Preparation and Performance Study of Modified Silica Sol/Phenolic Resin

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This study used silica sol, phenol, formaldehyde, *etc.* as raw materials to prepare silica sol/phenolic resin based on *in-situ* polymerization. The influence of silica sol content on the viscosity, solid content, and other properties of the composite resin were discussed. The structure and performance of the product were characterized and tested *via* laser particle size analyzer, infrared spectrum analyzer, thermogravimetric (TG) analyzer, and rheometer. The results show that the viscosity of the composite resin increased with increased silica sol content, and the solid content and the free formaldehyde content exhibited the opposite trend. The laser particle size analysis revealed that when the amount of silica sol was 40%, the particle size distribution of the composite resin was relatively uniform. Fourier transform infrared analysis illustrated a new chemical bond of Si-O-C formed between silica sol and phenolic resin. TG analysis showed that when the amount of modified silica sol was added at a 40% level, the decomposition temperature of composite resin (10% weight loss) increased from 294.8 to 324.4 °C, and the residual amount increased from 55.2% to 60.2%; rheological analysis revealed that when the content of silica sol was 40%, it had better flow properties, creating conditions for the composite resin to penetrate the wood.

Keywords: Silical sol; Phenolic resin; Particle size distribution; Thermal stability; Rheological properties

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INTRODUCTION

Phenolic resin (hereinafter referred to as PF) is the collective name for resins formed by the action of phenols and aldehydes in the presence of a catalyst. It is one of the three traditional thermosetting resins. They are widely used in artificial panels and furniture because of their simple preparation process, easy availability of raw materials, high gluing strength, weather resistance, and good water resistance. With the continuous development of the industry, new requirements for the performance of phenolic resins have been put forward, and a lot of research work has been conducted in domestic and international on the modification of phenolic resins. Due to the presence of phenolic hydroxyl groups and hydroxymethyl groups in phenolic resins, improving their toughness and heat resistance and reducing the free aldehyde content is the current development direction (Deng 2008).

In recent years, nanocomposites have become a hot spot for research, and inorganic nanomaterials are highly respected for their non-toxic and environmentally friendly properties. The main methods for preparing nanocomposites are sol-gel, physical blending, and *in situ* polymerization. The thermal decomposition temperature of the composite system is greatly increased (according to thermogravimetric analysis), and the heat resistance of the resin was optimal when the mass fraction of the added nano-SiO_2 particles was 3% (Tian *et al.* 2015). Huang *et al.* (2016) prepared composites of SiO_2 and phenolic resin using the sol-gel method, and the results showed that the nano-SiO_2 particles could be uniformly distributed in the phenolic resin, while the heat resistance of SiO_2/phenolic resin was improved (Sun *et al.* 2009). Dong *et al.* (2017) prepared a nano-SiO_2-modified WPU adhesive using the co-blending method and *in situ* polymerization, and they found that the nano-SiO_2 could improve the thermal stability of the polyurethane adhesive film and the performance of the adhesive prepared by the *in situ* polymerization method was better than that of the co-blending method (Huang *et al.* 2016).

Silica sol is a dispersion of nanoscale silica particles in water or solvent (Dong *et al.* 2017), which is widely used on account of its advantages of safety and environmental protection and no free formaldehyde (Chen *et al.* 2007). The surface of silica colloidal particles has a large number of hydroxyl groups and a high specific surface area and specific surface energy, but the compatibility and dispersion with polymers is poor (Zhou *et al.* 2016). Because the diameter of a nanoparticle is small, the Van der Waals radius of particles is always larger than the distance between centers of mass; this circumstance will lead to a higher functional energy among particles, stronger tendency of agglomeration of particles, and inferior distribution of nanoparticles (Wu *et al.* 2003). Therefore, the surface of nanoparticles needs to be modified, and modification by silane coupling agent is one of the most common chemical modification methods, which can make the size of nanoparticles stable (Wu *et al.* 2018). Xiang *et al.* used silica sol to modify waterborne polyurethane and found that the heat resistance and other properties were optimized when the amount of silica sol was added at 5% (Xiang *et al.* 2015).

Silica sol is a colloid with low viscosity. It can penetrate wherever water can penetrate, so it has excellent dispersibility and permeability when mixed with other substances, and the SiO_2 is a solid powder. In this study, silica sol was used to replace SiO_2 nanoparticles, and phenol, formaldehyde- and KH560 modified silica sol were used as raw materials and NaOH was used as catalyst to prepare synthetic composite resins based on *in situ* polymerization. The aim is to provide the necessary technical support and scientific and theoretical guidance for the development of the composite resin and the subsequent impregnation of modified wood.

EXPERIMENTAL

Materials

Reagents and instruments

Silica sol was purchased from Jinan Yinfeng Silica Products Co., Ltd. (Jinan, China) with an average particle size of 8 to 15 nm, solid content of 30%, pH 9.3. Phenol, formaldehyde, and sodium hydroxide, all of which were analytically pure, as well as KH560 (γ-epoxy propyl trimethoxysilane), were purchased from Shandong Youso Chemical Technology Co., Ltd. (Linyi, China). A rotary viscometer was purchased from Shanghai Institute of Geoscientific Instruments (Shanghai, China). An ultrasonic cleaner was purchased from Shanghai Shengyuan Ultrasonic Instrument Co. (Shanghai, China). A laser particle size meter was purchased from Malvern Instruments Ltd. (Malvern, UK). A Fourier transform infrared (FTIR) spectrometer was purchased from Beijing Ruili Analytical Instruments (Beijing, China). A thermogravimetric analyzer was purchased from NETZSCH (Selb, Germany), and a rotational rheometer was purchased from Anton Paar Ltd. (Shanghai, China).

