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RESEARCH ARTICLE

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Property of nano-SiO_2/urea formaldehyde resin

Abstract In this paper, we discuss the effects of a nanometer silicon dioxide (nano-SiO_2) coupling agent, dispersal methods and the amount of nano-SiO_2/urea formaldehyde resin. The results of our study indicate that when nano-SiO_2, using KH-550 silane as a coupling agent, was added to UF resin by discontinuous ultrasonic vibration, its properties improved effectively. When the content of nano-SiO_2 was below 1.5%, the amount of free formaldehyde decreased, and the viscosity and bonding strength of resin increased with an increase in the added nano-SiO_2, which did not prolong the curing time. The performance indices of plywood, particleboard and medium density fiberboard (MDF), hot-pressed by nano-SiO2 (1%)/UF resin (F/U molar ratio=1.2), exceeded the requirements of the National Standard. Their free formaldehyde emission reached E1 grade. Finally, we analyzed the mechanism of the strengthening effects of nano-SiO_2 on UF resin by means of infrared spectrum analysis and X-ray photoelectronic spectrum (XPS).

Keywords nanometer silicon dioxide, urea formaldehyde (UF) resin, bonding strength, free formaldehyde, X-ray photoelectronic spectrum (XPS)

1 Introduction

The study and applications of urea formaldehyde (UF) resin have a history of more than 100 years. Owing to its low cost, simple synthetic technique, and a certain water-resistant bonding strength, UF is one of the main glues used in wood industries so far (Tang, 2002). It contains free formaldehyde and its amount is directly proportional to its bonding strength. UF resin with a small amount of free formaldehyde can be produced by a low F/U molar ratio, but if the molar ratio was excessively lowered, bonding strength and the other properties of resin would deteriorate (Gu, 1999). The products bonded with UF resin still cause free formaldehyde emissions (F-emissions), which pollute the environment and harm people’s health (Levendis, 1992). Consequently, lowering the amount of free formaldehyde in UF resins and enhancing bonding strength have become the focus of study for many scientists.

Fillers have a modifying effect on the properties of UF resin (Du, 1995; Liang, 1996). But the fillers formerly used are all particles with sizes above micron grade, which have only small modifying effects. Nanoparticles with small diameters are surrounded by many atoms on the surface, which lack adjacent atoms and have dangling bonds and unsaturated properties. It easily combines with other atoms to become stable. Chemical activities of nanoparticles are excellent (Cao et al., 2001). Given this property, our test introduces nanometer silicon dioxide (nano-SiO_2), to be added to UF resin, which obtains favorable modifying results. The study focuses on the effects of nano-SiO_2 surface treatment, dispersal methods, and its effect on the properties of UF resin. We applied nano-SiO_2/UF resin to press panels and analyzed the mechanism of the strengthening effects of nano-SiO_2 on UF resin by means of infrared spectrum analysis and X-ray photoelectronic spectra (XPS).

2 Materials and methods

2.1 Experimental material

Both urea and formaldehyde are commercial products. The content of nano-SiO_2 was 99%, the average diameter of particles 20 nm and the specific surface area 440 m^2/g. There are four kinds of nano-SiO_2: 1) NMSi–0, non-surfacing; 2) NMSi–A, using a 1% KH-550 silane coupling agent for treatment (molecular formula

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$NH_2(CH_2)_3Si(OC_2H_5)_3$); 3) NMSi–B, using a 1% KH792 silane coupling agent for treatment (molecular formula $NH_2(CH_2)NH(CH_2)_3Si(OCH_3)_3$); 4) NMSi–C, using a 1% KH-570 silane coupling agent for treatment (molecular formula $CH_2=C(CH_3)COO(CH_2)_3Si(OCH_3)_3$). The veneer sheets, and rotary cutting sheets of Chinese red pine, were selected from the Sanming Plywood Factory, Fujian Province. The thickness was 1.3 mm and the moisture content was 8%–12% after drying. Wood particles were selected from the Particle Board Factory, Dazhou Timberyard, Nanping, Fujian Province. The ratio of pine to sundry wood was 7:3. Particles were 10–15 mm long, 2–3 mm wide, and 0.15–0.3 mm thick. Fibers were selected from the Yong'an Medium Density Fiberboard (MDF) Factory, Fujian Province. The ratio of pine to sundry wood was 6:4 and fiber resolution was about 11 s. Wood particle and fibers were dried to 5% moisture content for further use.

