Effect of Novel DOPO-g-Coupling Agent Treated Wood Fibers on Properties of Composite Phenolic Foams

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9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) graft γ-amino propyltriethoxy silane (APS), γ-glycidoxy propyltrimethoxy silane (GPS), and methacryloyl propyltrimethoxysilane (MPS) were synthesized and introduced on the surface of wood fiber. DOPO-g-APS (GPS and MPS) treated wood fibers (DAWF, DGWF, and DMWF) were used to prepare composite phenolic foams (DAWFCPF, DGWFCPF, and DMWFCPF). The chemical structures of DOPO-g-APS (GPS and MPS) were confirmed by Fourier transform infrared (FT-IR) spectra and nuclear magnetic resonance. The structures of DAWF, DGWF, and DMWF were confirmed by FT-IR. The diffraction peak positions were basically unchanged, but the crystallinity was slightly increased. Compared with WF, thermal stabilities were increased. The residue (800 °C) was slightly reduced. Compared with phenolic foam, the properties of DAWFCPF and DGWFCPF were better than others. Besides compression strength, the mechanical properties were increased dramatically, limited oxygen index was slightly enhanced, the cellular pore distribution was more regular, and the size of bubble cell was smaller and more uniform. By comprehensive analysis, the properties of DAWFCPF were best in all samples. The interfacial compatibility was significantly improved between DAWF and phenolic resin. These results confirmed that DOPO-g-APS is a suitable material for treating wood fibers and preparing composite phenolic foams.

Keywords: DOPO; Wood fiber; Coupling agent; Phenolic foam; Characterization

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INTRODUCTION

As an excellent retardant material, phenolic foams (PFs) have been widely applied in fields of thermal insulation such as buildings, oil and gas pipelines, and central air conditioning systems (Lei *et al.* 2010; Yang *et al.* 2012). However, the greatest defect of phenolic foam is its high brittleness, which greatly limits its large-scale application (Rangari *et al.* 2007; Ma *et al.* 2017a). As a kind of environmentally friendly natural material, wood fibers are characterized by low density and relatively high tensile and flexural moduli (Bledzki and Gassan 1999; Canche-Escamilla *et al.* 1999; Mitra *et al.* 1998; Rana *et al.* 1998; Xie *et al.* 2010), and treating wood fibers with a coupling agent not only can improve the interfacial compatibility between wood fibers and phenolic resin, it can also composite PFs to improve the mechanical properties and toughness of composite PF. The limited oxygen index (LOI) of wood fibers composite PFs are reduced compared to PFs (Ma *et al.* 2017a,b).

As a halogen-free phosphorous flame retardant, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) has received notable attention from researchers worldwide due to its advantages of smokeless, non-toxic, non-migration, durable flame retardant properties, and the multiple structural diversification by functionalization (Perret *et al.* 2011; Zhang *et al.* 2011; Sun and Yao 2011; Dumitrascu 2012; Wang and Cai 2017). The molecular structure of DOPO contains diphenyl and phenanthrene ring structures. The lateral phosphorous group is a circular O=P-O bond; therefore the thermal stability, chemical stability, and flame resistance of DOPO are higher than the normal organic phosphate ester. DOPO contains six-membered phosphorus heterocyclic structure, and phosphorus atoms have active lone pair electrons, which are prone to nucleophilic addition reaction. The active hydrogen of the P-H bond can be reacted with a variety of electron-deficient derivatives, leading to a wide range of compounds with a phosphaphenanthrene skeleton (Yuxiang and Jianjun 2006; Carja *et al.* 2014).

This study was devised to investigate the effects of chemical modification of wood fiber with DOPO-g-coupling agents on the properties of wood fibers and their composite phenolic foams. The aim was to improve the comprehensive performance of composite foam without reducing its flame retardancy. Fourier transform infrared spectroscopy (FT-IR) and nuclear magnetic spectra (^{1}H NMR) of DOPO-g-coupling agents were performed, and FT-IR, X-ray diffraction (XRD), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA) of modified wood fiber were determined. The mechanical properties, limited oxygen index (LOI), and microstructure of wood fiber composite phenolic foams were measured.