Methods

Preparation of KH560 modified silica sols

A total of 200 g of unmodified silica sol was placed into a mixture of ethanol and water. The mass of both ethanol and water was 100 g. The solution was placed in an ultrasonic cleaner for 30 min, and then the mixed solution was poured into a three-necked flask with a constant temperature water bath set at 60 °C. During the reaction, KH560 (9 g) was added dropwise to modify it, the reaction stirred for 6 h. At the end, a light blue modified silica sol solution was obtained after the reaction, and the KH560 modified silica sol was poured out and left to stand.

Preparation of composite resins

Preparation of silica sol/phenolic resins were based on *in situ* polymerization. Five experiments were conducted, and only the amount of KH560 modified silica sol was changed in the experiment. The molar ratio of phenol:formaldehyde = 1:2.1 was used to weigh 200 g phenol and 134 g formaldehyde into a beaker and 20, 40, 60, 80, or 100 g of KH560 modified silica sol was added separately (calculated as a percentage of the mass of phenol). The mixed solution of phenol, formaldehyde, and silica sol was subjected to ultrasonic shaking for 30 min to make the silica sol evenly dispersed in the solution, then placed in a three-necked flask. During the reaction, 16.7 g of catalyst, namely NaOH solution (concentration 30%) was added into the three-necked flask and the reaction temperature was set at 90 °C. The reaction was terminated after 2 h to obtain a translucent brownish-red liquid.

Samples information

Table 1 lists the compositions of the samples.

Table 1. Composition of Samples

Sample name	KH560 modified silica sol (g)	Phenol (g)	Formaldehyde (g)	Sodium hydroxide (g)	Mark
Phenolic resin	0	200	134	16.7	PF
Silica sol	0	0	0	0	Unmodified Silica sol
Modified silica sol	200	0	0	0	KH560 modified silica sol
Silica sol/Phenolic resin	20	200	134	16.7	10% silica sol/PF
	40	200	134	16.7	20% silica sol/PF
	60	200	134	16.7	30% silica sol/PF
	80	200	134	16.7	40% silica sol/PF
	100	200	134	16.7	50% silica sol/PF

Characterization

Basic adhesive performance testing

The solid content, viscosity, water mixing ratio, and free aldehyde content and other properties of the silica sol/ phenolic resin composite resin were tested according to the GB/T 14074 (2017) standard.

Particle Size Distribution Detection

Particle size distribution of KH560-modified silica sol

The silica sol before and after KH-560 modification was diluted to approximately 0.3% mass fraction concentration using anhydrous ethanol, was ultrasonically dispersed for 10 min, and then the particle size distribution of the samples was examined using a Malvern particle size analyzer.

PF and Silica sol/PF particle size distribution test with different levels of silica sol

The modifier was diluted with deionized water to a concentration of approximately 10% by mass fraction, and after 10 min of ultrasonic dispersion the particle size distribution of the samples was examined using a Malvern particle size analyzer.

Infrared spectroscopy analysis

The samples to be tested were dried to a constant weight and tested using the WQF-510A infrared spectrometer with a scan range of 400 to 4000 cm^{-1} and KBr press method to prepare samples for the determination and characterization of the structures of modified silica sol, phenolic resin, and silica sol/phenolic resin.

Thermogravimetric (TG) analysis

The dried PF and Silica sol/PF resin adhesives were tested using the TG209F3 thermogravimetric analyzer with a temperature rise rate of 10 °C/min. The scanning temperature range was 30 to 800 °C, with nitrogen atmosphere protection, and a sample size of 5 to 10 mg.

Rheological analysis

The MCR702 rheometer was used to measure the silica sol/phenolic resin composite resin at a constant temperature of 25 °C. The shear rate scanning range was 0.01 to 100 s^{-1}, and the apparent viscosity was measured with the shear rate. The variation of apparent viscosity with temperature was determined at a constant shear rate of 1 s^{-1}.

RESULTS AND DISCUSSION

Influence of the Amount of KH560-modified Silica Sol on the Properties of the Composite Resin

Figure 1(a) shows that the solids content and viscosity of the silica sol/ phenolic resin were influenced by the amount of silica sol added. The solids content of the silica sol/phenolic resin showed a decreasing trend with the increase of the silica sol content, while the viscosity increased. As the content of silica sol increased, the degree of polymerization of the composite resin gradually increased, and the cross-linked structure of the resin system also increased, thus making the viscosity of the composite resin also increase.

The current problem of free formaldehyde in adhesives is of concern and can be partially replaced by the addition of silica sol, so the free aldehyde content of silica sol/ phenolic resin made from different content of silica sol was tested and the results are shown in Fig. 1(b). From the figure, it can be seen that the free aldehyde content gradually decreased with the increase of silica sol content, indicating that the addition of silica sol can effectively reduce the free aldehyde content in the adhesive. Due to the high surface energy of the added silica sol, it is easy to interact with the hydroxyl groups in the phenolic resin, which can improve the bonding energy of the molecular bonds and make the polycondensation reaction with formaldehyde more adequate, and the degree of polymerisation in the synthesis of phenolic resin is improved, thus reducing the free aldehyde content in the composite system.

