of the cell walls of the wood composites (Fig. 1c,e). This indicates that the TBT precursor could penetrate into the cell walls before its hydrolysis and polycondensation, resulting in the formed TiO_2 gels becoming deposited principally in the cell lumens and partly in the cell walls. Since the inorganic gels are present in both cell walls and lumens, the physical and mechanical properties of the resulting wood composites would be expected to be altered to a different degree.

The relative weight gains of the wood-inorganic composites due to moisture absorption under various relative humidity (RH) conditions are given in Fig. 2a. Compared to the untreated control, the moisture uptake of the modified woods was reduced significantly at various RH conditions. The wood composites prepared from the moisture-conditioned and water-saturated wood showed, nevertheless, similar moisture absorption behavior in spite of their remarkably different WPGs. The reduction in the hygroscopicity of the modified wood is consistent with other results for wood that has been impregnated or coated with inorganic nanosols (Tshabalala and Sun 2007; Hübert et al. 2010; Sun et al. 2010; Tshabalala et al. 2011).

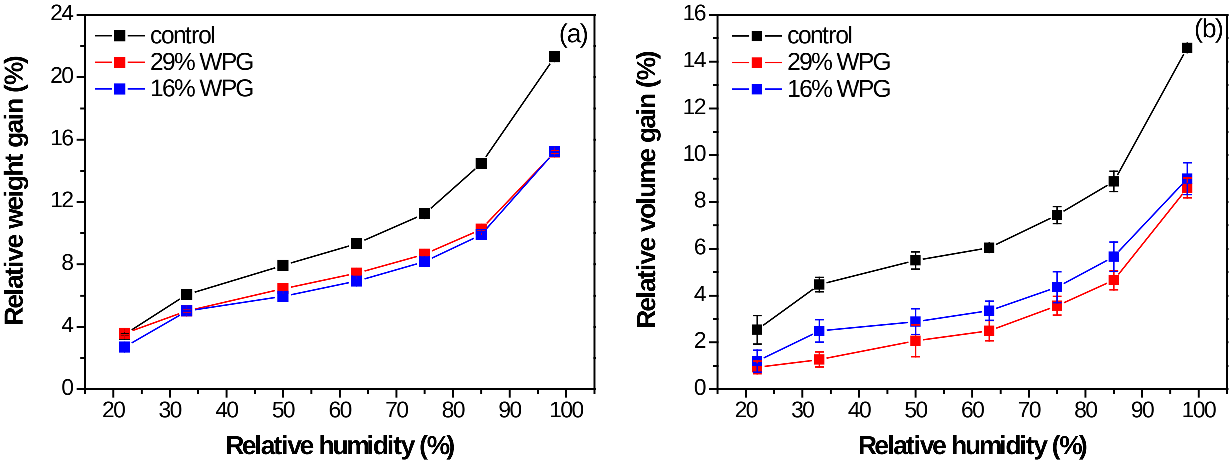

Fig. 2. Relative gains of weight (a) and volume (b) of the wood-TiO_2 composites with different WPGs (control, black line; 16% WPG, blue line; 29% WPG, red line) during storage in ambient atmosphere with varied relative humidity (RH). Values are given as mean of 10 replicates with the standard deviation as error bars. For part (a) no error bars are shown, since the intervals were small relative to the size of the plotted points.

As confirmed by ESEM-EDX analysis, the TiO_2 gels were incorporated into the cell wall and were probably occupying the void space (micropores) within the cell wall that would otherwise be accessible to water molecules, thus resulting in a reduction in the hygroscopicity of the modified wood (Donath et al. 2004; Hill 2006). On the other hand, the hydroxyl groups of cell wall components mainly responsible for moisture absorption possibly were blocked by formation of hydrogen bonds with the TiO_2 gels during hydrolysis and polycondensation of the TBT precursor, which could be a contributing factor for the reduced hygroscopicity.

