

Synthesis and Characterization of Phenolic Resol Resin Blended with Silica Sol and PVA

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ABSTRACT: The phenolic resol resin (PF) has a wide application in industry, but its poor tensile ductility and insufficient mechanical strength have severely limited its application. To overcome these limitations, in this study, the mixtures of silica sol and poly(vinyl alcohol) (PVA) were used to modify the PF. The structure, morphology, mechanical properties, and thermal stability of these hybrid materials were investigated by FTIR, SEM, tensile shear test (TSS), and TG. FTIR spectra indicated that the multiple reactive functional silanol group Si—OH on the surface of SiO₂ particles reacted with PVA and PF. Compared with pure PF, the com-

posite 50-50-3% exhibited the maximum shear strength which increased by 158%, whereas the elongation at break increased by 63%. Morphological results agreed well with the mechanical properties. The TG results suggested that the composite material 50-50-3% and pure PF had almost the same thermal stability because silica sol and PVA had opposite effects on the heat resistance of the hybrid materials. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 744–751, 2011

Key words: phenolic resol resin; silica sol; PVA; adhesives; tensile ductility

INTRODUCTION

Phenolic resol resin (PF), as one of the most common synthetic resins, has been widely used in the industry because the raw materials are easy to obtain and its some good properties can satisfy many applications.¹ For instance, compared to other resins, PF has good heat resistance, especially the outstanding performance of the instantaneous heat ablation.² As ablative materials, PF has played an important role in aerospace industry (space vehicles, rockets, missiles, etc.).^{3,4} In addition, the PF adhesive has excellent adhesive capacity, weather and water resistance, so it has been used extensively as adhesives for wood-based composite products such as plywood, oriented strandboard(OSB), and laminated veneer lumber.^{5–7}

Although PF has excellent adhesive strength, its toughness is very poor after curing. Meanwhile, the free formaldehyde and free phenol, as potential carcinogens, produced in the process of synthesis and curing, are harmful to human body. To overcome these shortcomings, a variety of modifying agents have been used to improve the toughness of PF, such as elastomers, tung oils, reactive liquid polymers, plastics, fibers, etc.^{8–10} However, in many

cases, the toughening agents may affect the heat resistance, adhesive strength and modulus, or other physical properties adversely. In recent years, with proposing of the organic-inorganic composite materials, and the application of nanotechnology, many researchers have introduced the nanomaterials into the resin matrix to achieve the purpose of toughening.^{11,12} However, nanoparticles have high surface energy and are easy to agglomerate, which does great damage to the performance of the system. So, the dispersion of nanoparticles becomes an important research branch. Some researchers expect to achieve uniform dispersion of the particles via different synthesis methods, such as the sol-gel method and intercalation method,^{13,14} and some other researchers hope to improve the interface compatibility of the nanoparticles and resin matrix by adding surfactants to the resin,¹⁵ or by employing different nanoparticles, which can lead to direct chemical bonds between the particles and the substrate.¹⁶ These methods basically achieve good effects.

In this article, the mixed solution of silica sol and PVA was employed to modify PF. In this case, SiO₂ particles could be distributed better, and this synthesis method also simplified the synthetic process and lowered the cost. By changing the ratio between the PVA and SiO₂, a series of hybrid materials were obtained. The structures of these materials were analyzed by FTIR. TG and SEM studies were also employed to characterize the hybrid materials with respect to their thermal and morphological properties.

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EXPERIMENT

Materials

Phenol (chemically pure grade) was supplied by the Tianjin Bodi Chemical Co., Ltd. (China). Formaldehyde (chemically pure grade) was purchased from the Chemical Factory of Hubei University (Wuhan, China). NaOH (chemically pure grade) was purchased from Shanghai Chemical Reagent (Shanghai, China). PVA was supplied by Sinopharm Chemical Reagent (Shanghai, China). Silica sol was provided by Chemical Factory of Wuhan University (Wuhan, China). The content of silica sol is 30 wt % and the particle size is about 10 nm.

Preparation of hybrid materials

Preparation of the mixture of silica sol and PVA: according to different requirements, different amount of PVA and silica sol were heated in water bath at constant temperature 85°C for about 2.5 h until the mixed solution turned transparent. Then, the solid content of the mixed solution was adjusted to 8% [eq. (1)] by adding distilled water into it.

$$\frac{M1 + M2}{M3} = 8\% \quad (1)$$

where $M1$ is the mass of SiO_2 particles in silica sol; $M2$ is the mass of PVA; $M3$ is the mass of the mixed solution.

