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Properties of phenol formaldehyde resin modified with silane coupling agent (KH550)

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Abstract: In the present work, the organic silane coupling agent KH550 (γ -aminopropyltriethoxysilane) was added in the preparation of phenol formaldehyde (PF) resin by direct copolymerization. Such an addition modified the thermosetting low molecular weight PF resin, blocking the phenolic hydroxyl and improving its electrical insulation performance in humid environments. The volume resistance and bonding strength of the resins were tested before and after soaking in hot water. The improvement of the properties was studied in terms of resin composition and curing behavior. A common PF resin and a commercial insulation PF resin were used for the comparison. The results showed that KH550 was grafted onto the PF resin, effectively blocking the polar phenolic hydroxyl group, reducing the water absorption and increasing the volume resistance of the cured PF resin. The preparation process was simple and the prepared resin was water-soluble. The low molecular weight PF resin modified with 5% in mass of KH550 (based on the mass of phenol) exhibited better curing properties and superior volume resistance and bonding strength in humid environments.

Keywords: phenol formaldehyde resin, silane coupling agent, electrical insulation performance, hot water soaking

1. Introduction

Phenol formaldehyde (PF) resin is widely used as coating, adhesive, and foam material due to its many advantages, such as the good mechanical and electrical insulation property, durability, and heat and flame resistance, producing low amounts of smoke during burning [1–2]. PF resin is an indispensable polymer material in electronic appliances, automobiles, residential applications, aerospace industry and military [3–6]; however, the resin is constantly modified to meet the changing requirements of high-tech applications.

The curing reaction of the PF resin mainly occurs among hydroxyl-methyl groups linked by methylene; thus, the chain possesses polar phenolic hydroxyl groups [7]. When PF resin is used as an electrical insulator, the phenolic hydroxyl tends to absorb atmospheric moisture, resulting in a decrease of the electrical properties, as well as the physical and mechanical properties [8]. In order to decrease the absorption of water, it is necessary to block the phenolic hydroxyl groups. The most commonly used modifiers achieve this through either a chemical reaction or physical blending with the phenolic hydroxyl.

Organo-silicones have been commonly used as modifying agents due to their environmental friendliness, non-toxicity, low tendency towards water absorption, and high thermal stability and flexibility [9]. Li et al. incorporated 4,4'-bis(3-dipropyl-tetramethyldisiloxane)-bis-2-methoxyphenol (SIE) when preparing novolac, in order to make sisal fiber reinforced phenolic composites. The authors showed that the water resistance and electrical properties were improved [10]. In another work, 4,4'-bis(1,3-diphenyl-1,1,5,5-tetramethyltrisiloxane)-bis-2-methoxyphenol was used to modify the PF resin. The resulting resin had lower flexibility and higher viscosity than the one modified with SIE [11]. Qi et al. used phenyltrimethoxysilane in the preparation of the PF resin to improve the thermal properties and curing behavior of the PF

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resin [10]. In published research, most silicone modified PF resins were either alcohol-soluble or thermoplastic and the modification process was complex, requiring, for example, vacuum dehydration and alcoholysis [10–13].

Another organic silicon polymer that has been used to modify resins in such a way as to improve the thermal, mechanical, and insulating properties, as well as increasing moisture resistance is γ -aminopropyltriethoxysilane [14,15]. Nonetheless, its use in the modification of a thermosetting PF resin has been rarely reported.

In the present study, γ -aminopropyltriethoxysilane was used to modify a low molecular weight PF resin with the aim of improving its electrical properties and bonding strength. This PF resin was prepared by a simple process in an aqueous state which is environmentally safer in comparison to alcohol-based PF resins. The volume resistance and bonding strength of resins were measured before and after hot water soaking. The resin composition and curing behavior were studied to gain an insight into the improvements of the material properties observed.

2. Materials and methods

2.1. Materials

Formalin (w/w 37%), phenol and a water solution of sodium hydroxide (w/w 40%) were bought from a commercial producer, Tianjin Kemiou Chemical Reagents Co., Ltd., Tianjin of CHN. The silane coupling agent, γ -aminopropyltriethoxysilane (KH550), was produced by Tianjin Yaohua Chemical Reagents Co., Ltd., Tianjin of CHN. Its molecular formula is $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$.