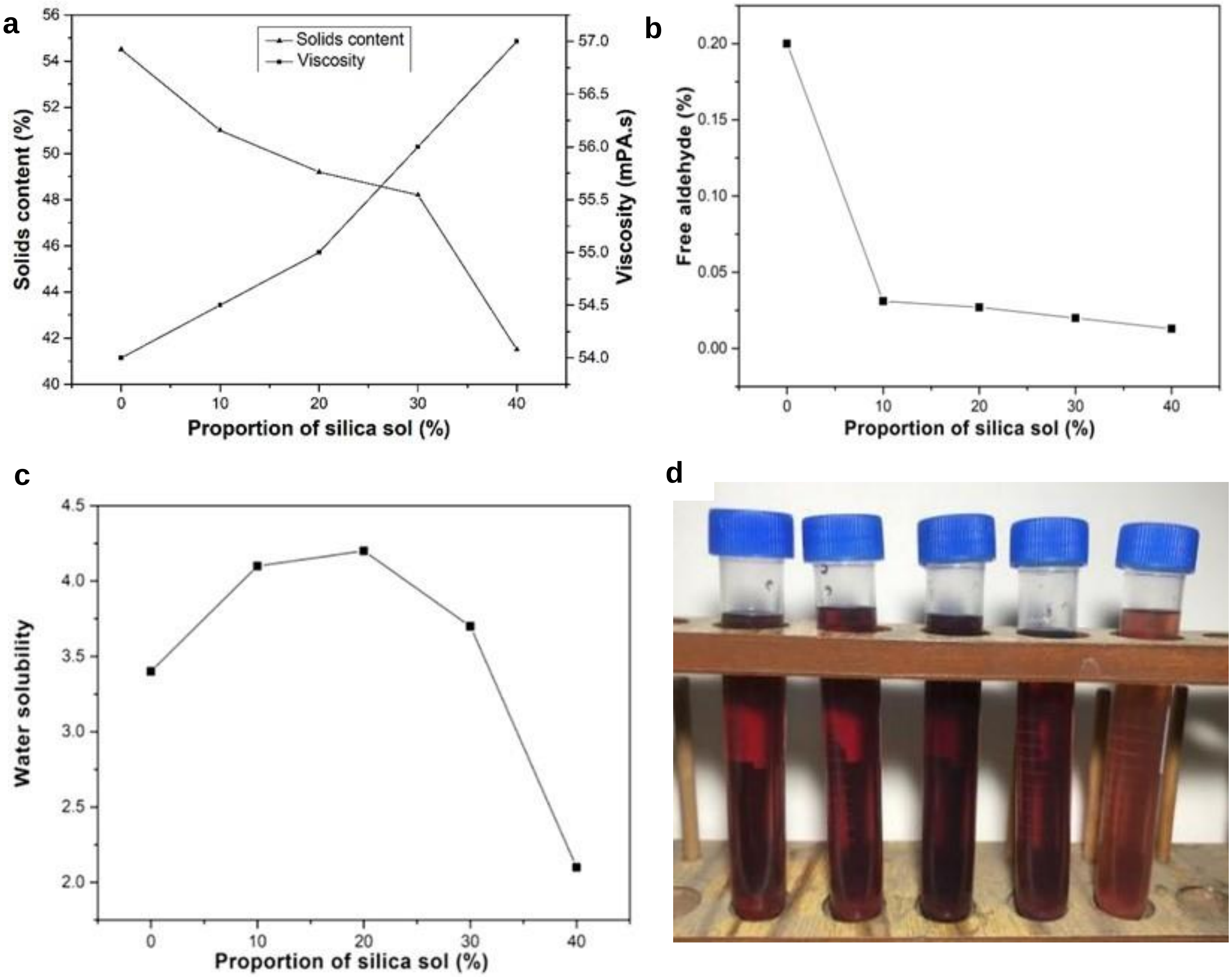


Fig. 1. Physicochemical properties of adhesives: (a) The solid content and viscosity of the adhesives prepared by different silica sol content; (b) Free formaldehyde content of adhesives made with different silica sol content; (c) Water solubility multiples of adhesives; (d) Physical view of adhesives made with different silicone sol content (From left to right KH560 modified silica sol content is 10%, 20%, 30%, 40%, and 50%)

Silica sol/phenolic resins was water-soluble, has low molecular weight in the range of 300 to 500. Figure 1(c) shows the water solubility multiples of silica sol/phenol-formaldehyde resin adhesives made with different levels of silica-sol. It can be seen from the figure that the water solubility multiplier decreased when the silica sol content was increased from 10% to 20%. Because the amount of silica sol was small, the polymerization of the resin was small and the degree of polymerization was low, so its solubility in water was strong. When the amount of silica sol was gradually increased, chemical cross-linking between KH-560 modified silica sol and phenolic resin, and condensation reaction between them occurred. The degree of polymerization of the resin became larger and the degree of cross-linking also became larger. In addition, the water solubility of phenolic resin decreased with the increase of the amount of modified silica sol. This is mainly because the modified silica sol was not soluble in water, but soluble in organic solvents. With the addition of modified silica sol, the water solubility of phenolic resin will inevitably decline.

The amount of silica sol added affected the stability of the phenolic resin. Figure 1(d) shows a physical diagram of the prepared composite resin with different levels of silica sol/ phenolic resin. The stability of the composite resin changed with the increase of the amount of silica sol. When added to 50%, the solution appeared turbid, the stability became poor, and it had a short storage stability. Since the wood is to be impregnated, a homogeneous and stable solution must be selected. Therefore, the following tests were not performed on 50% silica sol/ phenolic resin.

Analysis of particle size and distribution of KH560 modified silica sols

Figure 2 shows the particle size distribution of the unmodified silica sol and KH560-modified silica sol (temperature 60 °C, reaction time 6 h).