During the synthesis of PF, first weighed an appropriate amount of phenol (the molar ratio of formaldehyde and phenol is 1.9/1) and put it into a three-neck flask, and then heated the flask to 65°C, kept for a while, till the phenol melt into transparency liquid. According to the molar ratio of NaOH and phenol: 0.35/1, weighed a certain amount of catalyst, and divided it into 80% and 20% two parts. The 80% part was first added into the three-neck flask with fused phenol. Flask temperature was kept at 65°C, reacted for 30 min with stirring. Then poured 80% formaldehyde into the three-neck flask, heated up to 95°C and kept reacting for 120 min until the solution turned into micro-red. The remaining 20% catalyst was then added into the three-neck flask, reacted for 30 min at 95°C. Finally, the remaining 20% formaldehyde was poured in, reacted for 120 min at 95°C. Took a small amount of the solution and determined the solid content.

Preparation of the hybrid materials: first, the PF and the mixed solution were synthesized respectively, and then mixed them into a whole based on the weight ratio required. Finally, via vacuum distillation (80°C, 0.096 MPa), a series of hybrid materials with solid content of 50% were obtained.

The final composite materials are marked as: x - y - z . The x , y ($x + y = 100$) represents the mass ratio of SiO_2 particles and PVA of the nonvolatile components of the solution mixed with silica sol and PVA, respectively, and z expresses the SiO_2 content of the final hybrid material [eq. (2–4)]. Especially, when $x = 0$, z represents the PVA content of the final nonvolatile components.

$$\frac{M1}{M1 + M2} = x\% \quad (2)$$

$$\frac{M2}{M1 + M2} = y\% \quad (3)$$

$$\frac{x\%(M1 + M2)}{M1 + M2 + \eta \times M4} = z\% \quad (4)$$

where $M1$ is the mass of SiO_2 particles in silica sol; $M2$ is the mass of PVA; $M4$ is the mass of PF; η is solid content of PF.

Preparation of samples for shear strength

In this research, the shear strength test was performed as shown in Scheme 1. The dimensions of wood plates are 100 mm × 25 mm × 5 mm and the overlapping length is 20 mm. The two arrows indicate the directions of the shearing. The shear strength was tested by a universal testing machine.

In the curing process, the phenolic adhesive vacuum distilled was first coated on the wood plates until the coating was thin and bubbleless, then the samples were cured at 130°C, 1.2 MPa for 4 h.

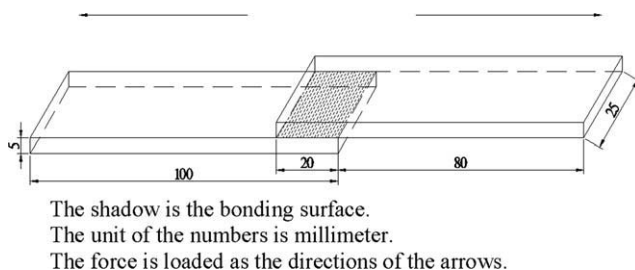
Characterization

The characterization of the chemical groups existed in the hybrid materials was carried out via a FTIR VERTEX 70 spectrometer. We first put the cured hybrid resole resin into a vacuum drying box for 24 h, then got it out, grinded and mixed with KBr-pellet. The mixture of PVA and SiO_2 were made into membranes and using attenuated total reflectance (ATR) technique.

The tensile shear strength of the hybrid materials was evaluated by using the test machine WDW3200 universal tester. Results of shear strength were the mean value among five tested specimens. The deviation are less than 10% of the mean value.

To study the morphology of modified PF, fractured surfaces obtained from shear adhesive tests were coated with gold. And then was performed on a PHILIPS Quanta 200 environmental scanning electron microscope (ESEM).

To characterize the heat resistance of the final hybrid materials, a TGA Pyris1 apparatus was employed. In experiment condition, the temperature



Scheme 1 The sample of the tensile shear test (TSS).

range 25–800°C and heating rate 20°C/min, nitrogen atmosphere are maintained.

RESULTS AND DISCUSSION

FTIR analysis

In Figure 1(a), the absorptions around 1130 cm^{-1} are attributed to asymmetry flexible vibration of C—O—C, Si—O—Si or Si—O—C in the hybrid materials,¹⁷ and the wide absorption at 3250 cm^{-1} indicates the abundance of —OH in the composites. No matter the PF was mixed with silica sol only or the mixture of silica sol and PVA, the absorptions of PF-based composites at 1130 cm^{-1} , representing the dissymmetry flexible vibration of linear Si—O—C, are obviously wider compared to that of pure PF. In Figure 1(b),¹⁶ we can also see the peaks at 1100 cm^{-1} are wider too. Meanwhile, the absorption at 3250 cm^{-1} , representing the abundance of —OH, become much lower as compared with that of pure PVA, which may imply that the silanol group Si—OH on the surface of SiO₂ particles has reacted with —OH of PVA, creating a new covalent bonding Si—O—C. The reason for wider absorption around 1100 cm^{-1} is that the symmetric Si—O—Si stretching peak at