A commercial insulation PF resin (HK-3150, alcohol-soluble) was produced by Shandong Jining Hongming chemical reagents Co., Ltd., Shandong of CHN. It was used as a control resin for comparison with the unmodified and modified PF resin.

The poplar veneer (2.2 mm thickness, 8%-12% moisture content, density of 0.46 g/cm^3), was provided by Jiangsu Liren Wood Flooring Co., Ltd.

2.2. Preparation of the phenol formaldehyde resin

Preparation of the low molecular weight water-soluble phenol formaldehyde (LPF) resin

Phenol and a water solution of sodium hydroxide were mixed in a three-necked flask and left to react for 10 min after which a part of the formaldehyde was added. The mixture was heated and kept at $80\text{--}85^\circ\text{C}$ for 60 min and cooled to $70^\circ\text{C}\text{--}75^\circ\text{C}$ before adding the remaining formaldehyde. The mixture was then heated again to $80^\circ\text{C}\text{--}85^\circ\text{C}$ and maintained at this temperature for 200 min, finally it was cooled to below 40°C .

Preparation of the KH550-modified low molecular weight water-soluble phenol-formaldehyde (LPF-KH550) resin

The preparation process was similar to that of the low molecular weight water-soluble PF resin. KH550 was introduced into the reaction system after the first batch of formaldehyde was added. The remaining procedure was the same as for the LPF resin. The amount of KH550 was fixed at 3%, 5%, and 8% based on the mass of phenol.

Preparation of the common phenol formaldehyde resin

The common PF resin, a common used adhesive in the wood industry, was prepared as a control for the present study. First, phenol, water, formaldehyde, and sodium hydroxide were

mixed and reacted at 70°C–75°C for 40 min in a three-necked flask. The mixture was then heated to 95°C–98°C, until the viscosity reached 20 s (Tu-4 cup/ 30°C). The liquid was cooled to 70°C–75°C and a second batch of liquid sodium hydroxide and water were added and reacted at this temperature for 30 min. After that, the third batch of formaldehyde and liquid sodium hydroxide were added and left to react for 30 min. The final batch of liquid sodium hydroxide was then added. The flask was heated to 90°C–92°C to further increase the viscosity to 36 s (Tu-4 cup/30°C). The mixture was cooled to below 40°C and the preparation was finished.

2.3. Preparation of the samples

Cured PF resin sample for property test

PF resin (about 10 g) was poured into a glass culture dish (100 mm in diameter, 1–2 mm in depth) and left at low temperature (40°C–50°C) for several days to cure. When a uniform resin sheet was formed, its electrical properties and water absorption were tested.

Plywood for bonding strength test

The prepared PF resin was used to bond plywood. Veneers dried to 7%–9% moisture content were coated on both sides with a PF resin load of $(280 \pm 10) \text{ g/m}^2$. The glued veneers were then laid up and hot pressed at 130°C and 1.2 MPa for 1.2 min/mm. The thickness of plywood was about 6 mm and the area was $300 \times 300 \text{ mm}^2$.

2.4. Performance test for phenol formaldehyde resin

Basic physical properties of the PF resin

The pH value of PF resin was obtained at 25°C with a digital pH meter. The viscosity of PF resin was tested at 30°C with a rotational viscometer. The solid content of PF resin was calculated after the sample was dried at $120 \pm 1 \text{ }^\circ\text{C}$ for $120 \pm 1 \text{ min}$.

Free formaldehyde content and free phenol content were tested according to the corresponding Chinese National Standard “testing method for wood adhesives and their resins” (GB/T 14074-2006). The titrated method was adopted. Free formaldehyde content was calculated from the formula (1), expressed as a percentage by mass:

$$w = \frac{3.003c (V_1 - V_0)}{m} \% \quad (1)$$

Where, w is free formaldehyde content(%), c is the actual concentration of sodium hydroxide solution (mol / L), V_0 is the volume of sodium hydroxide solution consumed in the blank test (mL), V_1 is the volume of sodium hydroxide solution consumed in the sample test (mL), and m is the mass of sample (g).

