

## Effects of Fiber Surface Treatments on the Properties of Wood Fiber–Phenolic Foam Composites

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Wood fibers were modified with alkaline solution and silane coupling agent to study changes on the fiber surface and the influence of these treatments on the mechanical properties, flame resistance, thermal conductivity, and microstructure of wood fiber-phenolic foam composites. Test results indicated that the lignin, waxes, hemicelluloses, and other impurities from the fiber surface were partially dissolved and removed. The mechanical properties of treated wood fiber-phenolic foam composites increased dramatically, the cellular pore distribution was more regular, the size of bubble cells was smaller and more uniform, and the thermal conductivity was reduced, and, in particular, the fragility of treated wood fiber-phenolic foam composites decreased. However, with increasing wood fiber content, the mechanical properties and limited oxygen index (LOI) of composite foam decreased. By comprehensive analysis, it was shown that the interfacial compatibility between the fibers and phenolic resin was improved. Nevertheless, the amount of wood used could not be too high, and the optimum amount was approximately 5%.

*Keywords:* Wood fiber; Surface modification; Silane coupling agent; Composites; Characterization

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### INTRODUCTION

Phenolic foams (PFs) are excellent retardant materials that are characterized by low thermal conductivity, excellent fire-resistant performance, low water absorption, and low generation of toxic gases during combustion and have been widely applied in the fields of agriculture, horticulture, thermal insulation, and sound insulation (Lei *et al.* 2010; Yang *et al.* 2012). However, the intrinsic brittleness and powdering of PFs have severely restricted their applications (Rangari *et al.* 2007). In general, the brittleness of PFs can be reduced by the introduction of fiber materials, such as glass fibers. However, there many shortcomings of this approach, including the costs and non-renewability which make it challenging (Shen *et al.* 2003; Shen and Nutt 2003; Yang and He 2015).

As a kind of environmentally friendly natural polymer-reinforced material, natural fibers are regarded as an abundant and low cost, biodegradable, flexible, and more energy-efficient material during processing with minimal health hazards, low density, desirable fiber aspect ratio, and relatively high tensile and flexural moduli (Mitra *et al.* 1998; Rana *et al.* 1998; Bledzki and Gassan 1999; Canche-Escamilla *et al.* 1999; Xie *et al.* 2010). Incorporating the tough and light-weight natural fibers into polymer (thermoplastic and thermoset) matrices produces composites that have some major advantages over conventional composite materials (Wambua *et al.* 2003; Baiardo *et al.* 2004; Wong *et al.* 2004). Although natural fibers can offer the resulting composites many advantages, the

polar fibers usually have inherently low compatibility with the non-polar polymer matrices (Bledzki *et al.* 1998; Cantero *et al.* 2003). This incompatibility may cause problems in composite processing and material properties. Hydrogen bonds may be formed between the hydrophilic fibers, causing the fibers to agglomerate into bundles and thus be distributed unevenly throughout the non-polar polymer matrix during the compounding process (Raj *et al.* 1989; Kazayawoko *et al.* 1999). There is also insufficient wetting of the fibers by the non-polar polymer matrices, resulting in weak interfacial adhesion.

By this token, wood fibers are often modified to improve the water resistance of fibers and to enhance the interfacial compatibility between natural fiber and polymers. A well-known surface treatment for natural fibers uses alkaline solution, which can change the chemical composition of fibers. Thus, the fiber surface becomes rough, which enhances the interfacial adhesion between fiber and resin, and this improves the mechanical performance of composite materials (Bledzki *et al.* 1996; Mohanty *et al.* 2002; Ouajai and Shanks 2005; Islam and Pickering 2007; Bachtiar *et al.* 2008). Silanes are recognized as efficient coupling agents used to enhance the interfacial compatibility of natural fiber/polymer composites (Rider and Arnott 2000; Mittal 2007). Silane coupling agents possess many advantages: at one end, they contain alkoxy silane groups that can interact with hydrophilic groups such as the -OH of natural fiber surfaces; at the other end, there are a large number of functional groups that can react with hydrophobic compounds such as polymers. Therefore, as a bridge, silane coupling agents can couple together hydrophilic and hydrophobic materials. Although the treatment is well established with natural fiber composites, its effect on natural fibers has not been extensively studied in natural fiber-phenolic foam composites (Colom *et al.* 2003; Pickering *et al.* 2003; Te-fu *et al.* 2005; Towo and Ansell 2008).

The objective of this study was to investigate the effects of alkali, silane coupling agents, and their complexes on the properties of wood fibers and their phenolic foam composites. Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), and scanning electron microscopy (SEM) of modified wood fibers were performed, and the mechanical properties, flame resistance, fragility, thermal conductivity, and microstructure of wood fiber-phenolic foam composites were measured.