1030–1100 cm^{-1} , C—O peak, and the new Si—O—C peak overlapped together. This has also been reported by Xu et al., that is, a lot of silanol groups have condensed with the hydroxyls on PVA chain to form a Si—O—PVA—O—Si bridge. The presence of Si—O—C and Si—O—Si bonds confirmed the existence of a chemical bonding linkage between the organic groups and silica.¹⁸

SEM and EDS characterization of hybrid materials

From Figure 2(a–c), we can see that with increasing SiO₂ content from 0 to 3%, the size of SiO₂ particles emerges a trend of growing bigger and the particles distribution becomes more homogeneous. The similar phenomena can also be seen from Figure 2(a),(d–f). The SiO₂ particles, which have been confirmed by EDS analysis (Fig. 3), distribute uniformly at 1%, 2%, and the sizes maintain about 1–2 μm . But when the SiO₂ content reaches 5%, the particles aggregated and no longer evenly distribute. The size comes up to 10 μm or even 20 μm .

In Figure 2(a), a lot of herringbones and small carved face can be seen on the smooth fracture surface of the pure phenolic resin, which implies a typical brittle fracture. A number of dimples, shear fiber, and microcracks can be seen on the fracture of the hybrid materials 40-60-1% and 40-60-2%. These morphologies indicate some typical ductile fractures. But the fractures turned into brittle fractures when the SiO₂ content reached 5% as shown in Figure 2(f). Thus with the increase of the SiO₂ content, a ductile-brittle transition process changing from the brittle to ductile and then turning into brittle, happened to the hybrid materials. The improved toughness is mainly because of two reasons. However, the hydroxyl groups in phenolic

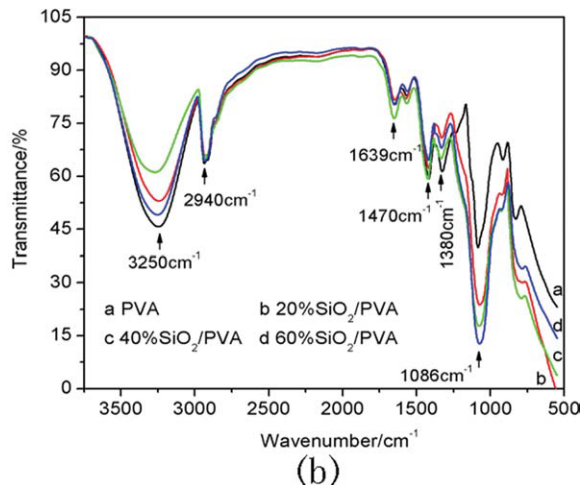
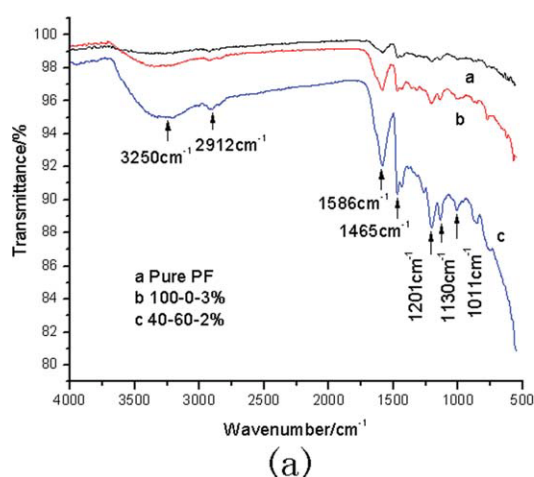


Figure 1 (a) FTIR spectra of PF and phenolic resin-based composites; (b) FTIR spectra of the mixtures of silica sol and PVA. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