2.2 Preparation of UF resin

The molar ratio of F/U was 1.05–1.30. We adopted an alkali-acid-alkali technique and applied three-times condensation. Formaldehyde and urea, applied for the first time, were conditioned with alkalescence at 90ºC for a period of time. Then, with the condition of weak acid, the reaction dropped to a definite temperature. After that, we applied urea for a second time. When the reaction terminated, we applied urea for a third time.

2.3 Analysis of resin properties

The usual properties were analyzed according to National Standards GB/T 14074–93; bonding strength of 3-layer plywood pressed was tested according to National Standards GB/T 9846–2004 for plywood Ⅱ.

2.4 Preparation of boards

Preparation of boards was accomplished in the laboratory. The dimensions of the plywood were 300 mm×300 mm×3.5 mm; the amount of prepared adhesive per unit area of wood surfaces (double spread) was 350 g/m. Hot-pressing technique: the temperature was 115±5ºC, pressure 0.97 MPa, and time 3 min. The dimensions of the particleboard were 360 mm×360 mm×10 mm and the amount of adhesive added was 10%. Hot-pressing technique: the temperature was 165±5ºC, the pressure 2.5 MPa, and pressing time 5min. The dimensions of the MDF were 360 mm×360 mm×10 mm and the amount of adhesive added was 12%. Hot-pressing technique: the temperature was 170±5℃, the pressure 2.8 MPa, and pressing time was 5 min.

2.5 Test of panel properties

According to the National Standards GB/T 9846–2004, GB/T 4897–2003, GB/T 11718–1999, and GB 18580–2001, the ultimate quantitative analysis of F-emissions was achieved by the method of acetylacetone.

2.6 Infrared spectrum analysis

For the infrared spectrum analysis, we used the following equipment: FOURIER AVATAR 360 (NICOLET, Inc, USA). Method: the powder sample was scanned after tabletting with KBr.

2.7 Analysis of XPS

For X-ray analysis, we used a QUANTUM 2000 SCANNING ESCA MICROPROBE X-ray (XPS) (PHYSICAL ELECTRONICS. Inc, USA). The based lowest degree of vacuum in the analysis room was above 5×10^{-8} Pa. The excitation source was a monochrome Al anode barn with energy of 1,458.8 eV, the X-ray beam spot 100 μm and power of 25 W. Method: after tabletting, the powder sample was submitted to the equipment for vacuum and scanning treatment.

3 Results and discussion

3.1 The effects of nano-SiO_2 coupling agent on the properties of UF resin

The properties of UF resin with F/U ratio 1.2, mixed with NMSi–0, NMSi–A, NMSi–B, and NMSi–C by discontinuous ultrasonic vibration are listed in Table 1.

From the results shown in Table 1, it can be seen that the properties of UF resin improved after the surface of nano-SiO_2 was incorporated with a silane coupling agent. Because of the active surface and high surface energy of the nanoparticles, they are apt to congregate (Pampach and Haberkc, 1983; Xu and Zhang, 2002). This aggregation can either be softened for intermolecular forces or hardened for bonding forces; the former can be dispersed again under an exterior force, while the latter cannot. In addition, the surface energy of UF resin is relatively low and incompatible with nano-SiO_2. When UF resin and nano-SiO_2 were mixed, the mixture was not easy to dissolve. Therefore, the properties of the UF resin, modified by NMSi–0 whose surface is not incorporated with a silane coupling agent, are relatively weak. Because there are two kinds of functional groups in the structure of silane coupling agents (Wang et al., 2002), these functional groups can decrease the surface energy of inorganic matter (nano-SiO_2) and improve its compatibility with UF resin. Thus, the dispersion of nano-SiO_2 and its compatibility with UF resin improved after incorporation with the silane coupling agent. However, the modified effects varied for different silane coupling agents (Yang et al., 2004a). From our experiments, it can be seen that the silane coupling agent KH-550 had the best effect. The UF resin, modified by this NMSi–A, had the lowest amount of free formaldehyde and the highest bonding strength.