## EXPERIMENTAL

### Materials

The formaldehyde (37%), phenol (> 99%), calcium oxide (CaO), phosphoric acid and hydrochloric acid (36%) were purchased from Nanjing Chemical Reagent (China), paraformaldehyde ( $\geq 95\%$ ), sodium hydroxide (NaOH), *p*-toluenesulfonic acid, polysorbate-80, petroleum ether and dicumyl peroxide were purchased from Sinopharm group Chemical Reagent Co. Ltd. (China). Vinyl trimethoxy silane (VTMOS) was obtained from GE Toshiba Silicones co. Ltd (Japan). Eucalyptus fiber was provided by Guangxi Fenglin Wood Industry Group Co. Ltd (China).

### Synthesis of High-Solid Resol Phenolic Resin

Formaldehyde (0.7 mol), phenol (2.15 mol), and CaO (0.0075 mol) were introduced into a 500-mL four-necked round-bottom flask fitted with a stirrer and condenser, and the mixture was allowed to react for 30 min under continuous stirring at 90 °C. The first part of paraformaldehyde (0.9 mol) and NaOH aqueous solution (50%, 0.15 mol) was added

into the reactor and continued to react at 90 °C for 60 min. Then, the second part of paraformaldehyde (0.9 mol) and NaOH aqueous solution (50%, 0.15 mol) was added and reacted at 85 °C for 60 min. Finally, the third part of NaOH aqueous solution (50%, 0.075 mol) was added to the reactor and the reaction was performed at 75 °C for 20 min. The high-solid resol phenolic resin (HSRPR) was obtained after cooling down to 40 to 50 °C. The solid content of HSRPR was approximately 80 wt%, calculated by oven-dry measurements.

## Pretreatment Method for Wood Fibers

### *Alkaline treatment*

Wood fibers were immersed in NaOH aqueous solution (4 wt%) for one hour at 25 °C. Then, they were washed with distilled water until the pH value of the washing solution was approximately 7. Subsequently, the wood fibers were dried at 60 °C for 24 h.

### *Silane coupling agent treatment*

Silane aqueous solution was used to treat both alkaline-treated and untreated wood fibers. The composition of the silane solution incorporated was 2 wt% VT MOS and 2 wt% dicumyl peroxide. The pH of the silane solution was adjusted to 3.5 with acetic acid. Then, the fibers were immersed in the solution for 4 h. Finally, the fibers were dried at 60 °C for 24 h.

**Table 1.** Nomenclature of Wood Fiber Surface Pretreatments

Sample No.	Surface treatment
WF	No treatment
SWF	Wood fiber treated with 4% aqueous NaOH solution
SVWF	Wood fiber treated first with 4% aqueous NaOH solution and then with VT MOS
VWF	Wood fiber treated with VT MOS

**Table 2.** Nomenclature of Wood Fiber-Phenolic Foam Composites

Keyword	Fiber phenolic foam composite
WFPFC	WF phenolic foam composite
SWFPFC	SWF phenolic foam composite
SVWFPFC	SVWF phenolic foam composite
VWFPFC	VWF phenolic foam composite

## Preparation of Wood Fiber-Phenolic Foam (PF) Composites

Surfactants (polysorbate-80), acid curing agents, blowing agents (petroleum ether), and wood fibers were added into HSRPR and mixed well; then, the mixture was poured into a mold. The PFs were obtained after foaming for 40 min at 70 °C.

## Measurements and Characterization

### *FT-IR measurements of wood fibers*

Vacuum-dried (60 °C, 24 h) samples were characterized using an FT-IR spectrometer (Nicolet IS10, USA).

#### *X-ray diffraction measurements of wood fiber*

All wood fibers were subjected to X-ray diffraction (Shimadzu 6000 X, Kyoto, Japan) measurements. The measurement parameters used were a Cu target, pipe pressure/flow of 40 kV/40 mA, scanning speed of 4°/min, sampling step width of 0.02°, shaft dynamic continuous scanning of 1, and  $2\theta = 5$  to 50°.