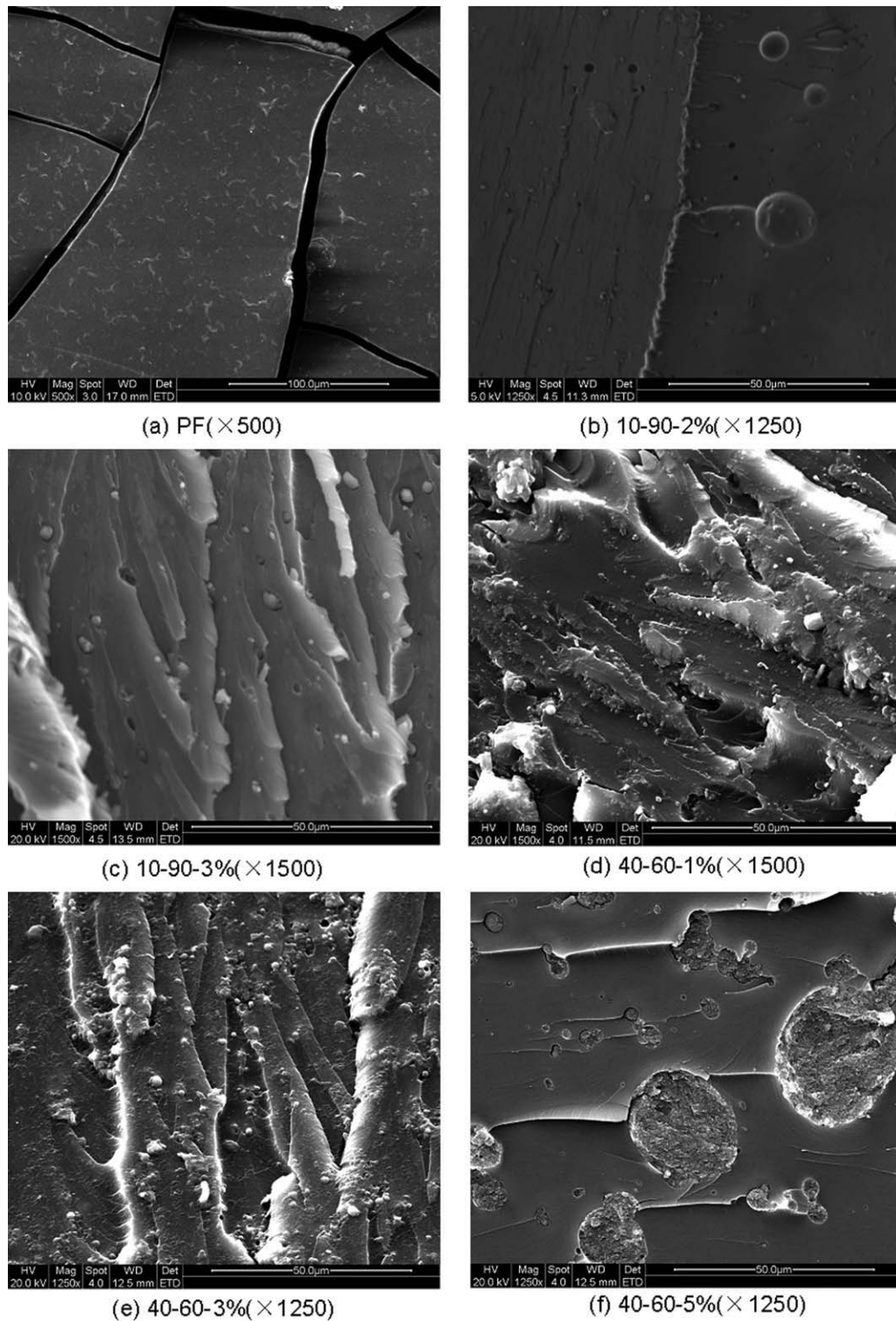


Figure 2 SEM micrographs of phenolic resole resin and modified phenolic resole resin. (a) PF (b) 10-90-2% (c) 10-90-3% (d) 40-60-1% (e) 40-60-2% (f) 40-60-5%.

resin matrix and on the surface of SiO_2 particles react and generate a new covalent bonding Si-O-C , which has been confirmed by infrared spectroscopy. So the debonding of SiO_2 particles requires greater force when the fracture takes place, and it absorbs more deformation energy so that the

toughness increased. The other reason is mainly the blocking effect of the second-phase particles. First of all, the existence of the second-phase particles leads to a stress concentration effect and is easy to lead the matrix resin to produce plenty of second-phase particles existed in the matrix passivate the