A reduction in the hygroscopicity of wood implies an improved dimensional stability. As shown in Fig. 2b, a significant reduction in volume swelling caused by moisture absorption at various RH conditions was observed for the modified wood, and the wood composite with a WPG of 29% seemed to exhibit slightly lower volume swelling than that of 16% WPG. This indicates that incorporation of the inorganic gels reduces the ability of cell wall to swell due to bulking and thus improves the dimensional stability of the impregnated wood. In fact, only the inorganic gels incorporated into the cell wall are expected to exert an influence on the hygroscopicity and dimensional stability of wood, whereas those deposited in the cell lumen would be expected to play a minor role. Therefore, it is speculated that almost the same amount of TiO_2 gels could be incorporated into the cell wall for the composites with WPGs of 16% and 29%, which could account for their similar moisture absorption and volume swelling behavior, although more TiO_2 gels are deposited in the lumens in the latter case.

Thermal analyses were performed to examine the thermal stability of the prepared wood-TiO_2 composites. The thermogravimetric (TG) results for the wood composites and the untreated wood are shown in Fig. 3a. The initial weight loss from room temperature to 200 ^oC is mainly attributed to the evaporation of adsorbed water. An abrupt weight loss was observed between 250 ^oC and 330 ^oC, followed by another remarkable weight loss between 330 ^oC and 485 ^oC. These distinct weight losses are due to oxidation and pyrolysis of wood components, in which the hemicellulose is most thermally unstable, followed in turn by cellulose and lignin (Fengel and Wegener 1984).

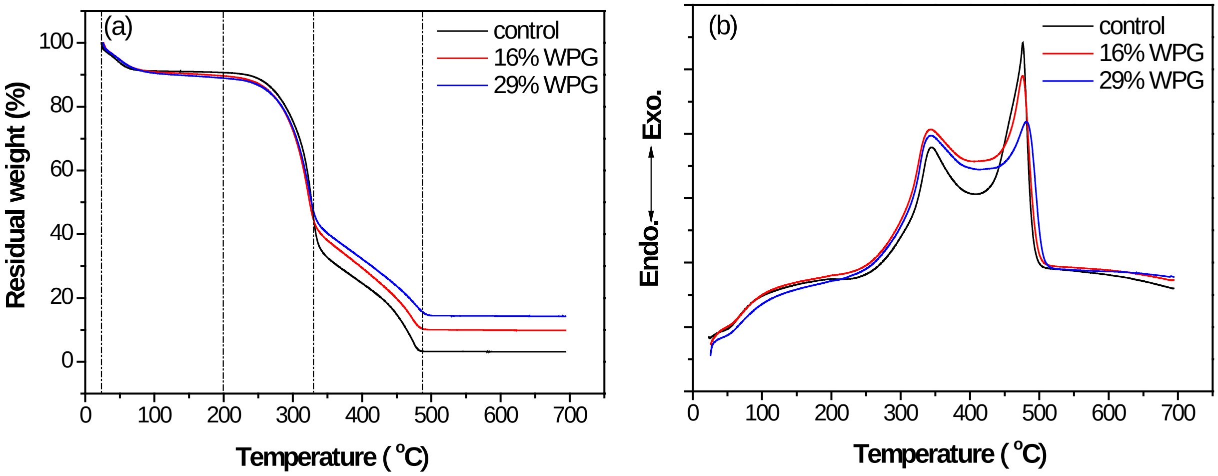

Fig. 3. Thermal behavior (a, TG curve; b, DTA curve) of wood-TiO_2 composites with different WPGs (control, black line; 16% WPG, red line; 29% WPG, blue line)

In comparison with the untreated wood, the wood-inorganic composites displayed similar TG curves up to 330 ^oC, after which a lower rate of weight loss was observed and eventually a higher amount of residues remained.