#### *Scanning electron microscopy (SEM) of wood fibers and foams*

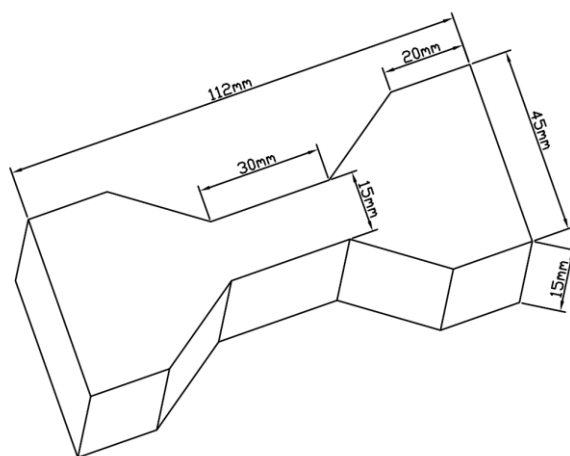
SEM images of all wood fibers and foams were acquired using a Hitachi S3400-N microscope (Kyoto, Japan). Prior to the analysis, the samples were coated with gold using E1010 Ion Sputter (Kyoto, Japan) to avoid sample charging under the electron beam.

#### *Compression and bending strength measurements of foams*

The compression strengths of the foams were tested by the ISO 844 (2014). The dimensions of the samples used for the test were 50×50×50 mm. The bending strength of foams was measured by the standard ISO 1209-1 (2007), and the size of samples used for the test was 120×25×20 mm.

#### *Tensile properties measurements of foams*

Tensile properties were measured using the standard ISO 1926 (2009). The shape and size of the samples used were as shown in Fig. 1. Approximately 5 measurements were made for each sample, and their arithmetic mean is reported.



**Fig. 1.** The schematic diagram of sample using tensile properties test

#### *Fragility test*

Fragility was determined in accordance with ISO 6187 (2001). The size of samples used for the test was 25×25×25 mm. Three sets of samples were tested, and the average is reported.

#### *Limiting oxygen index (LOI)*

The LOI test was carried out with a JF-3 oxygen index meter (LOI analysis instrument company, Jiangning County, China) according to ISO 4589-1 (2017). The size of samples used for the test was 100×10×10 mm.

### Thermal conductivity test

The thermal conductivity of foam samples was tested using a T322 thermal conductivity analyzer (C-THERM company, Canada), according to ISO 22007-2 (2015), using the transient heat method.

## RESULTS AND DISCUSSION

### FT-IR of Wood Fibers

Figure 2 shows the FT-IR spectra of wood fibers. It can be seen that the stretching vibration peak at  $1730\text{ cm}^{-1}$ , which can be ascribed to the C=O stretching of methyl ester and carboxylic acid groups in pectin or the acetyl group in hemicelluloses (Silverstein *et al.* 2014), disappeared from SWF and SVWF samples. This indicated that a portion of the lignin, pectin, and hemicelluloses can be successfully extracted by means of washing with an alkaline solution (Marchand 1985; Valadez-González *et al.* 1995; Lu *et al.* 2005). The characteristic absorption bands of SVWF were enhanced at  $1030\text{ cm}^{-1}$ , and the characteristic bands of VWF were enhanced at  $1030$ ,  $1230\text{ cm}^{-1}$ , and  $1730\text{ cm}^{-1}$ , respectively. This was because of the reaction that occurred between some of the hydroxyl groups of cellulose on the surface of the fiber and the hydroxyl groups of silanol (obtained after hydrolysis of silane). Thus, an ether bridge,  $-\text{Si}-\text{O}-\text{Si}-$ , and  $-\text{Si}-\text{O}-\text{C}-$  bonds were introduced on the surface of the fibers (Valadez-Gonzalez *et al.* 1999; Cui *et al.* 2008), which led to the appearance or the increase in the absorbance in the regions of  $1230$  and  $1030\text{ cm}^{-1}$ . The peak at approximately  $1730\text{ cm}^{-1}$  was due to the esterification of the hydroxyl groups, which resulted in an increased stretching vibration of the carbonyl (C=O) group present in the ester bonds (Silverstein *et al.* 2014).

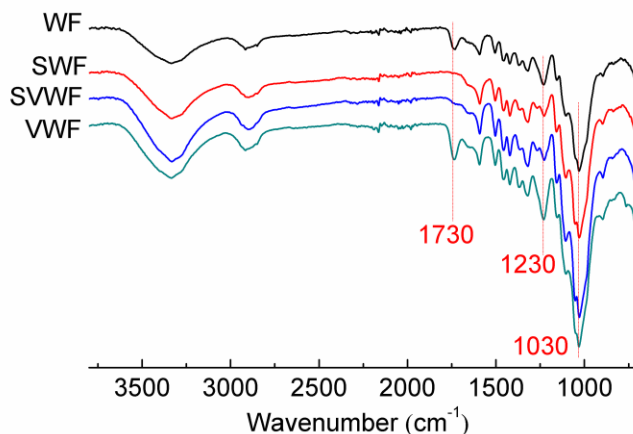


Fig. 2. FT-IR spectra of wood fibers

### XRD of Wood Fibers

Figure 3 displays the X-ray diffraction spectra of wood fibers. There were two X-ray diffraction peaks for wood fibers: a sharp high peak at  $2\theta = 22.6^\circ$  and a weaker diffraction peak at  $2\theta = 15.6^\circ$ , which could be assigned to the (002) and (101) planes (Wang *et al.* 2007). The positions of the diffraction peaks for all samples were basically unchanged. The results showed that the crystal form of the treated wood fibers was