Free phenol content of the resin was calculated according to formula (2):

$$p = \frac{(V_1 - V_2) \times c \times 0.01568 \times 1000}{m \times 50} \times 100\% \quad (2)$$

Where, P is free phenol content(%), V_1 is the volume of sodium thiosulfate solution consumed in blank test (mL), V_2 is the volume of sodium thiosulfate solution consumed by sample test (mL), c is the concentration of sodium thiosulfate solution (mol/L), m is the mass of sample, (g).

Water absorption of the cured resin

According to the criterion GB/T 1034-2008 (“Plastics-Determination of water absorption”) the cured resin samples from section 2.3 were weighed before and after complete immersion in

boiling water for 30 min. Water absorption (c) was calculated according to formula (3).

$$c=(m_2-m_1) \cdot 100/m_1 \quad (3)$$

Where m_1 is the absolute dry mass of the sample before immersion (g), m_2 is the mass of the sample after immersion (g).

Volume resistance of cured PF resin

According to GB /T 1410-2006 “Solid insulating material volume resistivity and surface resistivity test method”, the samples from 2.3 were tested on a Volume and Surface Resistance Tester (GEST-121, CHN). Sketch of the measurement of the volume resistance is shown in Fig.1.

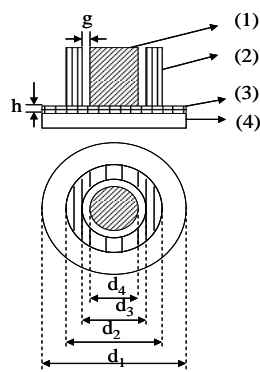


Fig. 1. Sketch of the measurement of the volume resistance

(1) Protected electrode (diameter d_4), (2) Protective electrode (external and inner diameter, d_2 and d_3), (3) Sample, (4) Unprotective electrode (diameter d_1), h : sample thickness, g : electrode gap.

Fourier transform infrared spectroscopy (FT-IR)

FT-IR was used to analyze the PF resins using a Nicolette 6700 (USA) with the attenuated total reflection technique called ATR method. The cured resin was oven dried at 120°C before being tested. The scanning range investigated was 600-4000 cm^{-1} and the distinguishability was 4 cm^{-1} .

Differential scanning calorimetry (DSC)

The curing behavior of PF resins were evaluated using a DSC Mettler (DSC Q20, TA instrument, USA) under a nitrogen atmosphere. Approximately 5 mg of frozen dried PF resin was placed in a sealed aluminum oxide crucible. The heating rates adopted were 10°C /min, 7.5°C /min, 5°C /min and the temperature limit was set at 200°C.

Shear bonding strength of plywood

The shear bonding strength of plywood was tested to determine the bonding strength of the resins. According to GB/T 17657-2013 (“Test methods for evaluating the properties of wood based panels and surface decorated wood-based panels”), the shear bonding strength of the PF bonded plywood was measured before and after water treatment. Specimens for wet strength were immersed in boiling water for 4 h followed by drying at (63 ± 3) °C for 20 h and further boiling for 4 h. After cooling in water at 30°C for 1 h, the shear bonding strength of plywood samples (Fig. 2) was tested.

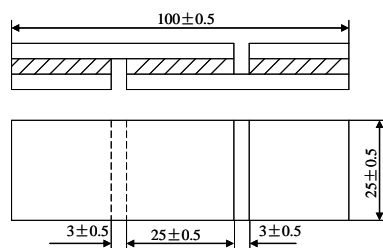


Fig. 2. Dimension and shape of bonding specimens

3. Results and discussion

3.1. Physical properties of phenol formaldehyde resin

The physical properties of the common PF resin, commercial alcohol-soluble insulation PF resin, KH550 modified and unmodified low molecular weight PF resins are listed in Table 1.