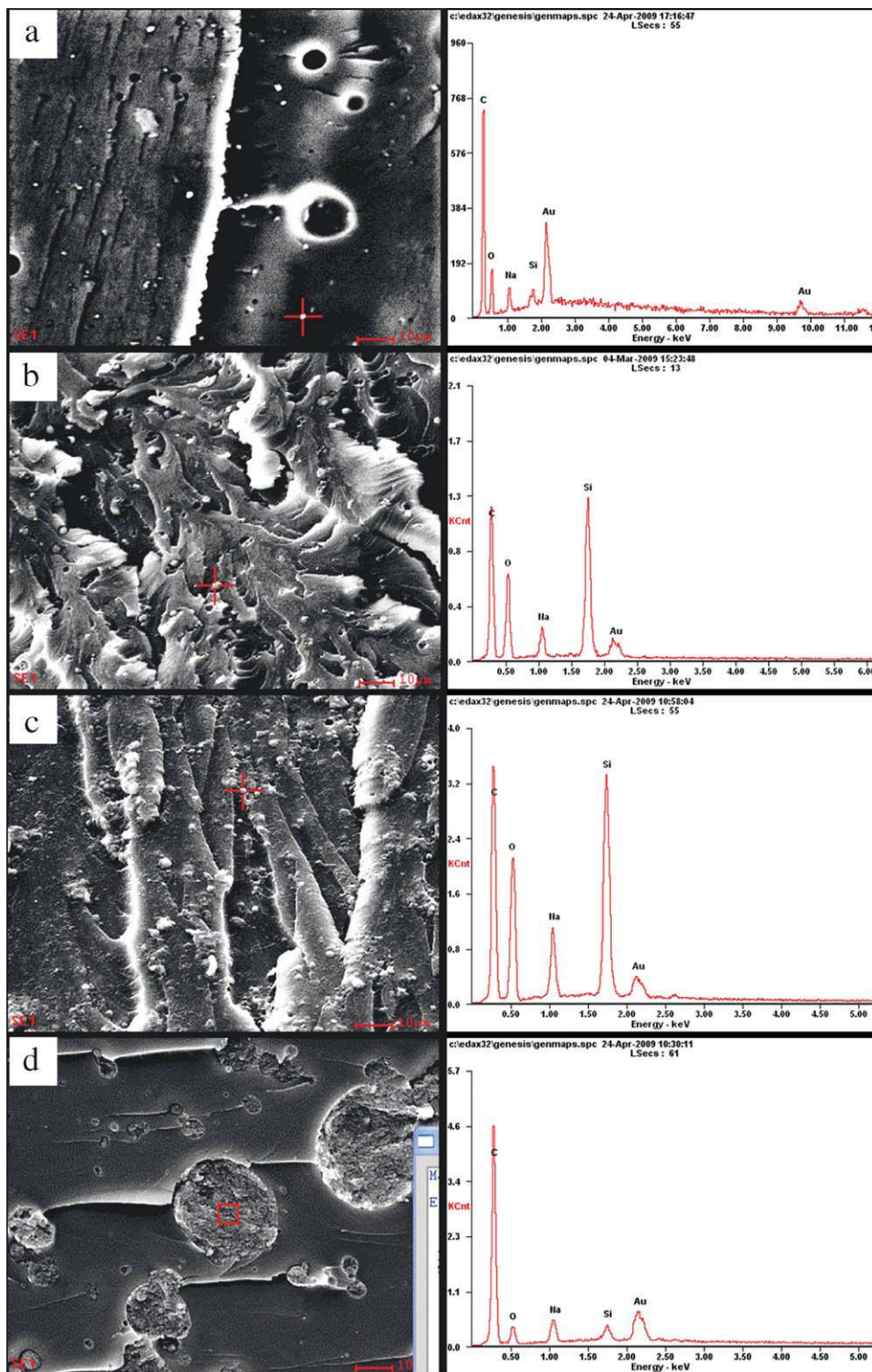


Figure 3 The EDS spectrum of phenolic resin-based composites. a:10-90-2% b:10-90-3% c:40-60-2% d:40-60-5%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

crack tips and delay the propagation of these cracks, so as to terminate the cracks developing into a destructive crack ultimately. However, if the second-phase particles is too large, microcracks can easily develop into a macrocrack so that the system

performance would turn worse, so to the material 40-60-5%.

By Comparing Figure 2(b,e), we can see that the hybrid material 40-60-2% has a greater particle diameter, which is mainly because of the chemical

TABLE I
The Shear Strength (MPa) of all Experimental Materials

Series	The content of SiO ₂					
	0%	1%	2%	3%	4%	5%
10-90	1.14	1.57	2.17	2.70	1.70	1.39
20-80	1.14	1.79	1.98	2.72	1.82	1.41
30-70	1.14	1.23	1.45	1.74	2.66	1.77
40-60	1.14	2.29	2.84	2.13	1.62	1.23
50-50	1.14	2.13	2.68	2.94	1.81	1.75
60-40	1.14	2.36	2.43	2.71	2.44	2.05
70-30	1.14	2.22	1.62	1.42	1.27	1.04
80-20	1.14	2.51	2.79	2.78	2.64	1.28
90-10	1.14	1.74	2.07	2.08	2.34	1.46
100-0	1.14	2.14	2.41	2.20	2.06	1.93
Average	1.14	2.00	2.24	2.34	2.04	1.53

reaction between PVA and SiO₂ particles. Because of the chemical bonds, the PVA molecular chain is attached to the surface of SiO₂ particles, which plays the role of steric hindrance. Therefore, for the SiO₂ particles, PVA is the surfactant and has a certain effect on the dispersion. From 40-60 series to 10-90 series, PVA ratio becomes higher, so the particles disperse better and the size becomes smaller.

Figure 3 displays the EDS photographs that can be used to confirm the aggregation of the SiO₂ particles. The EDS photographs of the cross mark demonstrated high Si intensity. For 10-90-2%, as the particles are smaller, the point analyzed is a little biased from the particle, so the content of element Si is lower. For 40-60-5%, as the particles have peeled off, the content of element Si is lower too.