unchanged, but the intensities of diffraction peaks were only slightly changed. This could be attributed to the partial removal of some impurities, waxes, pectin, oil, and hemicelluloses on the fiber surface by washing with an alkaline solution. Hence, the cellulose could adopt a better arrangement, causing the crystallinity of the fibers to slightly increase. By treating with a silane coupling agent, a portion of the low-molecular weight substances and impurities on the fiber surfaces were dissolved and removed; therefore, the crystallinity of the fibers also slightly increased.

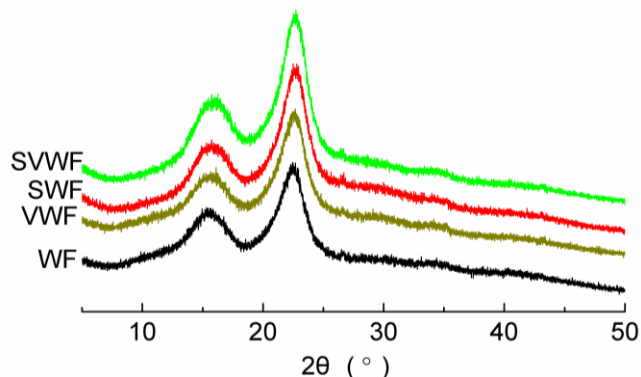


Fig. 3. X-ray diffraction spectra of wood fibers

### SEM of Wood Fibers

SEM micrographs of wood fibers are shown in Fig. 4.

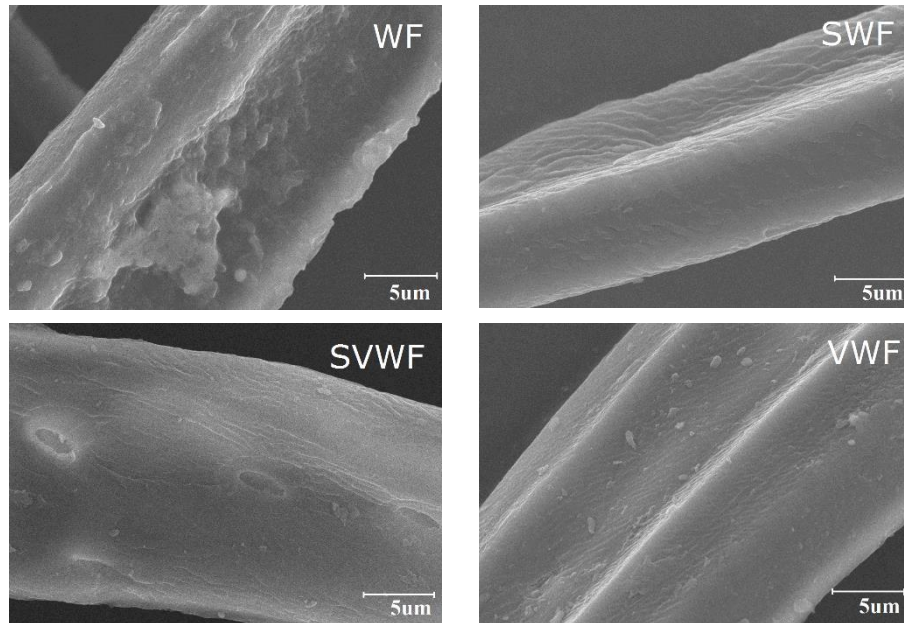


Fig. 4. SEM micrographs (4000 $\times$ ) of wood fibers

The surface of WF was not neat or smooth and was covered with pectin, lignin, hemicellulose, waxy substances, and impurities (Wang *et al.* 2007). The surface of SWF was etched after the treatment with alkaline solution and became rough (Valadez-Gonzalez *et al.* 1999). Thus, the interfacial compatibility between the fiber and polymer matrix was improved. The roughness of the SVWF surface decreased, as a reaction occurred between

the silane coupling agent and the hydroxyl groups on the surface of the fiber, which was advantageous to the bonding stability between the fiber and polymer matrix (Lu *et al.* 2005). The surface of VWF was also etched and became rough. This may be explained by the introduction of coupling agent groups on the fiber surface, as some of the impurities on the fiber surface were removed after the treatment.

