Effect of Silica Sol Content on Thermostability and Mechanical Properties of Ultra-low Density Fiberboards

Tingjie Chen, Min Niu, Zhenzeng Wu, and Yongqun Xie*

The thermostability and mechanical properties of ultra-low density fiberboard (ULDF) were improved with the different content of silica sol. Microstructure and properties of ULDF were tested using scanning electron microscope (SEM), thermogravimetric analyzer (TGA), and microcomputer control electronic universal testing machine. The microstructures and the relative density of ULDFs were different with changes in Si sol content. The TGA results showed that the residual weight of ULDF was increased with the increasing content of silica sol and that the thermostability of ULDFs was improved. The modulus of rupture (MOR), modulus of elasticity (MOE), and the internal bond strength (IB) of ULDF were significantly improved from 0.12, 10.86, and 0.020 MPa to their maximum values of 0.23, 23.36, and 0.031 MPa while 4% silica sol was added.

Keywords: Ultra-low density fiberboards; Si sol; Mechanical properties; Thermostability

*Contact information: Department of Material Science and Engineering, Fujian Agriculture and Forestry University, 350002, Fuzhou, Fujian; *Corresponding author: fafuxieyq@aliyun.com*

INTRODUCTION

Ultra-low density fiberboard (ULDF) is manufactured by a liquid frothing principle. It is a type of porous material that can be used as building insulation material and packaging buffer material (Xie *et al.* 2004; Xie *et al.* 2008a,b). Besides, it has some excellent properties such as ultra-low densities, low thermal conductivities, and good sound absorption, *etc.* (Xie *et al.* 2011; Niu *et al.* 2014), as well as some natural drawbacks in use. Due to its ultra-low density, its mechanical strength is very low, limiting its applications. On the other hand, the flammability of ULDF which used fibers as the matrix is also an intractable question. To overcome these disadvantages, several attempts have been made. For example, Xie *et al.* (2012) and Lin *et al.* (2013) improved the mechanical properties of ULDFs using sodium silicate and aluminum sulfate. Also, the fire resistance of different kinds of ULDFs treated by Si-Al compounds with different levels of additive amount was investigated (Niu *et al.* 2014).

Silicon materials have long been used as inorganic fillers to improve the fire resistance and mechanical properties of materials. Water glass, one of the silicon materials, was one of the earliest to be used as an additive and as a protective coating against fire. Not only can it significantly improve the fire resistance but also it can ameliorate the mechanical properties of composites. For example, it could protect wood against fire through retarding the formation of laevoglucose, which is regarded as the main fuel for burning the lignocelluloses' materials, and consequently minimizing the weight loss of volatilization stage (Saka and Ueno 1997; Mai and Militz 2004; Shabir Mahr *et al.* 2012; Pries and Mai 2013). However, the water glass coating is not stable in the long-term due to neutralization upon contact with air, which results in detachment of the coating from the substrate. And silicate usually is a hydrophilic material that may adversely affect the mechanical properties or waterproofness of materials (Shabir Mahr *et al.* 2012). Thus, other silicon compounds with better physico-chemical properties should be explored.

Another group of non-toxic silicon compounds worth noting is silica sol (Si sol) ($mSiO_2n$-H_2O), which is comprised of nano-SiO_2 particles. The colloidal particle is fine (10 to 20 nm) with large specific surface area, colorless, and transparent (Hayrapetyan and Khachatryan 2005; Yang and Ni 2012). It is a dispersion system of amorphous silica particles in water, which possesses variable aggregative stability, and can be liquid, semisolid, and solid-state. Many methods, including hydrolysis of ethyl silicate, electrolysis, dialysis, and electrodialysis of solutions of sodium silicate, *etc.*, have been employed to obtain Si sol (Freidenberg and Khvorov 1989). Because of the strong surface activity of hydroxyl groups on the surface of silica particles which can form hydrogen bonds with the organic polymers, it was widely applied in organic and inorganic composites (Labarre *et al.* 2002). The mechanical properties of composites and the interfacial interaction between these two components were significantly improved by adding silica sol in Wu *et al.* (2011). Besides, the properties of wood such as fire resistance, low capillary water uptake, and resistance to decay fungi were also improved by the cationic silica sol (Pries and Mai. 2013). Hopefully, physico-chemical properties of ULDFs manufactured by wood fibers are also improved by compositing the Si sol.