Table 1 Effect of nano-SiO_2 surface treatment on properties of UF resin

Nano-SiO_2 with different coupling agents	Content of free formaldehyde /%	Bonding strength /MPa
W*	0.31	0.82
NMSi–0/UF	0.27	0.95
NMSi–A/UF	0.18	1.28
NMSi–B/UF	0.22	1.08
NMSi–C/UF	0.22	0.97

The mark* denotes pure UF; the F/U molar ratio is 1.2, the same as in Table 2.

3.2 The effects of nano-SiO_2 dispersal methods on the properties of UF resin

In our experiments, the F/U molar ratio is 1:2 and the NMSi–A was added to the UF resin by six different methods. A: during the prophase of synthesizing UF resin (addition reaction phase); B: during the anaphase of synthesizing UF resin (after the end-point); C: mix NMSi–A and UF resin by mechanically stirring at the speed of 120 r/min; D: mix NMSi–A and UF resin by mechanically stirring at the speed of 1,000 r/min; E: mix NMSi–A and UF resin by continuous ultrasonic oscillation for 10 min; F: mix NMSi–A and UF resin by discontinuous ultrasonic oscillation for 10 min (alternately 30 s oscillation with a 30 s pause). The results are shown in Table 2.

Table 2 Effect of nano-SiO_2 dispersal methods on properties of UF resin

Nano-SiO_2 with different dispersal methods	Content of free formaldehyde /%	Bonding strength /MPa
W	0.31	0.82
A	0.32	0.80
B	0.28	0.99
C	0.25	1.10
D	0.20	1.18
E	0.22	1.16
F	0.18	1.28

From Table 2, it can be seen that when nano-SiO_2 was added to UF resin during the prophase of synthesis, the properties of the UF resin could not be improved. Because nano-SiO_2 participated in polymerization, which made the cross degree of UF resin insufficient, the amount of free formaldehyde increased and bonding strength decreased. When the nano-SiO_2 was added to the UF resin during the anaphase of the synthesis, the property of UF resin improved a little. Because it partly cross-linked with the active groups and free formaldehyde in the earlier resin, which increased the intermolecular force, the amount of free formaldehyde decreased and bonding strength increased. But nano-SiO_2 is apt to aggregate at a high temperature. Therefore, dispersal method B improved the properties of UF only by a small amount. The four dispersal methods C, D, E, and F improved the properties of the UF but each to a different extent. Among the four methods, the high rotation speed made nano-SiO_2 easy to disperse evenly and its effect was better than that of a low rotation speed, while the method of ultrasonic oscillation was better than that of mechanical mixing, especially F (the discontinuous ultrasonic oscillation) with the best effect. When the nano-SiO_2 was added to the UF by discontinuous ultrasonic oscillation, which produced cavitation in the mixture system (Xu and Zhang, 2002), a violent oscillating wave erupted along with the formation and cracking of tiny air bubbles and released energy. It brought about a short-lived microenvironment with high energy, weakened inter-nanoparticle bonding forces, prevented nanoparticles from aggregating and made nano-SiO_2 to be dispersed evenly. When nano-SiO_2 was added to UF by continuous ultrasonic oscillation, its microenvironment with high energy could easily bring about a partial high temperature, a partial high pressure, violent shock waves, and micro jets. If the oscillation time was too long, the probability of colliding with each other among the particles increased, which made the nanoparticles congregate again. Therefore, the effect of the E dispersal method was weakened. In conclusion, when the nano-SiO_2 was added, the UF by discontinuous ultrasonic oscillation at room temperature after the UF was synthesized, the UF, modified by nano-SiO_2, had the lowest amount of free formaldehyde and the highest bonding strength.