### Compression and Bending Properties of Phenolic Foam Composites (PFCs)

As shown in Figs. 5 and 6, from the overall trend, the bending and compression strengths of PFCs decreased with increasing contents of wood fiber used in composite foams. The compression and bending strengths of SWFPFC, SVWFPFC, and VWFPFC were higher than that of WFPFC, especially those of SVWFPFC. The reason was that the structure of the fiber surface changed after treatment with alkaline solution or coupling agent. These results were also confirmed by the SEM images of the wood fibers (Fig. 4). The interfacial compatibility was improved between the fiber and polymer matrix, and the surface groups of wood fibers crosslinked with certain groups of the phenolic resin. Therefore, the compression and bending strengths of the treated fiber composite foam were improved observably. Otherwise, the structure of the bubble wall was destroyed when the wood fiber was introduced into the composite foam, which reduced the bubble distribution uniformity. As the dosage of wood fibers introduced in the composite foam increased, a larger effect on the strength and the bubble wall was observed. Hence, with the addition of wood fibers, the influence of the fibers on the strength and distribution uniformity of the bubble increased gradually, which led to a reduction in the compression and bending strengths of the composite foam.

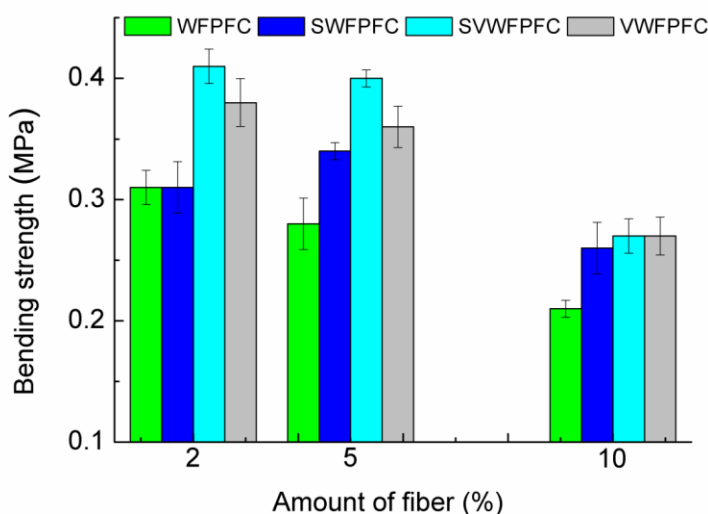
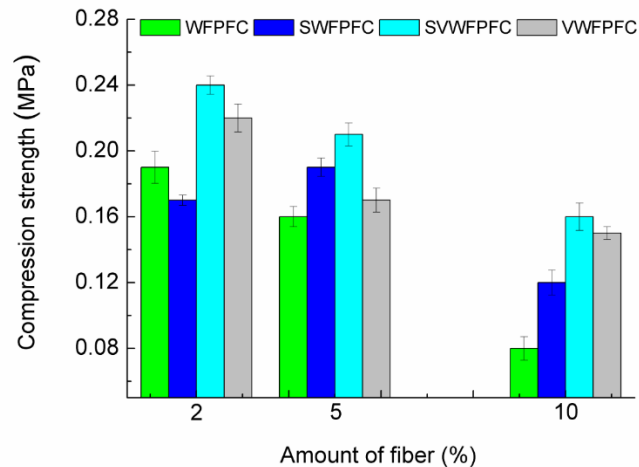