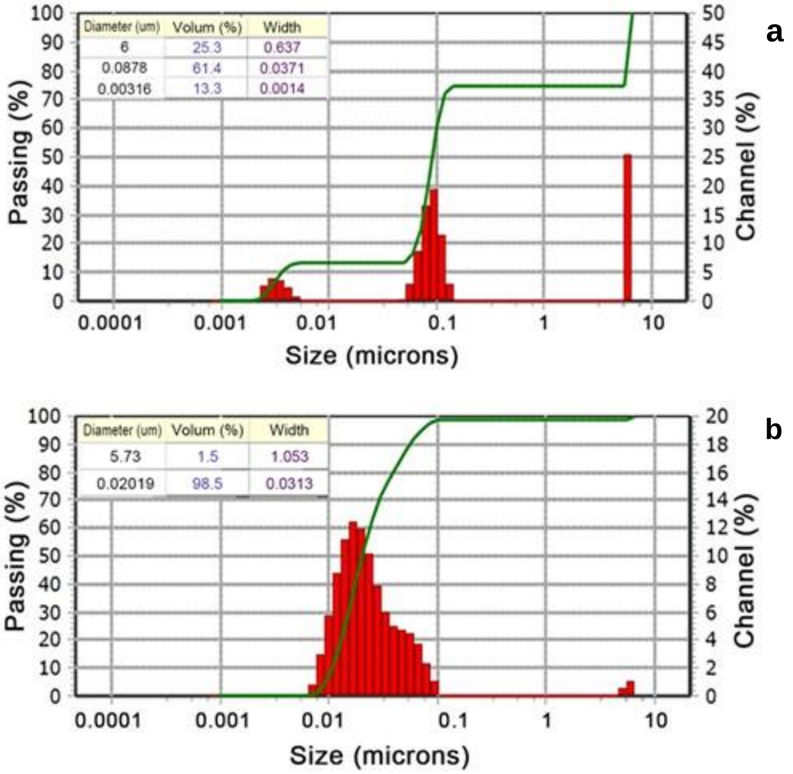
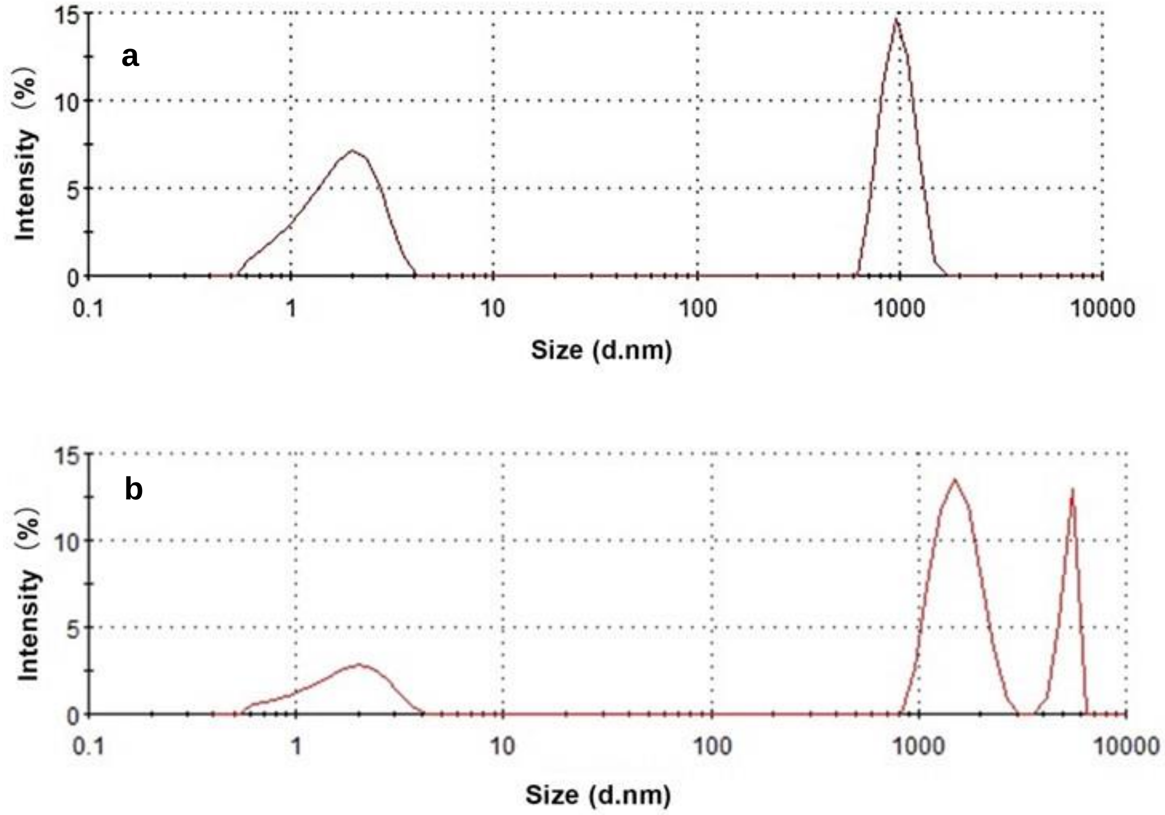


Fig. 2. Particle size distribution of unmodified and modified silica sols: (a) unmodified silica sol; (b) KH560-modified silica sol