Recently, the properties of composites affected by the Si sol have been widely investigated including fire resistance, mechanical properties, and so on (Labarre *et al.* 2002; Campos *et al.* 2014; Ye *et al.* 2014). However, few studies have focused on the effects of Si sol on thermostability and mechanical properties of the ULDFs. The specific objective of this study is to investigate the potential of Si sol in improving physico-chemical properties of ULDF.

EXPERIMENTAL

Materials

The main raw material used to manufacture the ultra-low density fiberboard was kraft pulp (KP, spruce-pine-fir) purchased from Tembec Inc. (Canada). The silicon sol was purchased from Jiangyin Saiwei Technology Trade Co., Ltd (China). The aluminum sulfate and sodium silicate which used to generate Si-Al compounds were purchased from Tianjin Fuchen chemical reagents factory (China).

Methods

Manufacture of ultra-low density fiberboard (ULDF)

ULDF with three-dimensional values of 200 × 200 × 50 mm ($L \times W \times H$) were manufactured separately under various conditions. With a target bulk density of about 55 kg m^{-3}, detailed preparation procedure and scheme were described in Xie *et al.* (2011) and Fig. 1. The amount of Si-Al compound, resin (amylan), water repellent (alkyl ketene dimer), surfactant (sodium dodecylbenzene sulfonate), and fire retardant (chlorinated paraffin) were 500 mL, 20 mL, 50 mL, 80 mL, and 46 g, respectively. Especially, the silica sol contents used in preparation process were under various levels of 0, 2.0, 4.0, 6.0, 8.0, and 10.0% in relation to the volume of Si-Al compound solution. And the related nomenclatures were Si0, Si2, Si4, Si6, Si8, and Si10, respectively.

Scanning electron microscopy with an energy-dispersive X-ray detector (SEM-EDS)

The micromorphology of specimens was characterized by a scanning electron microscopy (SEM, Phenom ProX, Netherlands, using an acceleration voltage of 15 kV). The surfaces of the specimens were coated with gold.

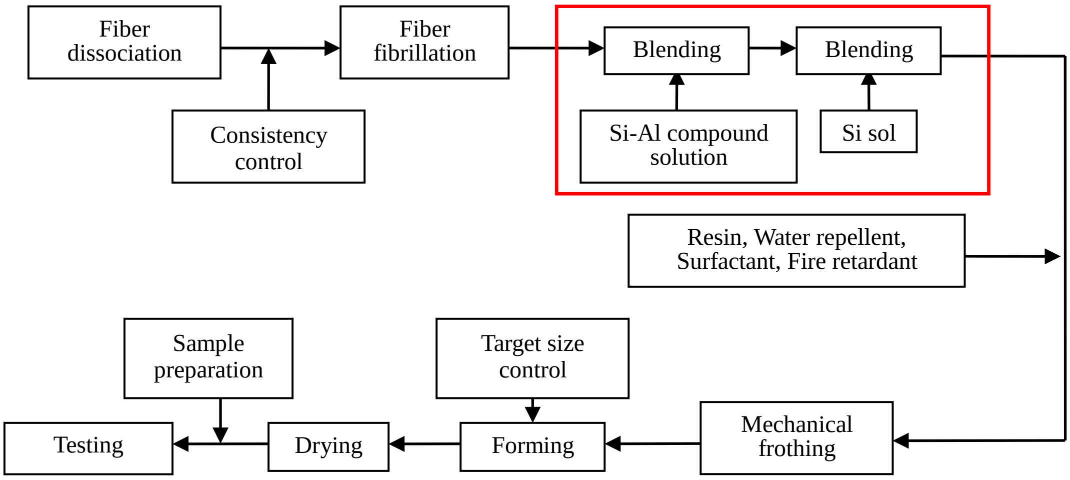

Fig. 1. The preparation process of ultra-low density fiberboard

Thermogravimetric analysis (TGA)

The thermal curves of TGA were obtained using a thermogravimetric analyzer (NETZSCH STA 449F3, Germany). The temperature range was from 20 °C to 500 °C with a heating rate of 10 °C min^{-1} under nitrogen atmosphere.