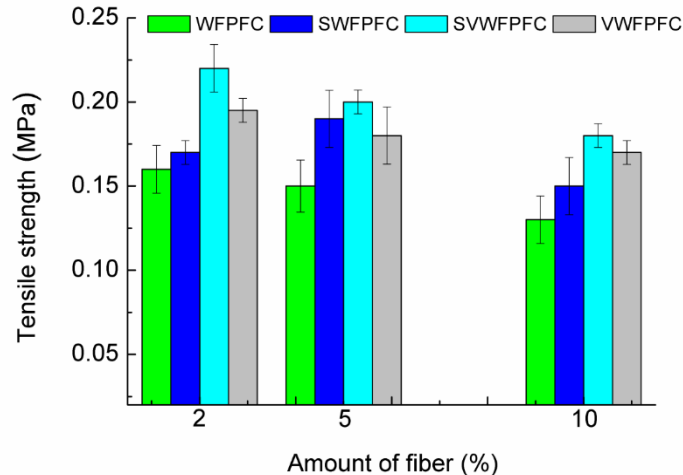
Fig. 5. Bending strength of PFCs



**Fig. 6.** Compression strength of PFCs

### Tensile Properties of PFCs

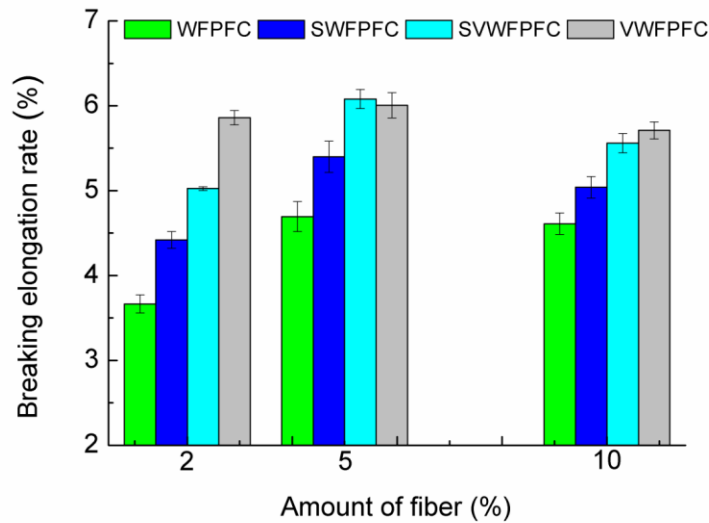
As shown in Figs. 7 and 8, compared with WFPFC, the tensile strength and breaking elongation rate of SWFPFC, SVWFPFC, and VWFPFC observably increased. This shows that the compatibility between fibers and the phenolic resin was enhanced after wood fiber surface treatment. Therefore, the resistance ability of tensile deformation improved considerably.



**Fig. 7.** Tensile strength of PFCs

The prominent improvement of the breaking elongation rate indicated that the compatibility between fibers and phenolic resin increased after wood fiber surface treatment. Nevertheless, with increasing amount of wood fibers, the influence of fibers on the strength increased gradually. Therefore, the tensile strength of treated fiber composite foams gradually decreased with increasing amount of wood fibers. However, with the increment of wood fiber content, the probability of crosslinking reactions also increased between the surface groups of wood fibers and phenolic resin. Hence, the breaking elongation rate of treated fiber composite foams observably increased with the addition of wood fibers.

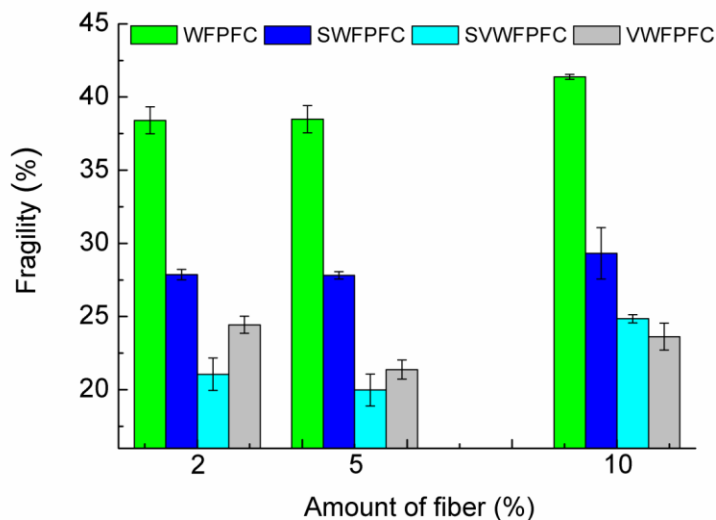




**Fig. 8.** Breaking elongation rate of PFCs

### Fragility Properties of PFCs

Fragility is one of the most important properties of phenolic foams and is measured using the ratio of mass loss from surface abrasion and impact damage: the smaller the ratio of mass loss is, the better the toughness is. Otherwise, it was a more fragile foam, as shown in Fig. 9. The analysis revealed that the ratio of mass loss of WFCF and SWFCF slightly increased with increasing dosage of wood fiber. The reason could be that with the increasing content of fibers, the original bubble structure was destroyed and the bubble uniformity decreased, which led to the increased loss of mass. However, with an increase in wood fiber content, the ratio of mass loss of SVWFCF and VWFCF was slightly decreased, and then slightly increased.