Table 1 Performance of several phenol formaldehyde resins

The type of the PF resin	pH	Viscosity (mPa · s)	Solid content (%)	Free formaldehyde content (%)	Free phenol content (%)
Common PF	11	161(±2.3)	44(±0.19)	0.09(±0.0032)	0.08 (±0.0007)
Low molecular weight PF (LPF)	9	63(±1.48)	50(±0.05)	0.14(±0.0033)	0.18 (±0.006)
Low molecular weight PF modified by 3% KH550 (LPF+3%KH550)	9	121(±1.92)	50(±0.05)	0.132(±0.0029)	0.16 (±0.001)
Low molecular weight PF modified by 5% KH550 (LPF+5%KH550)	9	161(±1.22)	50(±0.00)	0.12(±0.0036)	0.13 (±0.001)
Low molecular weight PF modified by 8% KH550 (LPF+8%KH550)	9	153(±3.03)	50(±0.00)	0.114(±0.0025)	0.1 (±0.004)
Commercial insulation PF	7	188(±4.28)	56(±0.16)	0.102(±0.0039)	0.1 (±0.02)

All these resins were alkaline except for the commercial, alcohol-soluble, insulation PF resin. Modification with KH550 did not change the pH of the LPF resin. Alkaline conditions would degrade wood components and enhance water sorption and thus, reduce the electrical insulation performance [16,17].

Usually, the viscosity of the resins relates to their molecular weight. In the present study, the viscosity of the common PF resin and the commercial insulation PF resin were higher than that of the LPF resin. This indicates that the latter had a lower molecular weight. Adding KH550 could significantly increase the viscosity of the LPF resin. When KH550 was added at 5% content, the resulting PF resin showed the highest viscosity among the modified resins. This indicated that a cross-linking reaction potentially occurred between the silane coupling agent and the PF resin which could be potentially beneficial to insulation. Compared to unmodified LPF, modification by KH550 resulted in a lower free formaldehyde and free phenol content due to the polar absorption. It is presumed that KH550 was grafted on the PF resin and consumed formaldehyde and phenol.

3.2. Water absorption and electric insulation performance of the cured PF resin

The volume resistance is an important indicator to describe a dielectric or insulating material. The higher volume resistance indicates better insulating properties. When polar compounds or

groups are present in the synthesis process or during material application, ion conductivity takes place and the electric insulation properties of the polymer become worse [18,19].

Compared to the LPF resin the common PF resin and commercial insulation PF resin absorbed more water and presented smaller volume resistance. The reason could be that these polymers still contain polar phenolic hydroxyl groups on the molecular chain, resulting in higher water absorption and worse electric insulation. As shown in Table 2, after absorbing water, the volume resistance of all resins decreased. This is because the polar group contained in the PF resins increased due to immersion in boiling water, favoring ion conductivity.

Compared to unmodified LPF, KH550-modified LPF presented higher volume resistance, both before and after treatment in boiling water. This might be attributed to the reduction of hydroxyl groups. In other words, the phenolic hydroxyl has been sealed by the silicone coupling agent.

Compared to 5% KH550-modified LPF, changing the content to either 3% or 8% resulted in lower R_v values, as shown in Table 2. A 3% KH550 content did not contribute sufficient silane alcohol to completely block the polar phenolic hydroxyl groups. Part of the polar phenolic hydroxyl groups was open and easily absorbed water. When KH550 was added to the level of 8%, an excessive amount of organic silicon was introduced and created high amounts of hydroxyl groups due to KH550 hydrolyzation. This could be shown by FT-IR spectroscopy.

Table 2 Water absorption and the volume resistance (R_v) of cured resin before and after boiling in hot water

The type of resins	Common PF	LPF	LPF+3% KH550	LPF+5%K H550	LPF+8% KH550	Commercial insulation PF
Water absorption (%)	5.28 (± 0.04)	3.15 (± 0.02)	2.14 (± 0.03)	1.28 (± 0.04)	1.79 (± 0.01)	6.93(± 0.02)
R_v before boiling in hot water ($10^9\Omega$)	0.13 (± 0.02)	0.27 (± 0.03)	1.14 (± 0.04)	2.38 (± 0.01)	1.4 (± 0.02)	3.06(± 0.06)
R_v after boiling in hot water ($10^9\Omega$)	0.071 (± 0.001)	0.068 (± 0.002)	0.45 (± 0.003)	0.58 (± 0.007)	0.29 (± 0.003)	0.16(± 0.005)

3.3. Fourier transform infrared spectroscopy (FT-IR)

In order to verify the reaction between the phenolic hydroxyl group and KH550, the FT-IR spectra of the cured PF resins are listed in Fig. 3.