Testing of mechanical properties

According to GB/T 17657 (1999), the bulk density (ρ) was measured on specimens (at 12% moisture content) with size of 100 x 100 x 30 mm ($L \times W \times H$). Each reported result was the average of five times replication.

The modulus of elasticity (MOE), modulus of rupture (MOR), and internal bond strength (IB) were tested in accordance with GB/T 17657 (1999). The size of the specimens for the testing of MOE and MOR was 120 x 50 x 10 mm ($L \times W \times H$). And the size for IB strength was 50 × 50 × 40 mm ($L \times W \times H$). All of the results were the average of five times replication.

RESULTS AND DISCUSSION

Micromorphology of ULDFs

The different microstructures of fiberboards with different contents of Si sol are presented in Fig. 2. Compared with the fiberboards with Si sol, the fiberboard A had a relatively smooth surface, which indicated that it was only covered by Si-Al inorganic films (Chen *et al.* 2015). The silica sol had both physical and chemical interaction on the fibers because of its strong surface activity. So, the compactness of surfaces, which might correspond to their mechanical properties, was growing higher with the increasing content of Si sol.

On the other hand, the large apertures were present on the fractured surfaces of Si2, Si4, and Si6 (Fig. 2 B, C, and D), whereas Fig. 2 E and F images only showed the silica particles tended to form clusters and the aggregation phenomenon without apertures. This might be attributed that the apertures on the fractured surfaces which were becoming smaller and smaller with the increasing content of Si sol were filled by the Si sol. In summary, the microstructures of ULDFs were affected by the different content of Si sol.