**Fig. 9.** Fragility of PFCs

The ratio of mass loss was least when the amount of fiber was at 5%. The reason is that with an increase in the amount of wood fibers, the influence of fibers on the strength and distribution uniformity of the bubble increased gradually. Nevertheless, the probability

of crosslinking reactions increased between the surface groups of wood fibers and certain groups of the phenolic resin. When the amount of fibers was 5%, a balance was formed between the adverse effects and the beneficial effects. Then, the adverse effects had the upper hand. Therefore, the ratio of mass loss of SVWFPFC and VWFPFC was least when the amount of fiber was 5%. Compared with untreated WFCF, the ratio of mass loss of SWFPFC, SVWFPFC, and VWFPFC obviously decreased, which further showed that after surface modification, the interfacial compatibility between the fiber and polymer noticeably improved.

### Limited Oxygen Index of PFCs

Limited oxygen index (LOI) is a very important indicator for the properties of phenolic foams. The LOI can be used to evaluate the difficulty of the material combustion by measuring the minimum oxygen concentration when the material is burnt. The higher the LOI is, the better the flame retardancy of the material is. As shown in Fig. 10, the LOI of PFCs remained at 33.9% to 40.7%, which is greater than 27%; thus, these composites can be considered flame-retardant materials (Cuicui and Dai Zhen 2010). With the addition of increased quantities of wood fibers, the LOI of PFCs decreased gradually, and the LOI of VWFPFC was reduced considerably. Compared with WFPFC, the LOIs of SWFPFC and SVWFPFC were slightly greater than that of WFPFC when the content of fibers was less than or equal to 5%. Then, the LOIs were slightly less than that of WFPFC. Nevertheless, the LOI of VWFPFC was less than that of WFPFC. The main reason was that the fibers are not flame retardant, and the flame resistance of the phenolic resin is greater than that of the wood fibers. After processing, the interfacial compatibility between fibers and polymers was greatly improved. When the amount of fibers was less than 5%, a large number of polymers adhered to the surface of the fibers, forming a “wick” effect; hence, the LOI slightly increased. However, when the dosage of fibers was greater than 5% (10%), there was not enough phenolic resin to cover the wood fibers and there was no effective heat transfer, which led to the dramatic reduction of the LOI of PFCs.

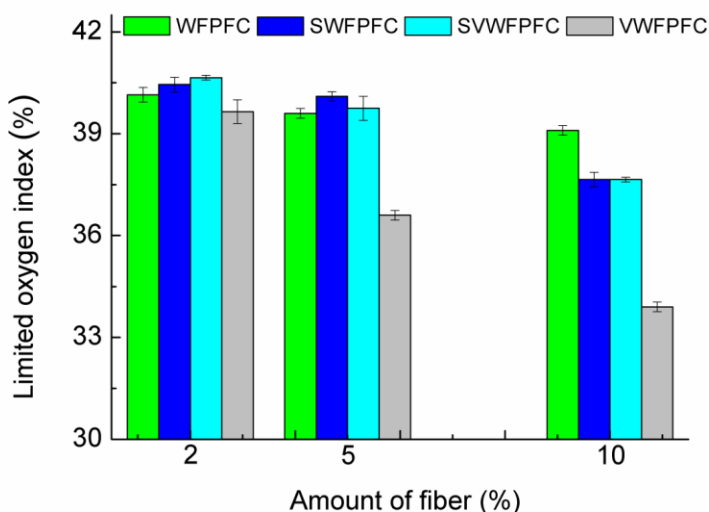


Fig. 10. Limited oxygen index of PFCs

### Thermal Conductivity of PFCs

Thermal conductivity is also an important indicator of foam properties and can be used to evaluate the insulation performance of materials. The lower the thermal conductivity is, the better is the insulation performance of materials. Figure 11 indicates the thermal conductivity of PFCs when the amount of wood fiber was 10%. It was shown that the thermal conductivities of SWFPFC, SVWFPFC, and VWFPFC were less than that of WFPFC, but the change was not obvious, and the thermal conductivity basically remained at approximately  $0.055 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ . The reason was that the compatibility between fibers and polymer was greatly improved after treatment, the influence of wood fibers on the foam pore was smaller than that of untreated wood fibers, the cell structure was regular, the size of cell was smaller, and the distribution of pores (Fig. 12) was uniform, so the thermal conductivity of the foam decreased (Ma *et al.* 2013).