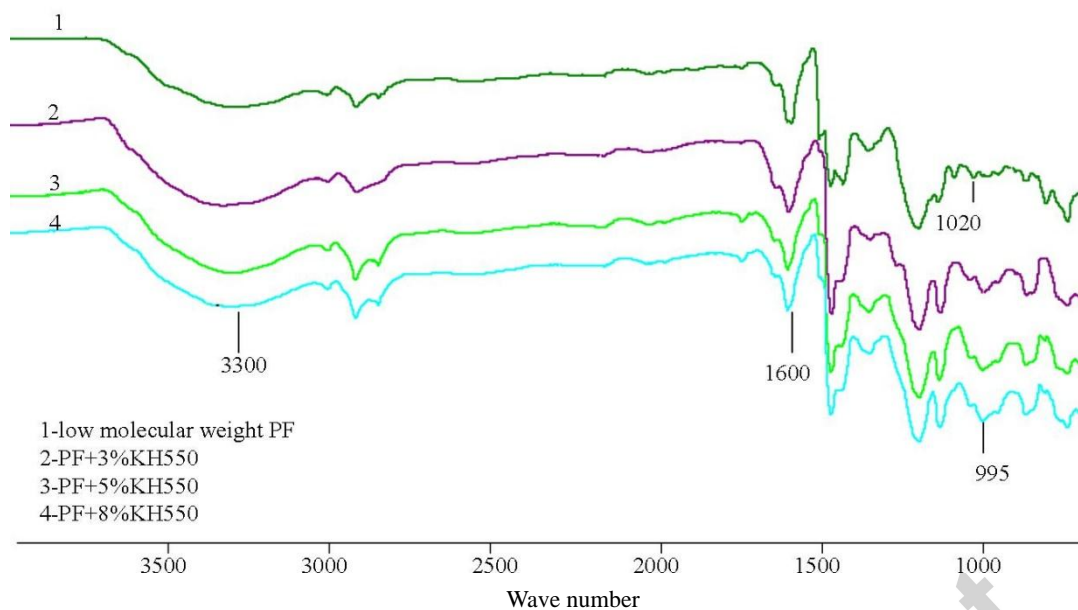
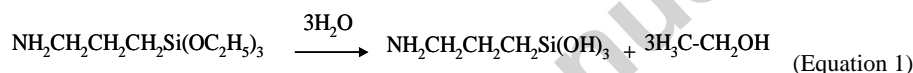
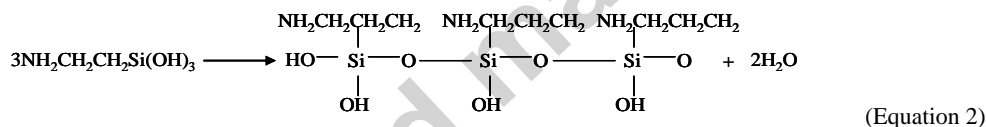


Fig. 3. FTIR spectra for cured phenol formaldehyde resins

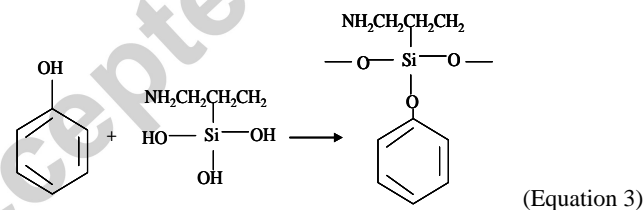
KH550 was easy to hydrolyze and generate silanol by reacting with the polar phenolic hydroxyl group. Dehydration condensation formed non-polar hydroxyl polymer Si-O-C₆H₅ (in equation 1,2,3). The supposed mechanism of organo-silicone-modified PF resin is described by equations (1), (2), and (3) [16].