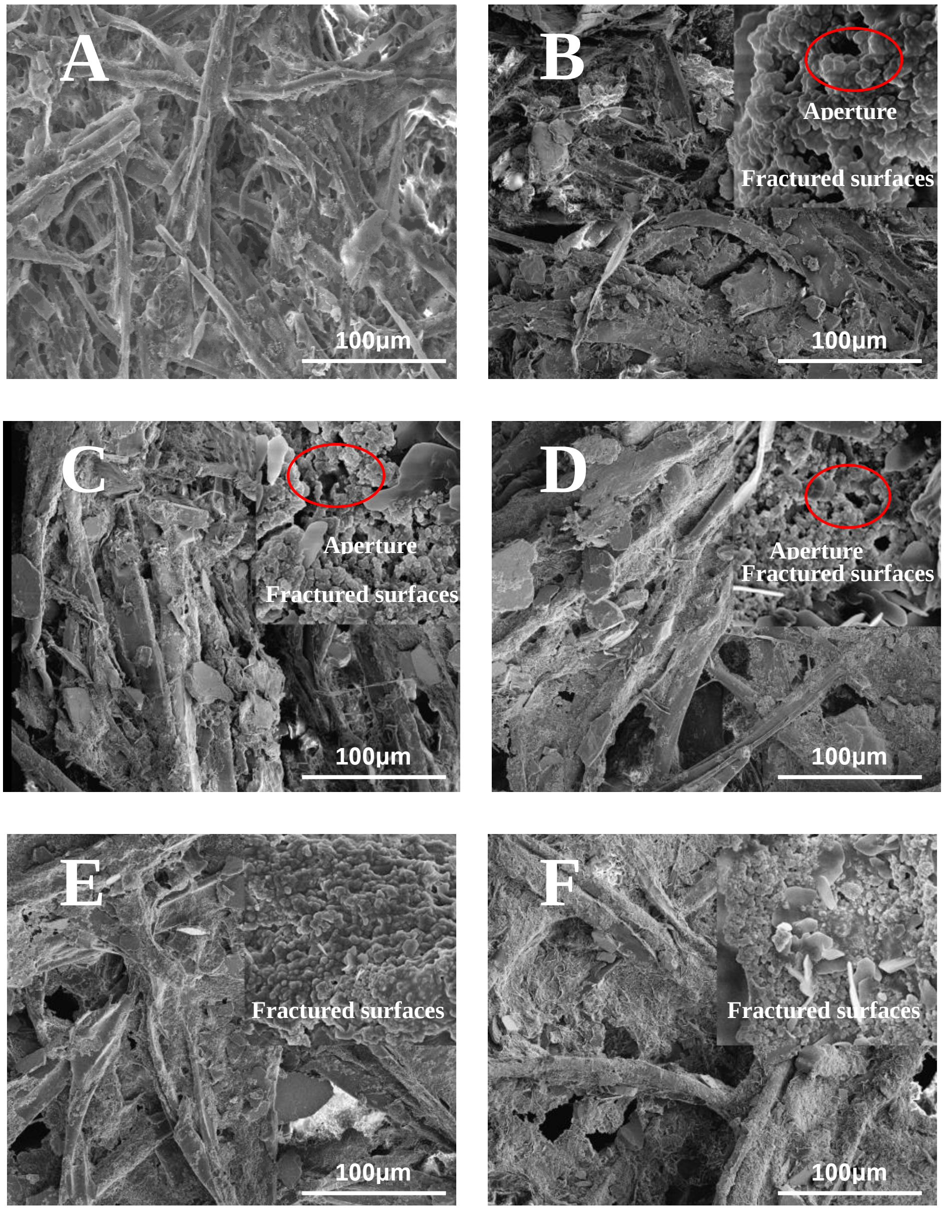

Fig. 2. SEM images of the fiberboards with different contents of Si sol: A(Si0), B(Si2), C(Si4), D(Si6), E(Si8), and F(Si10), respectively

Thermostability of ULDFs

Thermogravimetric analysis (TGA) was used to evaluate the thermostability of ULDFs and the effect of Si sol. The TGA and differential thermogravimetric (DTG) curves of control specimen and Si sol fiberboards are shown in Figs. 3a and 3b, respectively. The corresponding data, including the onset temperature, the temperature of maximum weight-loss rate ($T_{\max}$), and weight loss (WL), are listed in Table 1. It was evident that the thermostability of ULDFs was affected by the presence of silica sol. As can be seen in Fig.3b, the slight weight loss that occurred below 100 °C was caused by evaporation of imbibed water from the specimens (Vîlcu *et al.* 1985). The onset decomposition temperature of the control specimen was 215.4 °C, which was lower than all of the Si sol specimens, 241.7, 245.6, 244.2, 243.3, and 244.4 °C, respectively (Table 1). This higher degradation temperature for the Si sol specimens could be due to the Si sol component, embedded within and between the fibers. In the present study, TGA also presented the differences in $T_{\max}$ between control specimen and Si sol specimens. The onset of mass loss in the pyrolysis of control specimen was at lower temperature (301.6 °C) than all of the Si sol specimens. In particular, the Si8 specimen (310.9 °C) was nearly 10 °C higher than the control specimen. This might be ascribed to the Si sol, which would retard the formation of laevoglucose and prolong the degradation temperature. However, Table 1 does not show any obvious changes in onset decomposition temperature and T_{max} of Si sol specimens with the increasing content of silica sol.