It can be seen from Fig. 2(a) that the particle size of the unmodified silica sol was not uniformly dispersed and agglomerated, excluding the large particles caused by agglomeration, the particle size of the silica sol was mostly 3.16 nm. As shown in Fig. 2(b), the particle size of the silica sol was uniformly distributed after 6 h modification by the coupling agent KH560. The particle size of 20 nm accounted for 98.5%, which was mainly because KH560 was grafted onto the surface of the SiO_2 particles. During the grafting process, the polymer chains produced by the hydrolysis of KH560 can be grafted on the surface of multiple SiO_2 particles at the same time, and one SiO_2 particle can also adsorb multiple polymer chains at the same time. The SiO_2 particles act as physical cross-linkers between different polymer chains, thus forming a three-dimensional network structure (Wei *et al.* 2020), and indicating the modification of silica sol by KH560 can effectively prevent the agglomeration phenomenon, thus achieving the modification effect and playing a bridging role for the combination of silica sol and phenolic resin.

Analysis of the effect of modified silica sol content on the particle size and distribution of Silica sol/PF

The particle size and its distribution of phenolic resin with different content of silica sol/phenolic resin were tested by laser particle size meter. Figure 3 shows the particle size distribution of PF and 10%, 20%, 30%, and 40% silica sol/PF. The distribution of the modified silica sol in the phenolic resin can be seen from the figure.



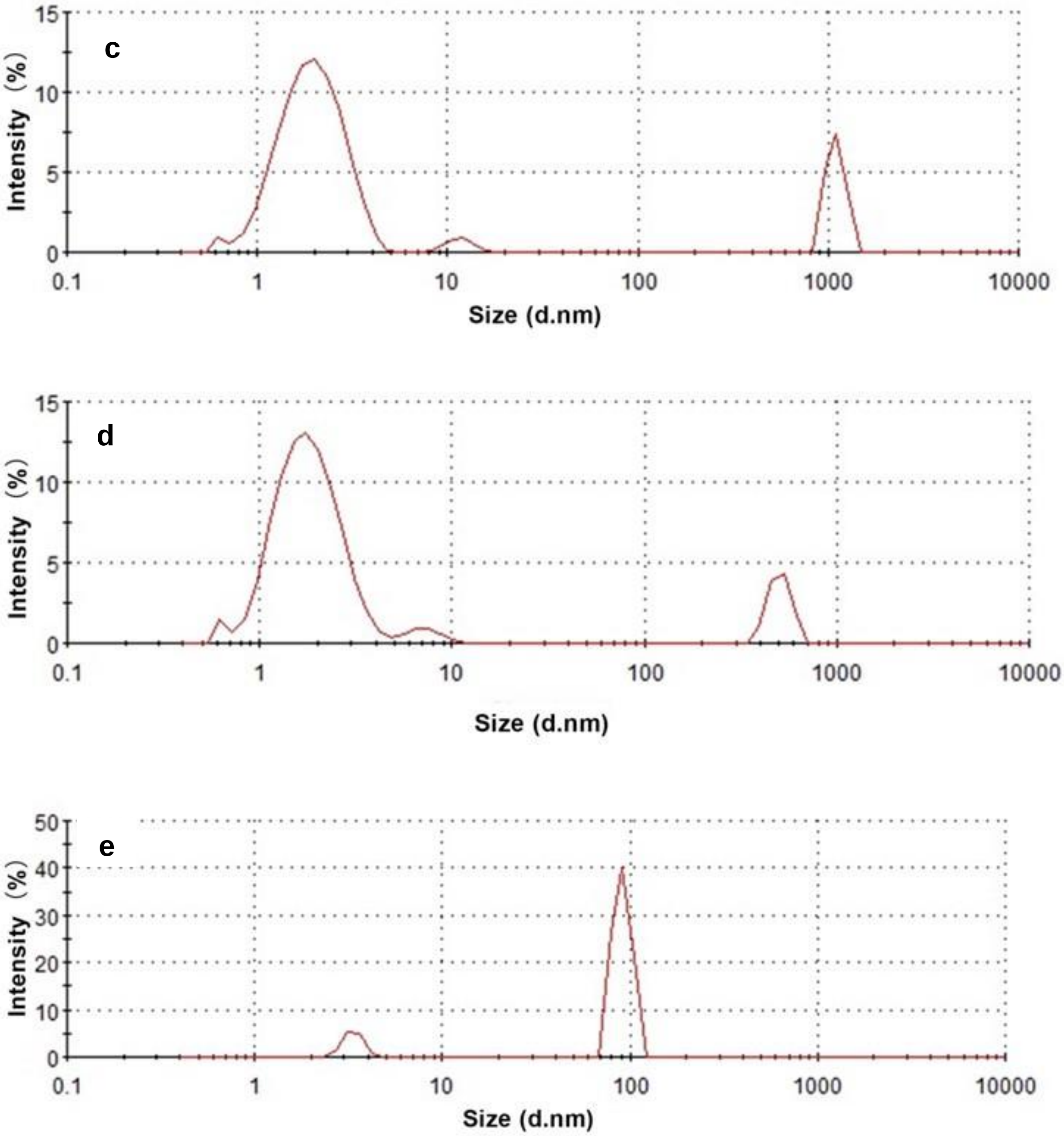


Fig. 3. Particle size distribution of silica sol/PF with PF and different contents of modified silica sols：(a) PF; (b) 10% silica sol/PF; (c) 20% silica sol/PF; (d) 30% silica sol/PF; (e) 40% silica sol/PF