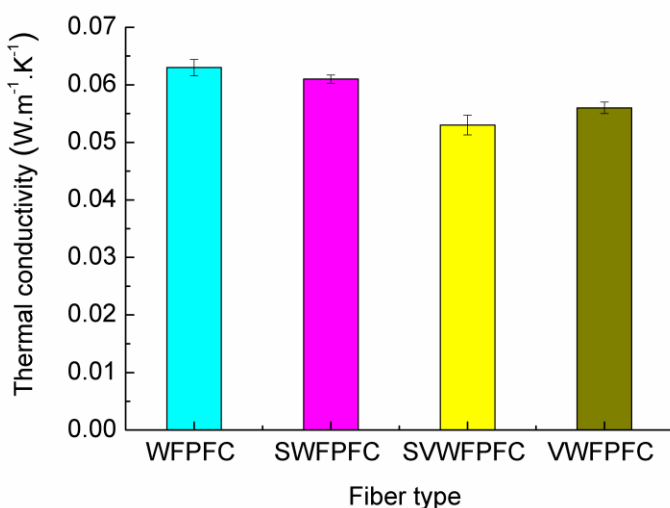


Fig. 11. Thermal conductivity of PFCs

### SEM Micrographs of PFCs

Figure 12 presents SEM images ( $\times 50$ ) of PFCs when the amount of wood fiber was 10%. There were many large cells in bubbles, and the distribution of cellular pores was uneven. The bubble cell size of WFPFC was approximately 150 to 450  $\mu\text{m}$ . The cellular pore distribution of SWFPFC was also uneven, and the bubble cell size of WFPFC was approximately 200 to 300  $\mu\text{m}$ .

The bubble cells of SVWFPFC and VWFPFC were smaller, and the cellular pores were also more uniformly distributed; the size of foam cells was approximately 100 to 200  $\mu\text{m}$ .

The results showed that the influence of untreated wood fibers on the pore structure of composite foams was greater with larger and more uneven bubble cells. On the contrary, the influence of treated wood fibers on the pore structure of composite foams was smaller when the bubble cells were smaller and more uniform; in particular, the influence of SVWF and VWF on the pore structure of composite foams was the smallest. The results also confirmed that the compatibility between treated fibers and phenolic resin was considerably improved.

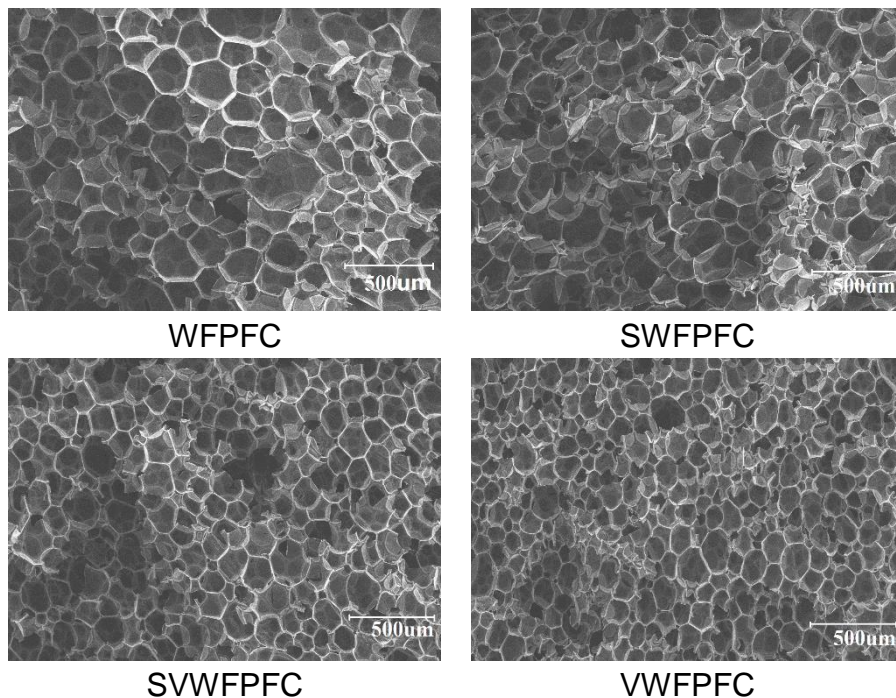


Fig. 12. SEM micrographs of PFCs

## CONCLUSIONS

1. After treatment with alkaline solution and silane coupling agent, the fiber surface was etched and became rough, but the position of the diffraction peak of wood fibers was basically unchanged, and the crystallinity of the fibers was slightly increased.
2. Compared with WFPFC, there were different degrees of ascension for the mechanical properties of SWFPFC, SVWFPFC, and VWFPFC; in particular, the mechanical properties of SVWFPFC increased dramatically. The LOI and thermal conductivity were reduced, and the cellular pore distribution was more regular, as the size of bubble cells became smaller and more uniform. With increasing wood fiber content, the mechanical properties and LOI of composite foams decreased.
3. The compatibility between fibers and phenolic resin was considerably improved; in particular, the processing effect was better after treatment with alkaline and VTMO aqueous solution. However, the amount of wood could not be too high, and the most suitable amount was determined to be approximately 5%.

## ACKNOWLEDGEMENTS

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