Tensile shear test (TSS)

Table I and II are summaries the TSS results, including the shear strength and the elongation at break of each series. Figure 4(a) represents the regular variation of the tensile shear strength and elongation of the 20-80 series. Figure 4(b,c) show the changes of the tensile shear strength and elongation of the five series, respectively. Figure 4(d) shows the changes of the average tensile shear strength and average elongation of all series.

From Table I and II, we can see that when the weight ratio of SiO₂ and PVA is 50 : 50 and the SiO₂ content is 3%, compared with the pure PF, the tensile shear strength and elongation at break of the hybrid material increase 158% and 63% respectively, reaching 2.94 MPa and 5.58%.

From Figure 4(a-c), we can see that for each series, with the increase of SiO₂ content, the shear strength first increases and then declines. The variation of the elongation at break is similar to that of the tensile shear strength. The higher the shear strength, the greater of the elongation at break. This indicates that the adhesive strength and the tensile

ductility of the PF are both improved simultaneously, when modified with the mixture of silica sol and PVA. The increase of the shear strength is mainly as a result of the second-phase particles pinning effect. The second-phase particles present in the matrix resin, hinder the movement of the polymer resin chain segment so that it needs greater force to lead to fractures. Therefore, the tensile shear strength is enhanced. Changes mentioned above is mainly because of two aspects. The first important influencing factor is the second-phase particles, that is, the size of SiO₂ particles and the degree of dispersion, and the volume fraction of the second-phase particles. Under the same conditions, with the reduction of the second-phase particle diameter, or with rising of the second-phase volume fraction, the shear strength increases significantly. In contrast, with the reduction of the second-phase volume fraction, or with the increase of the second-phase particles diameter, the shear strength of composite materials decreases a lot. The other influencing factor is hydroxyl (-OH) content of the hybrid materials. Because -OH is a strong polarity group, it plays the major role in the bonding. When SiO₂ content is low, the size of SiO₂ particle is small, they disperse evenly, and the adhesive tensile shear strength is positive correlation with the volume fraction of the the second-phase. That is, as the SiO₂ content increases, the shear strength increases too. When the SiO₂ content reaches a certain volume fraction, if the content continues to increase, serious agglomeration happens, particle size increases rapidly, and the distribution no longer keep uniform. Therefore, the intensity drops soon. Because of the modification, the tensile strength increases, so that in the same degree of deformation, the modified PF can withstand greater breaking strength, whereas under the same fracture strength, the modified PF can withstand a greater degree of deformation. Furthermore, PVA

TABLE II
The Elongation at Break (%) of All Experimental Materials

Series	The content of SiO ₂					
	0%	1%	2%	3%	4%	5%
10-90	3.43	3.60	5.00	4.50	4.02	3.35
20-80	3.43	4.25	4.60	5.70	4.30	4.10
30-70	3.43	3.45	3.88	3.65	4.60	3.80
40-60	3.43	4.78	6.15	4.95	4.05	4.10
50-50	3.43	5.15	5.20	5.58	4.13	4.13
60-40	3.43	4.90	4.70	5.85	5.55	4.53
70-30	3.43	6.35	4.43	4.05	3.58	3.43
80-20	3.43	4.73	5.90	6.97	4.90	3.48
90-10	3.43	4.18	4.33	4.26	5.30	4.08
100-0	3.43	4.55	5.63	5.02	4.68	4.15
Average	3.43	4.59	4.98	5.05	4.51	3.92