3.3 Effects of nano-SiO_2 content on properties of UF resin

The properties of modified UF resin whose F/U molar ratio were 1.30, 1.25, 1.20, 1.15, 1.10, 1.05, mixed with 0, 0.5%, 1.0%, 1.5%, 2.0% NMSi–A, respectively by discontinuous ultrasonic oscillation, are shown in Fig. 1.

Fig. 1A shows that the bonding strength of the modified UF resin decreased with F/U molar ratio decreasing, increased with an increasing amount of nano-SiO_2 under the condition of the same F/U molar ratio. When the nano-SiO_2 amount was over 1.5% of the UF resin, the bonding strength of the modified UF resin no longer improved. The lower the F/U molar ratio, the more obvious were the effects of the amount of nano-SiO_2 on the bonding strength of the modified UF resin. When the F/U molar ratio was 1.05% and 1.5%, nano-SiO_2 was added, the bonding strength of the modified UF resin improved from 0.42 to 0.87 MPa, nearly twice the bonding strength of pure UF resin. In general, the lower F/U molar ratio, the less the crossing degree of the modified UF resin and the weaker the bonding strength of pure UF resin. However, when the nano-SiO_2 was added, due to its surface effects, small size effects for its insufficient surface atoms and high reactivity, it could easily cross with the active groups of pure UF resin and improved cohesion and bonding strength of the modified UF resin. Those advantages did not apply to the general filler.