When no silica sol was added, the phenolic resin was more uniformly distributed. With the increase of the content of silica sol, the distribution of the composite resin was not uniform. When the content of silica sol was 10%, 20%, and 30%, particles having large size appeared. This was possibly due to the increase of the silica sol, since the system may contain some nanoparticles without KH560 surface modification. The unmodified nanoparticles are dispersed in the resin and cannot participate in the polymerization, which makes the polymerization reaction speed become sluggish, and the agglomeration of nanoparticles directly leads to a larger particle size and wider distribution of the composite resin, thus causing a poor polymerization effect of the resin (Chen *et al.* 2019). When the silica sol content was 40%, two peak positions appeared and the average particle size was

91.0 nm, accounting for 87.8%, so it can be seen that the particle size distribution of the composite resin with 40% silica sol added was more optimal. This probably was because of the interaction between the modified silica sol and the phenolic resin. A reduced agglomeration of nanoparticles in the modified silica sols would lead to a reduction in the average particle size, resulting in a more uniform distribution of the system. From Table 2, with the increase of the amount of KH560-modified silica sol, the particle size of the composite resin increased gradually, but it was smaller than that of the unmodified phenolic resin. This was mainly attributed to the fact that the measured particle size is the average particle size. Due to the small particle size of silica sol, the average particle size of phenolic resin is reduced after its addition. Of course, it is apparent that the particle size distribution index (PDI) increased gradually, indicating that the silica sol was evenly dispersed in the solution. (Zhang *et al.* 2014).

Table 2. Effect of KH560-modified Silica Sol Addition on Particle Size of Dispersion

Content of Modified Silica Sols (%)	Particle Size (nm)	PDI
0	708.8	0.894
10	371.6	0.562
20	395.5	0.600
30	425.9	0.699
40	491.9	1.000

Infrared spectroscopic characterization

To analyze the interaction between silica sol and phenolic resin, infrared spectroscopy was performed on silica sol, KH560-modified silica sol, phenolic resin, and silica sol/phenolic resin composite systems.

Figure 4 (a) shows the infrared spectra of phenolic resin as well as the composite system of silica sol/phenolic resin, and Fig. 4 (b) shows the infrared spectrum of silica sol and KH560 modified silica sol. The absorption peaks at 3415 cm^{-1} in the Fig. 4 (a) are the absorption peaks of –OH. The absorption peaks at 2920 and 1475 cm^{-1} are the characteristic peaks of asymmetric stretching vibration and asymmetric bending vibration of C-H bond. The absorption peak at 1595 cm^{-1} is the peak of C=C stretching vibration of aromatic ring. As shown in the Fig. 4 (a), when silica sol was added to the phenolic resin, a new absorption peak appeared at 1112 cm^{-1}, which is the antisymmetric stretching vibration peak of Si-O-C. The hydroxyl group of the surface phenolic resin and the Si-OH of the silica sol underwent a condensation reaction, making the hydroxyl absorption peak of the reactants weaker.

As shown in the Fig. 4 (b), 796 and 1101 cm^{-1} are the symmetric and antisymmetric stretching vibration peaks of Si-O-Si. The peaks at 3449 and 1641 cm^{-1} are the -OH stretching vibration peaks, which are weakened after modification. New absorption peaks appear at around 2936 and 2850 cm^{-1}, which are characteristic peaks of methylene and methyl groups. These indicate that physically adsorbed water and silicone hydroxyl groups on the surface of the silica sol are replaced by silane coupling agent, and the coupling agent is grafted on the silica sol.

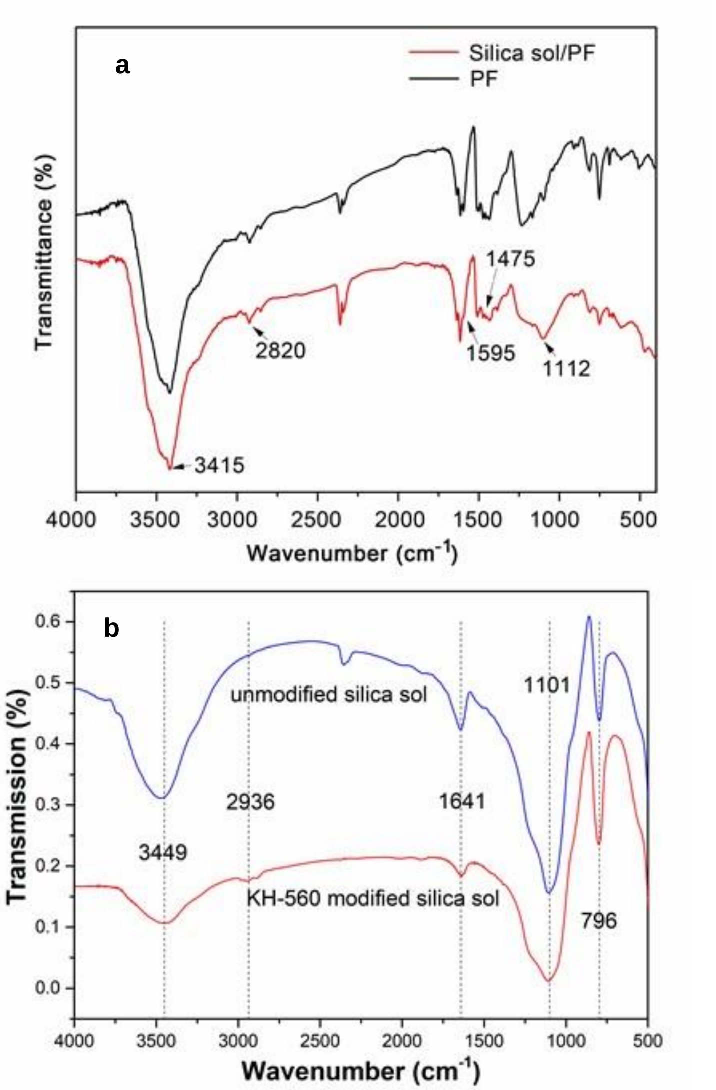


Fig. 4. Infrared spectra of silica sol, KH560-modified silica sol, phenolic resin, and silica sol-modified phenolic resin: (a) phenolic resin, and silica sol-modified phenolic resin; (b) unmodified silica sol and KH560-modified silica sol