EXPERIMENTAL

Materials

9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was purchased from Shenzhen Jinlong Chemical Technology Co., Ltd. (Nanjing, China). Phenolic resin (PR) was obtained from the Institute of Chemical Industry of Forestry Products (CAF; Nanjing, China). Polysorbate-80, petroleum ether, formic acid, and dicumyl peroxide (DCP) were obtained from Sinopharm Group Chemical Reagent Co., Ltd. (Shanhai, China); γ-amino propyltriethoxy silane (APS) was obtained from the United States Carbon Company (Danbury, USA). γ-Glycidoxy propyltrimethoxy silane (GPS) and methacryloyl propyltrimethoxysilane (MPS) were purchased from Dow Corning (Midland, USA). Eucalyptus fiber was obtained from Guangxi Fenglin Wood Industry Group Co., Ltd. (Nanning, China).

Methods

Preparation of DOPO-g-coupling agent

DOPO (0.26 mol) was introduced into a 250 mL four-necked round bottom flask fitted with a stirrer, aerated with nitrogen for 5 min, and heated to 140 °C to 150 °C. After the DOPO melted, a coupling agent (0.1 mol APS, GPS, MPS) was introduced into the reactor, aerated with nitrogen for 5 min, and reacted for 5 h in an anaerobic environment. The temperature was then brought to 120 °C, toluene was added (60 mL), and vacuum suction filtration was performed. The temperature was brought down to 75 °C, tetrahydrofuran was added (50 mL), and vacuum suction filtration was performed. Subsequently, the reaction product (DOPO-g-APS, DOPO-g-GPS, DOPO-g-MPS) was dried to a constant weight in a vacuum drying oven at 50 °C. The yields of DOPO-grafted silane (APS, GPS, and MPS) were 87.1%, 87.5% and 87.7%, respectively.

DOPO-g-coupling agent pretreatment of wood fiber

The composition of coupling agent water solution incorporated 2 wt.% DOPO-g-APS or DOPO-g-GPS or DOPO-g-MPS and 2 wt.% DCP. The pH was adjusted to 3.5 with formic acid. The wood fibers were immersed in the solution for 4 h. Finally, treated wood fibers were filtrated and dried at 60 °C for 24 h.

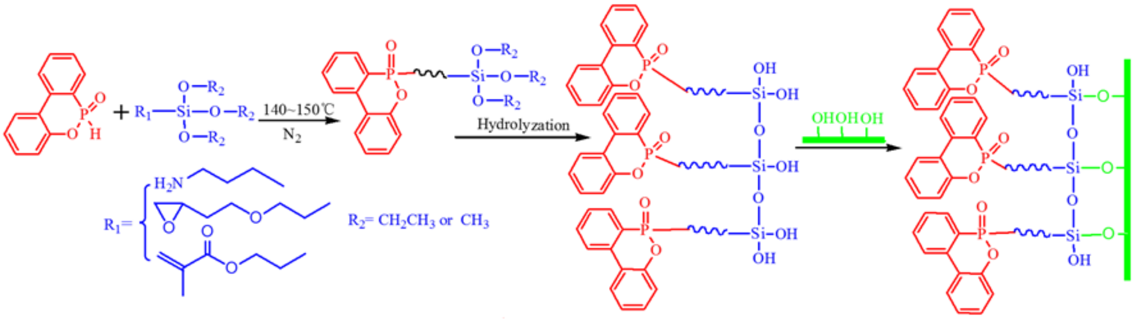


Fig. 1. Scheme of DOPO-g-GPTS modified wood fiber composite PFs

Table 1. Nomenclature of Wood Fibers Pretreatment

Keyword	Pretreatments
WF	wood fiber
DAWF	wood fiber treated with DOPO-g-APS
DGWF	wood fiber treated with DOPO-g-GPS
DMWF	wood fiber treated with DOPO-g-MPS

Preparation of wood fiber composite PFs

Surfactants (Polysorbate-80, 5%/PR), acid curing agents (22%/PR), blowing agents (petroleum ether, 5%/PR), wood fibers (6%/PR), and treated wood fibers (6%/PR) were added into phenolic resin and mixed well, then poured into the mold. The PFs were obtained after foaming for 40 min at 70 °C.