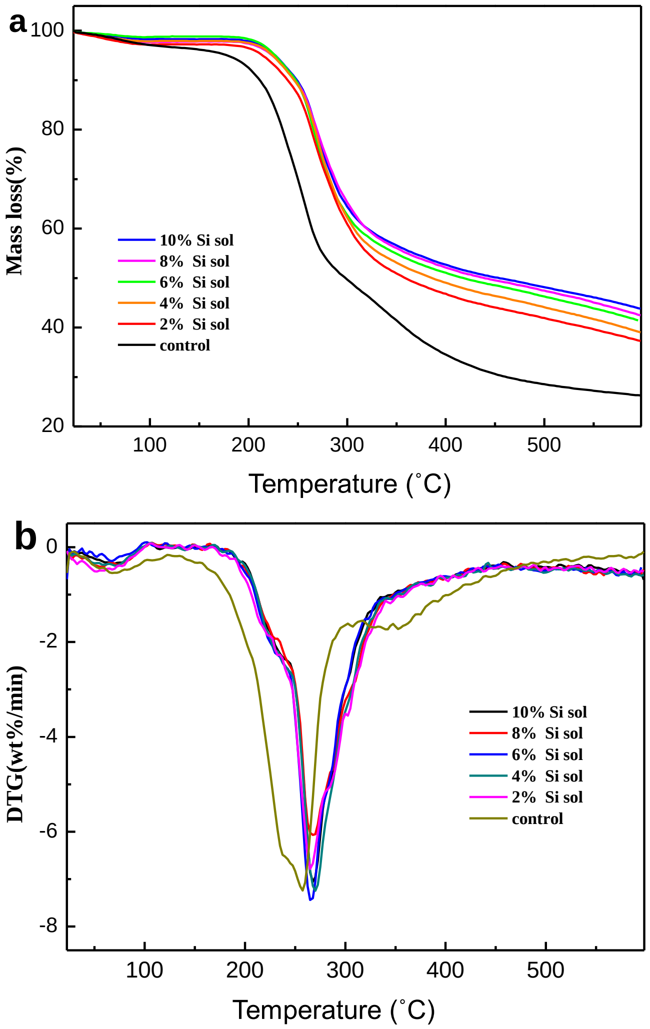

Fig. 3. (a) TG and (b) DTG curves of the control specimen and the Si sol fiberboards with different contents

Table 1. Onset Temperature, Degradation Temperature (T_{max}), and Weight Loss (WL) in the Thermal Degradation Processes of the Different Fiberboards Obtained from the TG and DTG Curves

Sample	Onset temp (°C)	T_{max} (°C)	WL (%)
Control specimen	215.4	301.6	73.73
2% Si sol	241.7	310.7	62.73
4% Si sol	245.6	304.9	61.00
6% Si sol	244.2	302.4	58.56
8% Si sol	243.3	310.9	57.55
10% Si sol	244.4	304.3	56.23

As can be seen in Fig. 3a and Table 1, the total weight loss of Si0 (73.73%) was 11 percent higher than the total weight loss of Si2 (62.73%). And, the total weight loss of Si sol fiberboards decreased with the increasing content of silica sol. They were 62.73% (Si2), 61.00% (Si4), 58.56% (Si6), 57.55% (Si8), and 56.23% (Si10), respectively. Because the remainder weight of the specimen was inorganic fillers and charcoal, this could be explained that why the residual weight values of ULDF were increased with the increasing content of silica sol. Combined TGA with DTG results, it could be concluded that the thermostability of ULDFs was improved by Si sol. This phenomenon could be explained by the following reasons. On the one hand, incorporation of Si sol into the fibers lumens might hinder the release of volatile gases and thus reduce the combustibility. When ULDF was heated, combustible gases were released from the cell wall and exited the ULDF network structure through the hole to burn outside material. On the other hand, the increased density might cause a higher heat capacity; or silica sol incorporated into the lumen might increase the thermal conductivity of the fiber. So, more energy was needed to heat the material which resulted in an improvement in the thermostability of ULDFs.

Mechanical Properties of ULDFs

The bulk densities of specimens are shown in Table 2. The values were raised with the increasing of the Si sol. The bulk density of control specimen was only 55.02 kg·m^{-3} which was lower 13.0% and 22.1% than that of Si2 and Si10, respectively. This was due to the residual Si sol in ULDF. This result coincided with SEM and TGA illustration. Additionally, the densities of Si sol specimens were not increased with the increasing content of Si sol.