Equation 1 Three- OC₂H₅-group connected to silicon hydrolyzed to silanol



Equation 2 Silanol condensed to oligomer



Equation 3 Presumed reaction between oligomers and phenol [16]

The phenolic hydroxyl absorption peak is located at 3300 cm⁻¹, and silanol is also present between 3200 cm⁻¹ and 3400 cm⁻¹. Thus, it is difficult to judge whether the phenolic hydroxyl was blocked based on the change in peak strength at 3200–3400 cm⁻¹. Silanol came from the hydrolyzed KH550 coupling agent reacted with phenolic hydroxyl. The generated Si-O-C₆H₅ is visible at 995 cm⁻¹. This characteristic peak should be considered. In the present study, the internal standard method was adopted to understand the changes in functional groups. The absorption peak of the benzene ring at 1600 cm⁻¹ was used as the internal standard object. The ratio of A₃₃₀₀/A₁₆₀₀ and A₉₉₅/A₁₆₀₀ was used to detect the changes in -OH and Si-O-C₆H₅ [20].

When KH550 increased from 0 to 3%, the ratio of A₉₉₅/A₁₆₀₀ for the resulting Si-O-C₆H₅ was generated and the strength increased from 0 to 1.89% (Table 3). Correspondingly, the ratio of hydroxyl was reduced. It is presumed that phenolic hydroxyl was consumed. This could

potentially improve water resistance and electrical insulation resistance.

When KH500 was increased from 3% to 5%, A_{995}/A_{1600} was higher and A_{3300}/A_{1600} lower. This testified that more phenolic hydroxyl reacted with the silanol and more $\text{Si-O-C}_6\text{H}_5$ was generated when KH500 was added at 5% level. When the KH500 was continuously raised to 8%, the ratio of A_{995}/A_{1600} for the produced $\text{Si-O-C}_6\text{H}_5$ was the same as of the one obtained with a 5% content; however, the ratio of hydroxyl groups (A_{3300}/A_{1600}) increased (Table 3). This indicated that the usage of 8% KH500 introduced new polar hydroxyl groups from hydrolyzation.

Table 3 The variation of the absorbance for parts of the functional groups

	low molecular weight PF	PF+3% KH500	PF+5% KH500	PF+8% KH500
A_{3300}/A_{1600}	1.02	0.94	0.89	0.95
A_{995}/A_{1600}	0	1.89	2.17	2.18

The results obtained indicate that the amount of modifier is critical. Testing results summarized in Table 2 proved that only a reasonable amount of KH500 can decrease the number of polar phenolic hydroxyl group, reduce water absorption and improve the electrical insulation performance. In the present study, 5% KH500 presented the lowest water absorption, highest volume resistance and persistent better electrical insulation in a hot and humid environment.

3.4. Differential scanning calorimetry (DSC)

DSC was carried out at different heating rates ($5^\circ\text{C}/\text{min}$, $7.5^\circ\text{C}/\text{min}$ and $10^\circ\text{C}/\text{min}$) from room temperature to 200°C with the aim of studying the non-isothermal curing behavior of PF resins.

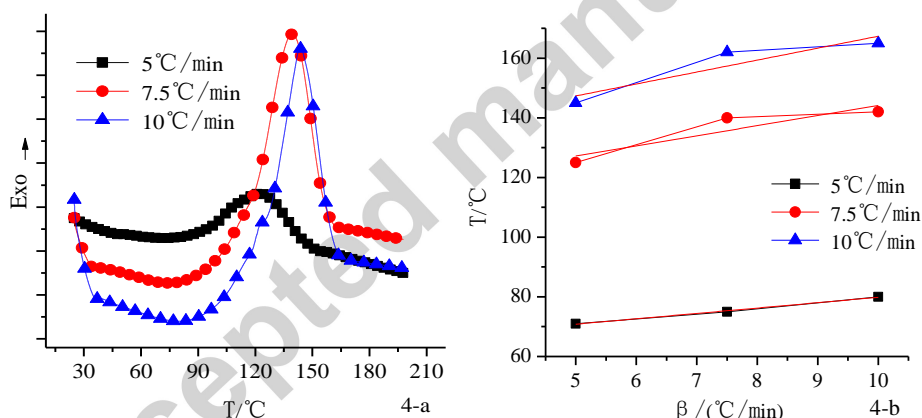


Fig. 4. Non-isothermal curing curves of the low molecular weight PF resin modified by 5% KH500 under different heating rates (a) and curves of the relationship between heating rates (β) and temperature (T) (b)