TG characterization

The phenolic resin was characterized by thermogravimetric analysis using a TG209F3 thermogravimetric analyzer with different contents of silica sol/phenolic resin, as shown in Fig. 5. Figure 5 shows that within the temperature range between 100 and 300 °C the sample underwent dehydration and condensation of the silicone hydroxyl group, and after 300 °C the thermal decomposition process of the sample was apparent. It can be seen from the graph that the weight loss reduced around 100 °C, which indicates that the addition of the silica sol reduces the presence of moisture, allowing the Si-OH bond to condense into a Si-O-Si network structure. Due to the large specific surface area of the nano-silica and the large number of hydroxyl groups it contains, it is easy to condense with the hydroxyl groups on the surface of the substrate, thus forming a Si-O-Si network structure.

Below 350 °C, the resin exhibited a weak weight loss, mainly attributable to the volatilization of free phenol and intermolecular water in the resin. In the range 350 to 400

°C, the resin weight loss produced an inflection point, after which the slope of weight loss suddenly increased, which can be ascribed to the carbonization of phenolic resin, producing CO, CO_2, cresols, and dimethyl phenol gases. It can be seen from the Fig. 5 that the thermal stability of the silica-sol/phenolic resin composite system was better than that of the phenolic resin. At the same weight loss, the thermal decomposition temperature of the composite system was remarkably higher and it can be seen that the addition of silica sol was able to remarkably increase the thermal stability of the phenolic resin. This is due to the role of silica cross-linked network to limit the thermal movement of polymer chain breaks; meanwhile, the silica sol itself is a colloidal solution formed by SiO_2 particles in water, which has good thermal stability and plays the role of the cross-linked point in the resin, thus making the thermal decomposition temperature improved (Jeon *et al.* 2007).

The thermal stability of the modified and unmodified phenolic resins was judged by comparing the thermal weight loss temperature at 5% degradation ($T_{5\%}$), the thermal weight loss temperature at 10% weight loss ($T_{10\%}$), and the residual amount at 800 °C. The corresponding thermal weight loss parameters are shown in Table 1, from which it can be seen that the thermal degradation temperature of the composite resin tended to increase as the addition of silica sol increased. The greatest effect on the thermal degradation of the phenolic resin was observed when 50% of the silica sol was added, resulting in an increase in the thermal weight loss temperature of 26.1 °C for 5% degradation of the phenolic resin and 29.6 °C for 10% weight loss, with the residual amount increasing from 55.2% to 60.2%, indicating that the heat resistance was remarkably improved.

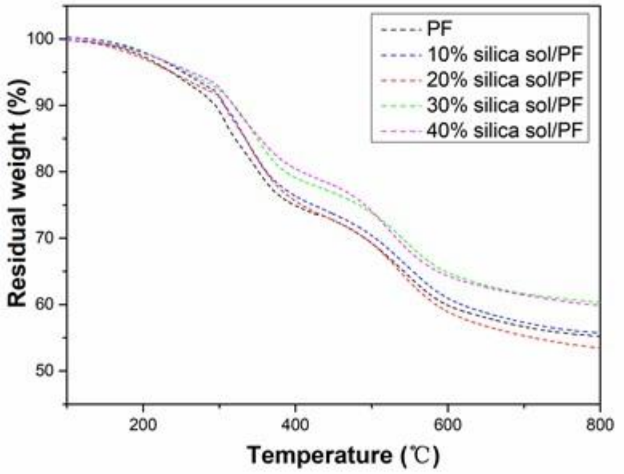


Fig. 5. Heat loss curves of phenolic resins with different contents of silica-sol-modified phenolic resins

Table 3. Thermogravimetric Weight of Modified Phenolic Resins

Modified Silica Sol Content (wt%)	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	Residuals (%) (800 °C)
0	236.88	294.78	55.20
10	252.66	306.86	55.61
20	237.57	307.02	55.74
30	256.08	317.80	59.86
40	263.00	324.39	60.22

Rheological performance analysis

Rheology is an expression of the nature of the flow and deformation of a substance under the action of external forces and refers to the relationship between stress, deformation, deformation rate, and viscosity during processing (Li *et al.* 2013). Figure 6 shows a graph of the apparent viscosity of phenolic resins with different contents of silica sol/ phenolic resin composite resins with shear rate.

Figure 6 represents the variation curve of apparent viscosity with shear rate at 25 °C. It can be seen from the graph that as the amount of silica sol added increases, the apparent viscosity of the composite system shows a decreasing trend with increasing shear rate. In other words, there was a trend of shear thinning, indicating that the fluid was a non-Newtonian fluid. This phenomenon can be attributed to the behavior of solids and polymers in the fluid under the action of shear, which will occur in the entanglement point of the unravelling and reconstruction. As the shear rate increases, the rate of opening the entanglement point is greater than the rate of reconstruction, resulting in a decreasing trend of apparent viscosity with increasing shear rate. It is also possible that the effect of shear causes the orientation of molecular chains along the direction of flow and a reduction in resistance, making the relative movement between macromolecules easier and thus causing the viscosity of the solution to decrease (Xu *et al.* 2012).