To further understand the thermal behavior of the composites, a differential thermal analysis (DTA) was conducted (Fig. 3b). In the DTA curve of the untreated wood, two characteristic exothermic peaks were observed, with the first one appearing at 350 ^oC, followed by a second one at 476 ^oC. The second exothermic peak was weakened and broadened by the chemical treatment, such that the peak was shifted to higher temperatures with increasing loads of the inorganic gels, indicating an improved thermal stability of wood achieved by the inorganic modification. By incorporation of TiO_2 gels into the cell wall, the cell wall components are likely to be shielded by the fire-retardant inorganic gels, which may hamper the cell wall components from being accessible to oxygen and retard their combustion, thus enhancing the thermal stability of wood (Miyafuji and Saka 1997).

To gain more insight into the structure-property relationships of the wood-inorganic composites, their mechanical behavior under compression in the longitudinal direction was characterized. Since the WPGs due to the sol-gel treatment were almost the same (approximately 5%) for the moisture-conditioned and water-saturated wood, a typical stress-strain curve of the modified wood under compression is given in comparison with the untreated wood (Fig. 4). The stress-strain curve of the untreated wood showed a linear elastic region at the beginning of compression, followed by a yield point, indicating the onset of cell wall buckling and collapse, after which wood continued to deform under compression with a steadily decreasing stress. The wood-inorganic composites showed a deformation behavior generally similar to that of untreated wood. However, a higher Young's modulus indicated by the slope of the initial linear portion of the stress-strain curve and an elevated stress threshold required to initiate cell wall collapse were observed for the composites. In addition, after the yield point the composites showed an initially abrupt and then steady decrease in compressive stress. This indicates that the wood stiffness and yield strength in compression were improved by the inorganic modification.

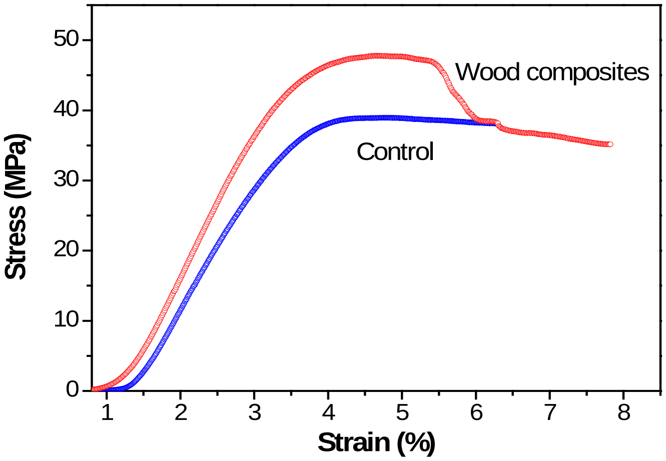

Fig. 4. Typical stress-strain curves of wood-TiO_2composites (red line, upper) and untreated control (blue line, lower) under compression in the longitudinal direction

The effect of incorporation of TiO_2 gels into wood matrix is probably to densify and stiffen the cell walls by filling their void space with relatively rigid inorganic particles, thus increasing the resistance of the cell walls to deformation and collapse in compression. On the other hand, the reduction in the cell wall moisture content due to TiO_2 infiltration may also contribute to the improved mechanical properties (Fig. 2a).

CONCLUSIONS

Inorganic modification of wood to form wood-TiO_2 composites was achieved by the sol-gel process, in which wood was impregnated with the precursor solution prepared from tetrabutyl titanate (TBT), followed by a curing step. The porous structure of wood was retained, and the formed TiO_2 gels were deposited mainly in the cell lumens and partly in the cell walls. Incorporation of the inorganic TiO_2 gels into wood matrix reduced the hygroscopicity of wood significantly and consequently improved its dimensional stability. The thermal stability of wood was also enhanced, and preferable effects were achieved with increasing loads of the inorganic gels.

Our results indicate that wood could be functionalized with enhanced dimensional stability by inorganic modification without posing a negative influence on its porous structure and mechanical properties. The treatment of wood with inorganic nanosols to develop functional wood composites with enhanced properties may be a promising novel technology for value-added utilization of wood.

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