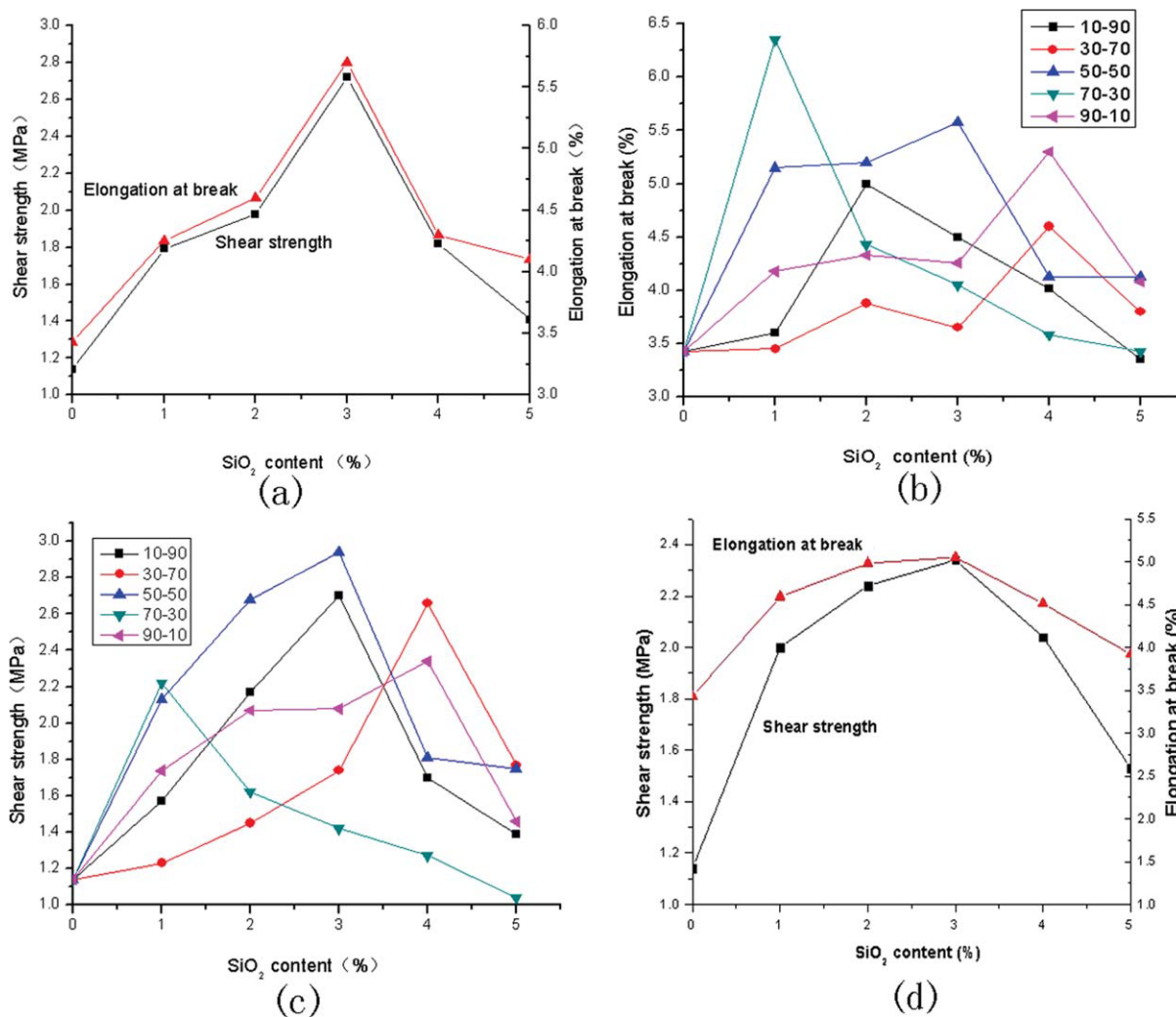


Figure 4 (a) The shear strength and elongation at break of 20–80 series; (b) The shear strength of five series; (c) The elongation at break of five series; (d) The average shear strength and average elongation at break of all series. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

modification introduces long aliphatic chains, which have better plasticity and reduces the fraction of rigid segments.

For each column of Table I, from top to bottom, that is, with the decrease in relative content of PVA, the changes in shear strength have no rules. This is mainly because, when the SiO_2 content is fixed, the adhesive properties of the hybrid materials are mostly affected by the number of hydroxyl. Because the hydroxyl exist in the silica sol, PVA, and phenolic resin, when the ratio among the three changes, the final amount of hydroxy in the hybrid materials changes too. Therefore, the final bond strength appears a certain volatility and complexity. In addition, when the content of the surfactant PVA changes, the dispersion of SiO_2 particles and the particle size alters, which also have an appreciable effect on the shear strength. This increases the complexity of the stretching rules further.

In Figure 4(d), with the increase of SiO_2 content, the average tensile shear strength of all series first increases and then declines, which indicates that the dispersion of SiO_2 particles and the particle size play a major role in the adhesive bonding strength of the modified PF.

TG measurements

The TG results are shown in Table III and Figure 5. The heat resistance of the PF modified with silica sol

TABLE III
5, 10, 15, and 25% Mass Loss Temperature ($^{\circ}\text{C}$)

	T-5%	T-10%	T-15%	T-25%
50–50–3%	196.9	292.7	407.0	544.8
Pure PF	201.7	289.0	398.8	543.7
100–0–2%	240.8	378.5	471.0	602.3
0–100–25%	258.6	317.2	389.1	478.3

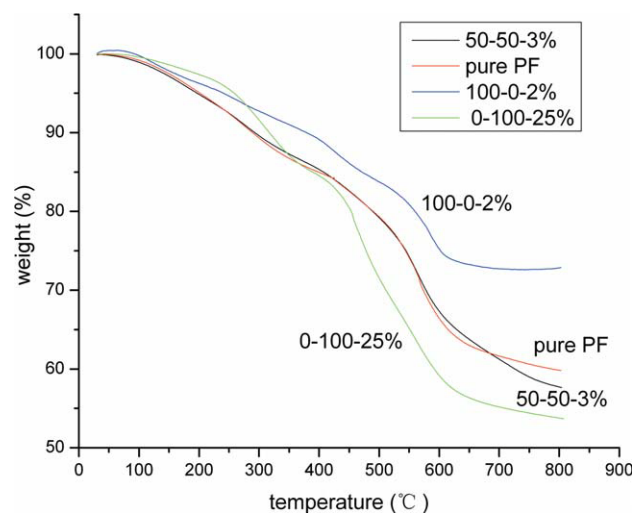


Figure 5 TG curves of phenolic resole resin and modified phenolic resole resin. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

is the best, whereas the PF modified with PVA is the worst. The hybrid material 50-50-3% and pure PF have considerable heat resistance.