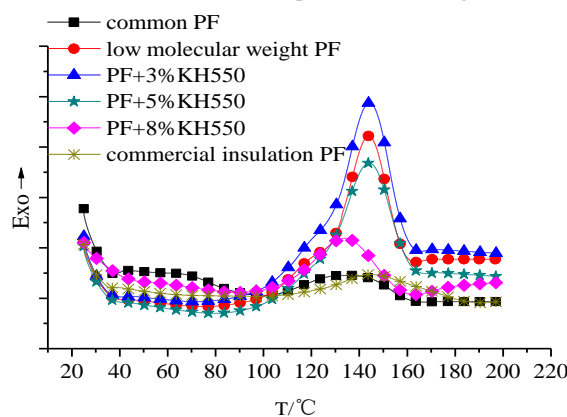


Fig. 5. DSC curing curve of different resins ($10^\circ\text{C}/\text{min}$)

The curing curves (Fig.4-a) show that as the heating rate increased the thermal response became more evident and the temperature difference correspondingly increased. When the heating rate exceeded the rate of poly-condensation reaction of PF resins, hysteresis took place [21–24] and the exothermic peak for the curing reaction was correspondingly shifted to higher temperatures. As shown in Fig. 4-a, a heating rate of 10°C/min presented the highest exothermal temperature.

The curing curves at the same heating rate (10°C/min) for the different types of resins (Fig. 5) show that the exothermic peak due to the cross-linking reaction for common PF resin, commercial insulation PF resin, and 8% KH550-modified LPF were broad. On the other hand, the curing curves of the unmodified and 3% and 5% KH550-modified LPF resins exothermic peaks were sharp during the curing process. This result may be due to the high reactivity [25]. The KH550 hydrolyzed to form silanol which possesses hydroxyl groups that can react with the polar phenolic hydroxyl. The reaction activity therefore increased and the peak was sharp compared to other resins. When KH550 was added at 8% level most of the phenolic hydroxyl groups were blocked and the resultant of Si-O- C₆H₅ was not easy to break. No more phenolic hydroxyl groups were exposed and the excessive KH550 was able to react weakly with the polar hydroxyl-methyl groups so that the reaction reactivity of curing was weakened and the exothermic peak was broad[25]. Therefore, by judging the activity of the reaction from the width of the peak, it was further proved that an excessive addition of KH550 was useless.

From the non-isothermal curing curves of the PF resins under different heating rates the initial curing temperature (T_i), peak curing temperature (T_p), termination curing temperature (T_f) and curing time of PF resins at different heating rates can be obtained. The curing times of PF resins at the heating rate of 10°C/min are listed in table 4. Compared to the common PF resin and commercial alcohol soluble PF resin, the modified and unmodified LPF resin presented a shorter curing time. This means that energy consumption is lower. The gel temperature (T_{gel}) and curing temperature (T_{cure}) were obtained from extrapolation. Based on that the characteristic temperature at different heating rates were extrapolated to the zero heating rates (Fig. 4-b)[26,27] and are shown in Table 4. All resins in the study showed a curing temperature around 130°C. Commercial insulating PF resin owned the highest gel temperature. When enough KH550 was used, the modified LPF resin showed a lower gel temperature. When these resins are used to impregnate sheets attention should be paid to the drying time in order to avoid excessive curing. On the other hand, the lower curing temperature reduced energy consumption during curing.

Table 4 Curing temperature and curing time of different phenol-formaldehyde resin (10°C/min)

	Curing time, t (min)	Gel temperature, T_{gel} (°C)	Curing temperature, T_{cure} (°C)
common PF	9.2	70	128
LPF	9.2	75	133
LPF+3%KH550	8.3	75	135
LPF+5%KH550	8.5	70	125
LPF+8%KH550	7.8	72	127
commercial insulation PF	10	95	130

3.5. Shear bonding strength of plywood

The bonding strength of the resins is expressed in terms of the shearing strength of plywood, shown in Fig. 6. When tested in dry state, all samples failed in wood veneer. After wet treatment,

more than 80% samples failed in wood veneer for KH550 modified PF resin, mean while 65- 75% for other resins.