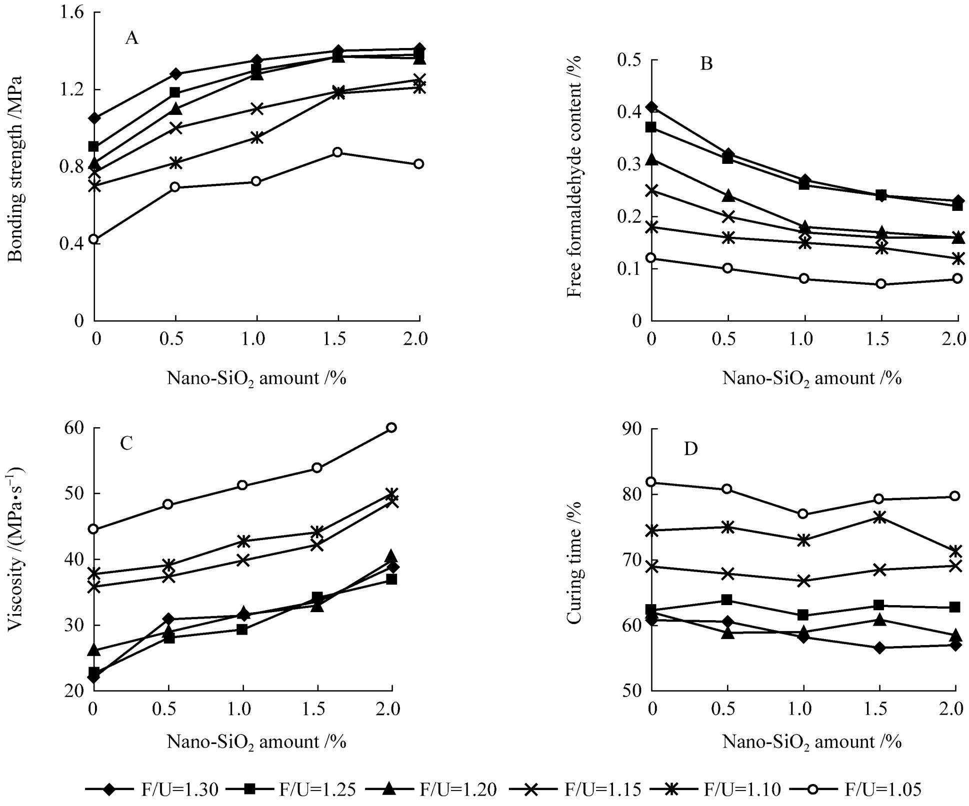


Fig. 1 Effect of nano-SiO_2 dosage on properties of UF resin

Fig. 1B shows free formaldehyde of the modified UF resin increased with an increase in the F/U molar ratio. The amount of free formaldehyde of the modified UF resin gradually reduced with the amount of nano-SiO_2 increasing at the same the F/U molar ratio. When the amount of nano-SiO_2 was more than 1.5% of pure UF resin, the amount of free formaldehyde no longer decreased. Therefore, the higher the F/U molar ratio, the more obvious the effects of the increase of nano-SiO_2 on the decrease in the amount of free formaldehyde. Because nano-SiO_2 has very strong absorbability, the nano-SiO_2 particles can react with the active groups of the pure UF resin and absorb free formaldehyde, the amount of free formaldehyde of the modified UF resin was reduced.

Fig. 1C shows that the viscosity of the modified UF resin increased with increasing amounts of nano-SiO_2. Because hydrogen bonding or van der Waals forces were formed between nano-SiO_2 and the hydroxy, amido of the pure UF resin, the intermolecular forces were increased, the resistance inside the liquid, which counteracted their relative fluxion, increased, so that the viscosity also increased (Yang et al., 2004b). Within our chosen experimental range, the increased viscosity could not yet affect the operating performance of the modified UF resin. In fact, the opposite occurred. It could prevent too much of the adhesive from filtering into the wood to create the phenomena of permeation or inadequate bonding so that the dosage of general flour additive could be reduced.

Fig. 1D shows that the time for curing the modified UF resin was hardly affected by the amount of nano-SiO_2. So the hot-press conditions of the modified UF resin need not be altered.

3.4 Pressing different kinds of wood-based panels using nano-SiO_2/ UF resin

UF resins G–0 and H–0 were prepared by using molar ratios (F/U) 1.2 and 1.1 separately. One percent NMSi–A was added to UF resins G–0 and H–0 separately by a discontinuous ultrasonic vibration method, which produced nano-SiO_2/UF resins G–1 and H–1. These four kinds of resins were used to press plywood, particleboard and MDF. The property indices of the panels are presented in Table 3. Table 3 shows that the strengths of the panels can meet the

National Standard, but the F-emission only reached the E_2 grade when using pure UF resin with a F/U molar ratio of 1.2 to press wood-based panels; the strength of the panel could not meet the National Standard when the F/U molar ratio was 1.1; the strength of each of the panels exceeded the National Standard and the F-emission reached the E_1 grade when adding 1% nano-SiO_2 in the UF resin with a F/U molar ratio of 1.2. The property indices of the panels improved to some extent, while they fluctuated around the critical value of the National Standard when the F/U molar ratio was 1.1. So it is difficult to ensure the manufacture of eligible products when the F/U molar ratio is 1.1. The result of the test indicates that all the physical and mechanical property indices of the different panels, which were produced using nano-SiO_2 (1%)/UF resin with F/U molar ratio of 1.2, can meet National Standards and the F-emission can attain the E_1 grade.