Among 300–600°C, compared with the pure PF, the heat resistance of the PF modified with silica sol increases more than 60°C, and at the temperature higher than 600°C, the PF modified has much better heat resistance. As inorganic phase, SiO₂ itself has much better heat resistance than the organic resin. Meanwhile, when the silica sol is added into the PF, the Si—OH on the surface of SiO₂ particles reacts with the phenolic resin of the phenol hydroxy or hydroxymethyl of PF and creates a chemical bond Si—O—C with high energy. Destruction of such chemical bonds require a higher temperature.

Below 350°C, because of the small proportion of phenolic resole resin in the hybrid 0-100-25% and the less volatile monomers phenol and formaldehyde, compared with the pure PF, the weight loss of 0-100-25% was smaller. But above 350°C, the weight loss of 0-100-25% is greater. It appears bad high-temperature heat resistance. It is mainly because PVA modification introduces long aliphatic chain, and the methylene groups in which are very easily oxidized. Therefore, heat resistance decreases badly.

It is precisely because silica sol and PVA have opposite effects on the thermal stability of the hybrid materials, the adhesive 50-50-3% and pure PF had almost the same heat resistance.

CONCLUSIONS

In this study, we have prepared the modified PF with the mixture of PVA and silica sol for the first time. This study clearly shows that the method of modifying can improve the tensile ductility and bonding strength of PF at the same time. Infrared spectroscopy confirmed that the reactions among PVA, silica sol, and the PF occurred in the process of preparing hybrid materials and produced a new chemical bond Si—O—C. Furthermore, Silica sol and PVA have opposite effects on the thermal stability of PF; the hybrid material 50-50-3% and pure PF have almost the same heat resistance. Therefore, the modified PF will be useful for potential applications of wood adhesives and molding compound.

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References

- Zhangxiong, W.; Yan, M.; Dongyuan, Z. *Micropor Mesopor Mat* 2010, 128, 165.
- Ahmad Reza, B.; Mehrdad, K.; Mohammad Hossein, N. F.; Mohammad Hossein, B. *Polymer* 2006, 47, 3661.
- Mohamed, O.; Abdalla, L.; Temisha, M. *Polymer* 2003, 44, 7353.
- Higgins, A. *Int J Adhes Adhes* 2000, 20, 367.
- Cihat, T.; Barry, G.; Roberto, L.-A.; Michael, P.; William, H.; Jody, J. *Int Biodeterior Biodegradation* 2003, 51, 157.
- Byung-Dae, P.; Bernard, R.; Yoon Soo, K.; Won Tek, S. O. *J Appl Polym Sci* 2002, 83, 1415.
- Svetlana, P.; Kaichang, L. *J Biotechnol* 2003, 102, 199.
- Gietl, T. D.-I.; Lengsfeld, H. D.-I.; Altstadt, V. D.-I. *J Mater Sci* 2006, 41, 8226.
- Hongbin, S.; Steven, N. *Compos A* 2003, 34, 899.
- Changsong, L.; Paul, E. *Compos Sci Technol* 2007, 67, 1475.
- Paul, D. R.; Robeson, L. M. *Polymer* 2008, 49, 3187.
- Maurizio, N.; Josè, K.; Luigi, T. *Compos Sci Technol* 2010, 70, 571.
- Schmidt, H.; Jonschker, G.; Goedicke, S.; Mennig, M. *J Sol-Gel Sci Technol* 2000, 19, 39.
- Permpoon, S.; Berthomé, G.; Baroux, B.; Joud, J. C.; Langlet, M. *J Mater Sci* 2006, 41, 7650.
- Paqui, I.; Jin, F.; Jordi, E.; Tharward, F.; Tadros, C.; Dederen, G.; Núria, A. *J Colloid Interface Sci* 2005, 285, 388.
- Juan, L.; Jinping, S.; Runzhi, D. *J Reinf Plast Comp* 2010, 29, 618.
- Hernández-Padrón, G.; Rojas, F.; García-Garduño, M.; Canseco, M. A.; Castano, V. M. *Mater Sci Eng A* 2003, 355, 338.
- Xu, Y.; Li, Z.; Fan, W.; Wu, D.; Sun, Y.; Rong, L.; Dong, B. *Appl Surf Sci* 2004, 225, 116.