In addition, when silica sols are modified by coupling agents, they are able to increase compatibility and interfacial bonding with the phenolic resin matrix, which is more conducive to maintaining the dispersion of the silica sol in the phenolic resin. Due to the small size, large specific surface area, and high activity of the nanoparticles, they are able to form a good physico-chemical bond with the polymer matrix, and more silica sol content results in more opportunity to bond with the phenolic resin (Gao *et al.* 2003). The effect of shear stress can play a lubricating role between the phenolic resin, making the resistance to flow of the whole system smaller, which leads to a reduction in viscosity, as can be seen from the graph after adding 40% silica sol, the viscosity is the lowest, so the fluidity is optimal at this point and it has a better advantage for impregnating wood afterwards.

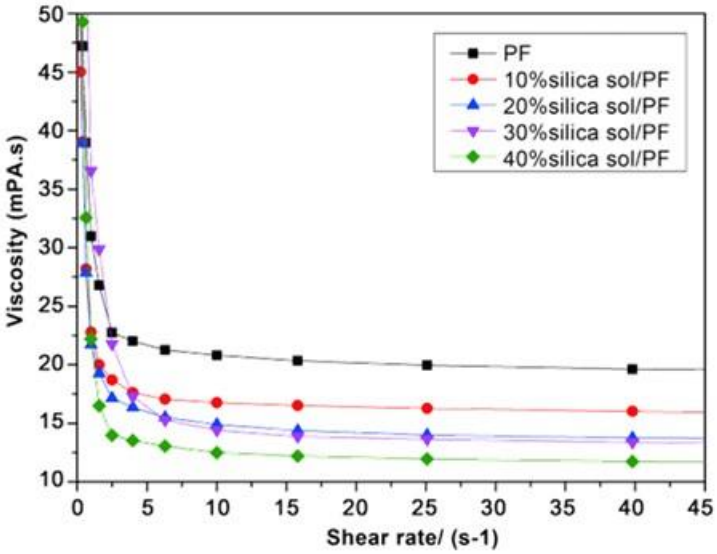


Fig. 6. Variation of apparent viscosity with shear rate for phenolic resins and silica sol/ phenolic resins with different contents

Figure 7 shows the change in viscosity of phenolic resin and 40% silica sol/ phenolic resin with temperature. It can be seen that as the temperature increased, the viscosity of both dropped sharply and stabilized after 80 °C. Due to the increased temperature, the energy of the molecular chain increases, the attraction between molecules decreases, and the frictional force decreases. Of course, the increase in temperature increases the free enthalpy of chain-breaking movement and generates more cavities to increase the space for chain-break activity, and the increase in temperature weakens the interaction forces between molecules. These effects will lead to an increase in material fluidity. Therefore, the modifier can only be in a good flow state when the temperature is above 80 ℃ and the viscosity of the silica sol/phenolic resin is lower than that of the phenolic resin. This ensures that the modifier is in a good flow state during impregnation and thus creates the conditions for the impregnating solution to penetrate into the wood.

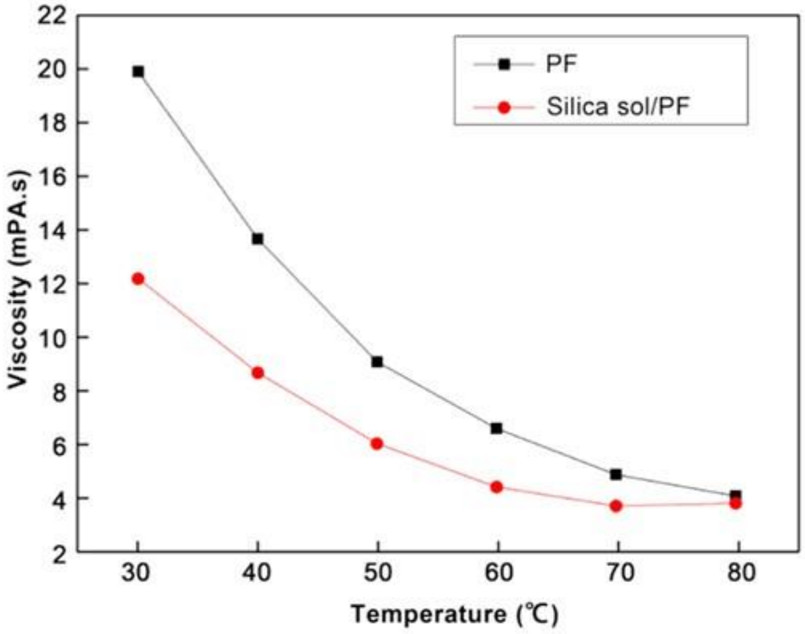


Fig. 7. Variation of apparent viscosity with temperature for phenolic resin and 40% silica sol/ phenolic resin

CONCLUSIONS

1. The silica sol/phenolic resin composite resin prepared by *in situ* polymerization method, the addition of silica sol can reduce the free aldehyde content of the resin to a certain extent.

2. The laser particle size analysis revealed that when the amount of silica sol was 40%, the particle size distribution of the composite resin was relatively uniform.

3. A new Si-O-C chemical bond is formed between the silica sol and the phenolic resin, and the thermal stability of the composite resin is remarkably improved compared to the phenolic resin. A total of 40% of the thermal stability and rheological properties of the silica sol/phenolic resin composite resin are optimized.

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