Table 3 Properties indices of wood-based panels

Board kinds	Resin kinds	Bonding strength /MPa	Formaldehyde emission*	Bending strength /MPa	Thickness expansion ratio after water absorption /%	Density /($kg·m^{-3}$)
Plywood	G-0	0.82	7.55			
	G-1	1.28	1.23			
	H-0	0.70	6.93			
	H-1	0.95	0.71			
Particle board	G-0	0.48	18.21	16.8	5.19	702
	G-1	0.63	5.17	18.5	2.98	695
	H-0	0.33	12.78	14.8	6.01	696
	H-1	0.42	3.22	15.7	4.45	697
Medium density fiberboard	G-0	0.73	22.09	24.83	7.94	703
	G-1	0.97	8.58	25.22	7.00	718
	H-0	0.55	10.16	16.37	9.98	712
	H-1	0.68	4.97	22.80	8.20	709

* Units of formaldehyde emission: plywood mg/L; particle board and medium density fiberboard mg/100g.

3.5 Infrared spectroscopic analysis

Small amounts of UF resin and nano-SiO_2/UF resin (3:100) were dried to become solid for 2 h under conditions of 40–50ºC and a degree of vacuum 0.095 MPa. Two kinds of powders were obtained by grinding these solids. After a small amount of nano-SiO_2/UF resin (3:100) dried to become solid at 115ºC, powder was obtained by grinding this solid. Fig. 2 shows the result of infrared spectrum analysis from NMSi–A and the three samples mentioned above (Wang, 1989).

Spectrum A in Fig. 2 shows the infrared spectrum of nano-SiO_2. There is a big dome peak, which is a hydroxy peak at 3,444.27 cm^{-1}. It indicates that there are abundant hydroxyls on the surface of nano-SiO_2. The highest absorption peak occurs at 1,094.67 cm^{-1}, which is the assymmetric flexing vibration of the Si–O–Si bond in the amorphous nano-SiO_2. The absorption peak of symmetrical flexing vibration of Si–O–Si bond was at 796.37 cm^{-1}.

Spectrum B in Fig. 2 shows the infrared spectrum of pure UF resin. Intermolecular hydrogen bonds of hydroxyl and hydroxyl, hydroxyl and amido, and amido and amido form in UF resin molecules. This resulted in an associative phenomenon, the absorption peaks of flexing vibration of O–H and N–H to move in the direction of low frequencies, and a broad and strong absorption peak occurred at 3,354.37 cm^{-1}. The flexing vibration of the C–H of methylene occurring at 2,958.00, 1,654.48 and 1,544.15 cm^{-1}, are acylamino absorption bands; the bands 1,384.79 cm^{-1} and 1,249.94 cm^{-1} are the deformation vibrations of the plane of methylene; the band 1,131.44 cm^{-1} is the absorption band of ether linkage of CH_2OCH_2 and 1,008.85 cm^{-1} absorption band of the methylol of CH_2OH.

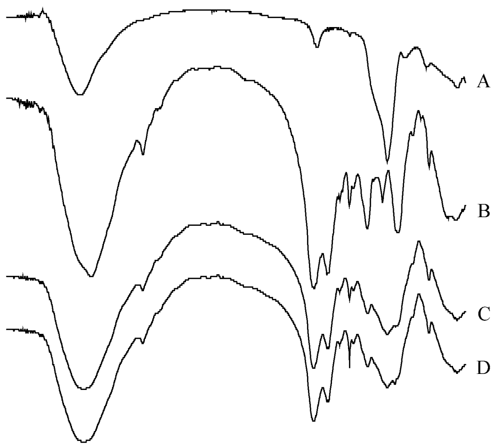


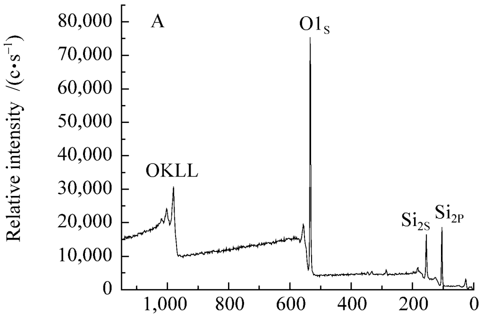
Fig. 2 FTIR spectra of samples

Spectrum C in Fig. 2 shows that there were absorption peaks of nano-SiO_2 and the main characteristic groups of UF resin in the infrared spectrum of the nano-SiO_2/UF resin mixture.