Table 2. Bulk Density of the Specimens

Sample	Si0	Si2	Si4	Si6	Si8	Si10
Bulk Density (kg m^{-3})	55.02 (±1.81)	62.20 (±2.43)	63.01 (±1.43)	63.84 (±0.87)	64.47 (±1.42)	67.20 (±1.05)

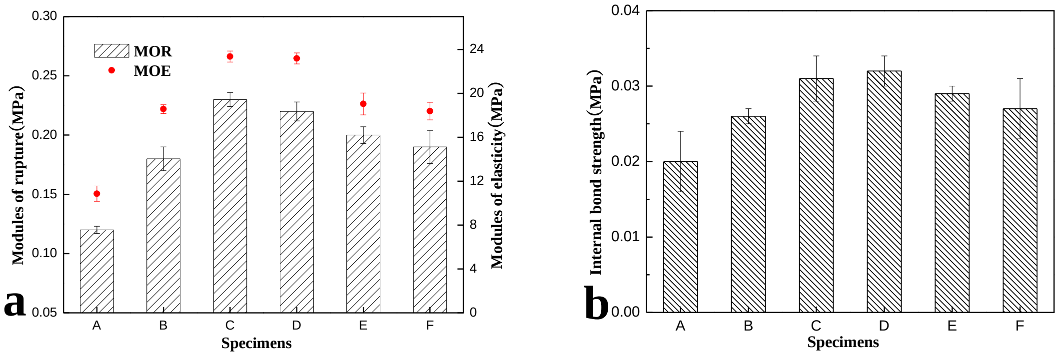

Fig. 4. (a) MOE and MOR and (b) internal bond strength of the control specimen (A) and the fiberboards with different contents of Si sol: A(Si0), B(Si2), C(Si4), D(Si6), E(Si8), and F(Si10), respectively

The results of MOE, MOR, and IB testing are shown in Fig. 4. As shown by the experiments, the MOR, MOE, and IB of B were 0.06, 7.71, and 0.006 MPa higher than A, respectively. Comparing C to A, the MOR, MOE, and IB were increased by 91.7%, 115.1%, and 55.0%, respectively. It was confirmed that the mechanical properties of ULDF had improved by the Si sol. As depicted in Fig. 4a, the MOR and MOE increased first and decreased later. The amount of energy required for fracture increased when only 4% amounts of Si sol were incorporated in the ULDF. But the MOR and MOE were decreased with the increasing content of Si sol when it was over 4%. This is because the Si sol is inorganic filler, which could make the material become brittle. The lower modulus of the material is, the more fragile will be the material (Lin *et al.* 2013). So the ULDFs were fragile materials when excess Si sol was added.

From another aspect, when the silica content was 6%, its maximum IB was 0.032 MPa. It climbed with the increasing of the Si sol mass fraction when the amounts were over 6%. The incorporation of the silica nanoparticles in the ULDF had a notable effect on their IB strength. This was due to the strong surface activity of hydrogen groups on the surface of silica particles which could mix and react with fibers and form hydrogen bonds to construct a mesh structure in the system could improve the interconnection between fibers (Labarre *et al.* 2002). Thus, the IB strength was increased when the content of Si sol was lower than 6%. However, the redundancy of Si sol would make the IB of ULDF decreased. When a lot of Si sol was added in system, it not only led to the formation of clusters and aggregation phenomena of the silica particles, but it also influenced the opportunity of interconnection between fibers.

In summary, the introduction of Si sol was beneficial to improve mechanical properties of ULDFs. This was due to the covalent or physically crosslink interaction between fibers and nano fillers, which is available to the improved the energy dissipation mechanism compared to the pure hydrogen bonding cross-linked interaction between fibers.

CONCLUSIONS

As reported in this article, ULDFs were successfully prepared through adding Si sol as the inorganic filler. The investigation on the thermostability and mechanical properties of ULDF demonstrated the fact that Si sol played an important role in the thermostability and mechanical properties of the ULDFs. The properties were affected by different content of Si sol. Micromorphology analyses indicated that some Si sol particles were left on the surface of fibers, leading to the improvement of interfacial adhesion between fibers and inorganic fillers. Additionally, the ULDF showed improved thermostability and mechanical properties, which could expand its application as value-added product.

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