Table 2. Nomenclature of Wood Fibers Composite Phenolic Foams

Keyword	Fiber Composite Phenolic Foam
PF	phenolic foam
WFCPF	WF composite phenolic foam
DAWFCPF	DAWF composite phenolic foam
DGWFCPF	DGWF composite phenolic foam
DMWFCPF	DMWF composite phenolic foam

FT-IR measurements

Fourier transform infrared spectra were taken on a Nicolet IS10 FT-IR spectrometer (Thermo Fisher Scientific, Waltham, MA, USA).

^{1}H NMR Measurements

The ^{1}H NMR spectra were recorded at 400 MHz on a Bruker DRX 500 NMR spectrometer (Karlsruhe, Germany) with tetramethylsilane (TMS) as an internal reference.

X-ray diffraction measurements

All wood fibers were used for X-ray diffraction (Shimadzu 6000 X, Kyoto, Japan) measurements. The measurement parameters were as follows: Cu target, pipe pressure, 40 kV; flow, 40 mA; scanning speed, 4°/min; the sampling step width was 0.02°; and shaft dynamic continuous scanning was one time, $2\theta = 5$ to 50°.

Scanning electron microscopy of wood fibers and foams

All wood fibers and foams were examined using a Hitachi S3400-N SEM microscope (Kyoto, Japan). Prior to the analysis, the samples were coated with gold to avoid sample charging under the electron beam.

Thermogravimetric analysis

Thermogravimetric analysis was conducted on a NETZCSH TG 209 F3 TGA system (Selb, Germany), ramping from 35 to 800 °C with a rate of 10 °C/min.

Mechanical properties measurements of foams

Compression strength was measured by the standard ISO 844 (2014), and the samples used for the test were 50 × 50 × 50 mm. Bending strength was measured using the standard ISO 1209-1 (2012); the samples used for the test were 120 × 25 × 20 mm. Tensile properties were measured by the standard ISO 1926 (2009). The number of parallel tests was five.

Limited oxygen index (LOI).

The LOI test was carried out with JF-3 oxygen index meter (LOI analysis instrument company, Nanjing, China) according to ISO 4589-1 (2017). The samples used for the test were $100 \times 10 \times 10$ mm^3. The test was repeated 5 times.

RESULTS AND DISCUSSION

The structure of DOPO-g-coupling agent

The FTIR spectra of DOPO-g-coupling agent are shown in Fig. 1. The FTIR analysis of DOPO was shown as follows: 3061 cm^{-1} (C–H in phenyl group), 2436 cm^{-1} (P-H), 1593 cm^{-1} and 1603 cm^{-1} (phenyl group), 1477 cm^{-1} (P-phenyl), 1236 cm^{-1} (P=O), 903 cm^{-1} (P-O-phenyl). In the structures of DOPO-g-coupling agent, a peak of P-H (around 2436 cm^{-1}) disappeared. In addition, the absorptions around 1595 cm^{-1} and 1606 cm^{-1} corresponded to the phenyl group, the absorptions around 1238 cm^{-1} corresponded to P=O, and the absorptions around 906 cm^{-1} corresponded to P-O-phenyl. Figure 2 shows the ^{1}H NMR spectra of the DOPO-g-coupling agent. In the structure of DOPO, around 6.85 ppm to 8.23 ppm corresponded to the phenyl protons. The phenyl protons also appeared in the DOPO-g-coupling agent structure. These absorptions and protons supported the idea that the reaction occurred between DOPO and the coupling agents (APS, GPS, and MPS), and that the DOPO-g-coupling agent could be successfully synthesized (Min *et al.* 2016; Ni *et al.* 2017; Shan *et al.* 2017; Tang *et al.* 2017).