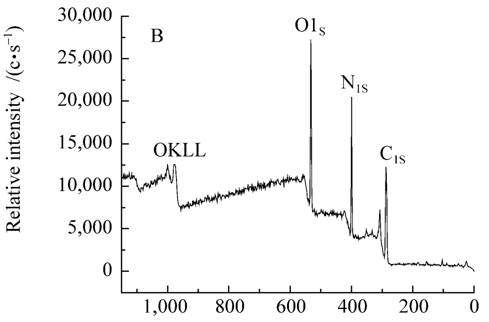
Spectrum D in Fig. 2 shows the infrared spectrum of the reactant of nano-SiO_2/UF resin. The deformation vibration peak of methylene is very obvious at 1,380.70 cm^{-1} compared with C in Fig. 2, which indicates a further poly-condensation reaction in UF resin at a high temperature. In addition, an aiguillette absorption peak at 1,041.54 cm^{-1} occurred near 1,094 cm^{-1}. Will the UF resin react with nano-SiO_2 and form the C–O–Si bond? Since the force constant of C–O–Si is similar to that of C–O–C, the question could be answered by further XPS spectra.

3.6 XPS analysis

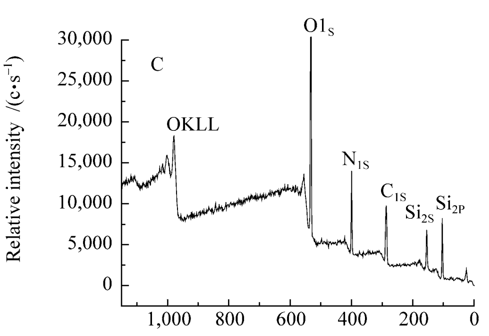
The sample process is similar to 2.5. Fig. 3 shows the total element analysis of the sample surface by XPS analysis (Wu, 2002) of NMSi–A, pure UF resin, and nano-SiO_2/UF resin at an 115ºC process. Table 4 shows the bonding energy and chemical state of every element, and Fig. 4 shows the narrow element section of the spectrum of O (oxygen) by setting the scanning area of the narrow element section of the spectrum according to a total analysis.



A. XPS survey spectra of nano-SiO_2

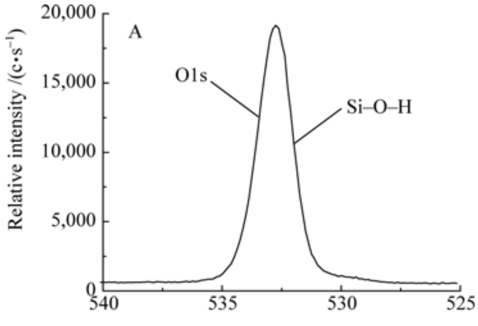


B. XPS survey spectra of UF resin

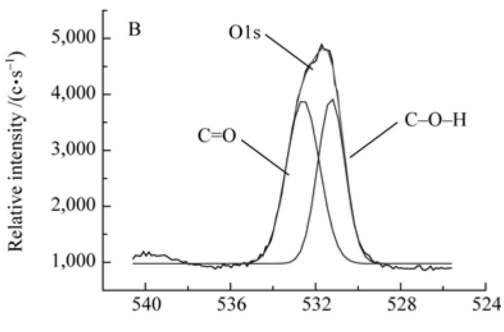


C. XPS survey spectra of nano-SiO_2/UF resin

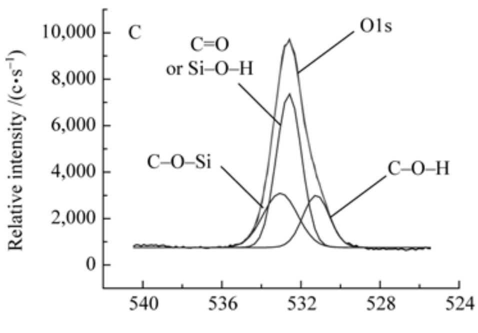
Fig. 3 XPS survey spectra of the samples