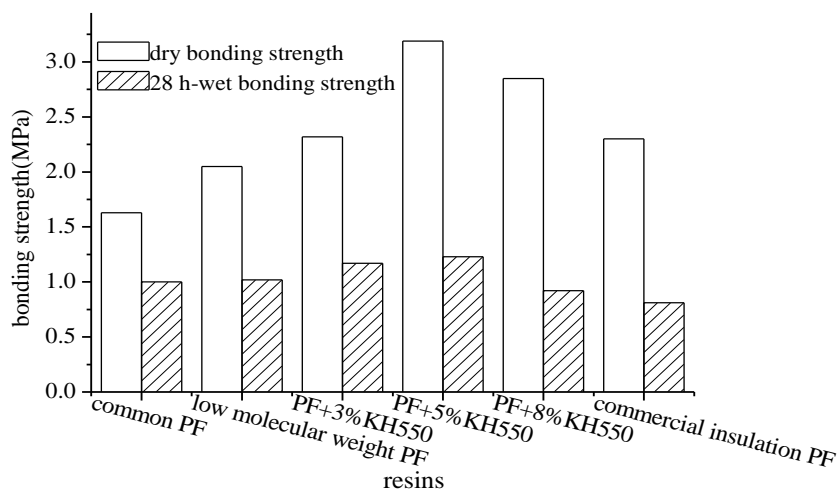


Fig. 6. Shear bonding strength of the plywood

The interlayer performance of plywood depends on the cross-linking force of the cured resin matrix [28,29]. The bonding strength of the low molecular weight PF resin modified by KH550 was higher than that of the others in both the dry and wet states. The presence of the coupling agent strengthened the interface bonding between wood and resin. The assumed mechanism is shown schematically in Fig.7.

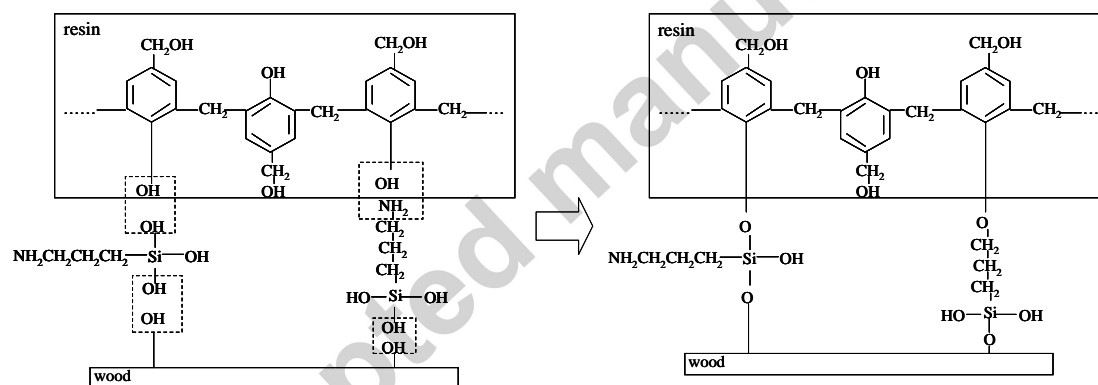


Fig. 7. Schematic diagram of the bonding that promoted by KH550

In hot and humid environments the interface phase will inevitably suffer from water invasion. The resulting swelling will affect the interface bonding. After modification by KH550 the polar phenolic hydroxyl group was blocked which reduced water absorption and thus, improved the interfacial bonding. On the other hand, the coupling agent could strengthen the interaction between resin and wood, and further increase the interface adhesion [13,30,31].

In summary, the KH550 modified resin provided plywood with a higher bonding strength and water resistance. A 5% content was shown to result in the highest bonding strength.

4. Conclusions

In this paper, KH550 was introduced successfully to modify a low molecular weight PF resin. The electrical, physical and bonding properties of the PF resin and the mechanism of improvement were discussed.

(1) The non-toxic, non-polluting, environmentally friendly, and biodegradable modifier KH550 was added to the reaction system through a simple procedure resulting in the preparation

of a water-soluble resin. After curing the modified PF resin has improved water resistance, volume resistance and bonding strength. The volume resistance, and the physical and mechanical properties of the 5% KH550 were the best.

(2) DSC analysis showed that the curing temperature of all resins was moderate, about 130°C, with similar cure times. The curing speed of the LPF resin modified by KH550 was moderate and the curing process was faster than others, reducing energy consumption.

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