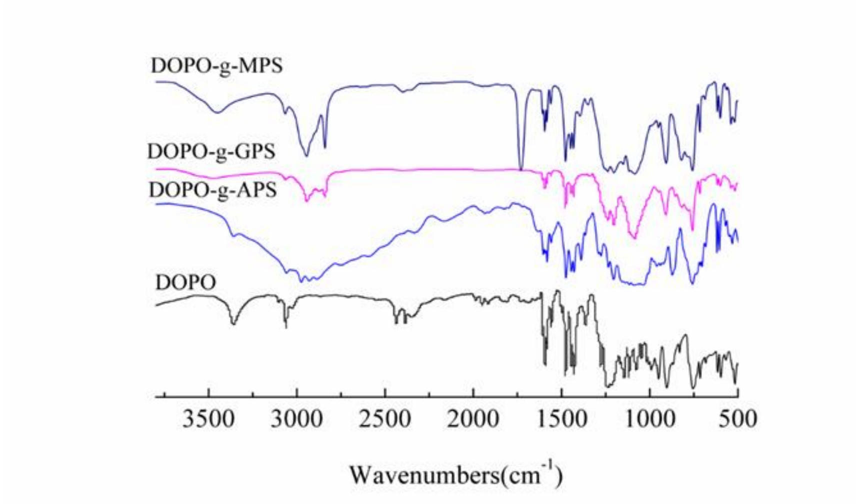


Fig. 1. FTIR spectra of DOPO-g-coupling agents

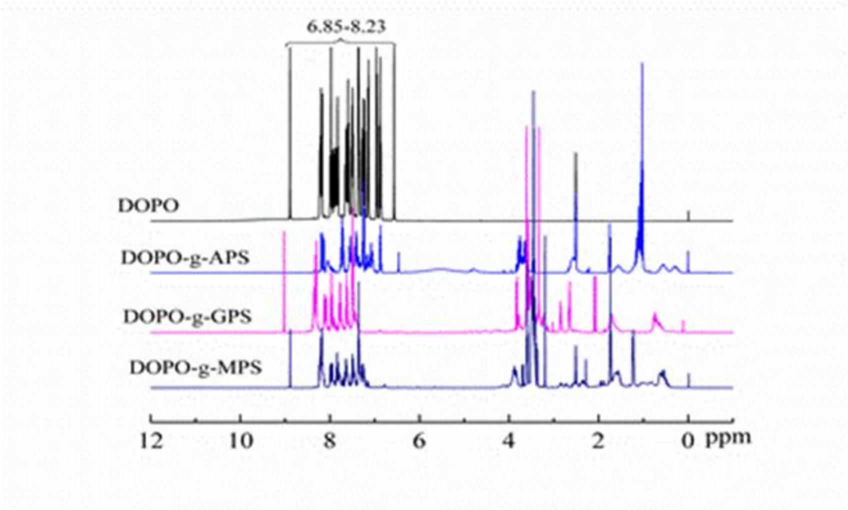


Fig. 2. ^{1}H NMR spectra of DOPO-g-coupling agents

The Properties of Wood Fibers

FTIR

Figure 3 shows the FTIR spectra of wood fibers. The characteristic absorption bands of DAWF, DGWF, and DMWF were enhanced at 2900 cm^{-1}, 1425 cm^{-1}, and 1050 cm^{-1}, which were respectively ascribed to –CH_2, P=O, and Si–O. These results indicate that reactions occurred between some of the hydroxyl groups on the surface of wood fiber and the hydroxyl groups of silanol (obtained after hydrolysis of silane), which thus generated an ether bridge, –Si–O–Si–, –Si–O–C– (around 1050 cm^{-1}), and an aliphatic chain (CH_2 in coupling agent) was introduced on the surface of fiber (Valadez-Gonzalez *et al.* 1999; Cui *et al.* 2008; Tang *et al.* 2017). These absorptions led to the appearance or the increment of the absorbance in the regions around 2900 cm^{-1}, 1425 cm^{-1}, and 1050 cm^{-1}. These absorptions also suggested that DOPO-g-coupling agents were successfully introduced on the surface of the wood fiber.