A. O1s spectra of nano-SiO_2



B. O1s spectra of UF resin



C. O1s spectra of nano-SiO_2/UF resin

Fig. 4 O1s spectra of the samples

Fig. 3 shows that there were two major elements of Si and O in nano-SiO_2, three main elements of C, N, and O in UF resin and four main elements of C, N, Si, and O in nano-SiO_2/UF resin.

There were some C–O–Si bonds. The initial chemical states of nano-SiO_2 and UF resin remained after nano-SiO_2 was added to the UF resin and reacted at a high temperature (115ºC) by analyzing the narrow section of each sample of the spectrum from Table 4 (Moulder et al., 1995). The results can be seen more directly by the contrast of the XPS spectrograms of O1s in every sample. This result indicates that both physical adsorption and a combination of chemical bonds exist between nano-SiO_2 and UF resin. It is the main reason that a small amount of nano-SiO_2 can improve the UF resin's bonding strength and reduce the amount of free formaldehyde.

Table 4 Bonding energy and chemical state of elements in different samples

Sample	Element	Bonding energy /eV	Chemical state
Nano-SiO_2	Si	103.4	Si–O
	O	532.7	Si–O–H
UF resin	C	284.8	C–H
		286.1	C–O
		287.1	C–N
		288.8	C=O
	O	531.3	C–O–H
		532.6	C=O
	N	399.7	C–N
Nano-SiO_2/UF resin	C	284.8	C–H
		285.8	C–O
		286.8	C–N
		288.7	C=O
	O	531.3	C–O–H
		532.6	C=O, Si–O–H
		533.3	C–O–Si
	N	399.6	C–N
	Si	103.3	Si–O

4 Conclusions

When nano-SiO_2, using a 1% KH-550 silane coupling agent for surface treatment, was added to UF resin by discontinuous ultrasonic vibration, this nano-SiO_2/UF resin had the best properties.

The amount of nano-SiO_2 has variable effects on the performance of UF resins with different F/U molar ratios. Under the condition of the same F/U molar ratio, when the amount of nano-SiO_2 was below 1.5%, the amount of free formaldehyde decreased, bonding strength increased with the increase of the added nano-SiO_2. The lower the molar ratio of F/U, the more obvious the effects of nano-SiO_2 on enhancing bonding strength. The higher the molar ratio of F/U, the more obvious the effects of nano-SiO_2 on lowering the amount of free formaldehyde. By increasing the amount of nano-SiO_2, the viscosity of resin increased. But within the scope of our experiment, the increase of viscosity did not affect the processing properties. On the contrary, it could avoid a squeeze-out and reduce the amount of common filler. The amount of nano-SiO_2 had little effect on curing time, and so it was not necessary to change the hot press conditions.

When the F/U molar ratio of UF resin was 1.2 and nano-SiO_2 (1%) was added to UF resin by discontinuous ultrasonic oscillation, we used this nano-SiO_2/UF resin to press plywood, particleboard and MDF. The physical and mechanical property indices of the panels meet the demands of the National Standard and their F-emission reached the E1 grade.

There were many hydroxide groups on the surface of nano-SiO_2, which could be seen from infrared spectrum analysis. The reactant of nano-SiO_2 and UF resin presented a band absorption peak at 1,041.54 cm^{-1}. The reason is that nano-SiO_2 probably had reacted with UF resin.

XPS analysis indicated that the O1s bonding energy and chemical condition of the reactant of nano-SiO_2 and UF resin had changed and there are C–O–Si bonds. From this, we can conclude that nano-SiO_2 has reacted with UF resin, which is the main reason why a small amount of nano-SiO_2 was able to increase the bonding strength of UF resin and decrease F-emissions.

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