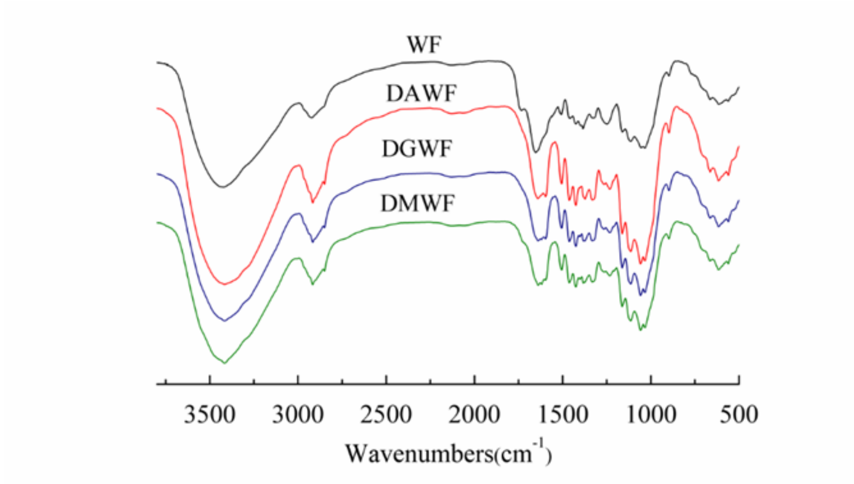


Fig. 3. FTIR spectra of wood fibers

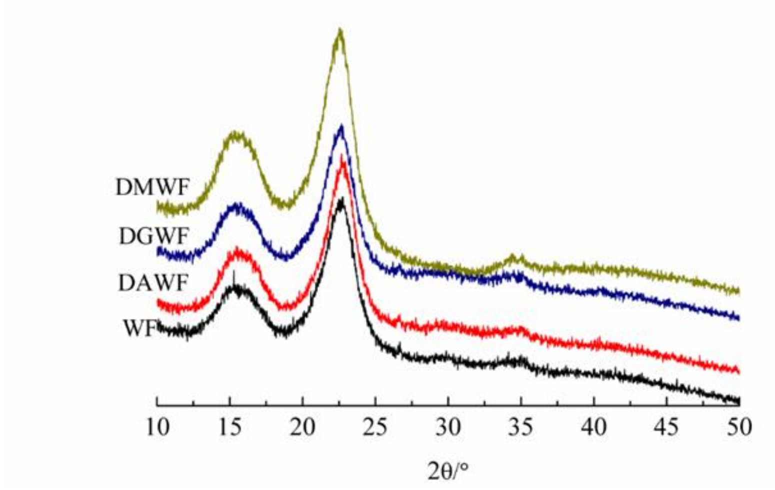


Fig. 4. XRD spectra of wood fibers

X-ray diffraction (XRD)

XRD spectra of wood fibers are shown in Fig. 4. There were two diffraction peaks: a sharp high peak (2θ = 22.6°) and a weaker diffraction peak (2θ = 15.6°) (Wang *et al.* 2007). The wood fibers' peak positions were basically unchanged, which suggested that the crystal form of treated wood fibers were unchanged. But the treated wood fibers' peak intensities were only slightly enhanced. The reason for this could be that during the process of pretreatment, wood fibers were immersed in the acidic solution, and so a part of the impurities, the small and soluble molecules on fiber surface were dissolved and removed by suction filtration (Valadez-González *et al.* 1995; Lu *et al.* 2005). Hence the cellulose could have a better arrangement, and the crystallinity of wood fiber was slightly increased.

SEM

As shown in Fig. 5, the surface of WF was not smooth, and it was covered with pectin, waxy substances, and impurities (Wang *et al.* 2007). The surface of DAWF, DGWF, and DMWF was etched and became smooth. The surface of DAWF was the smoothest. A thin layer of material covered the surface of DAWF, DGWF, and DMWF.

This could be attributed that during the process of treatment, some of the small and soluble molecule impurities present on the surface of the wood fiber were dissolved and removed by suction filtration (Valadez-Gonzalez *et al.* 1999). In the meantime, DOPO-g-coupling agents were introduced on the surface of wood fibers, which was advantageous in enhancing the bonding stability between the fiber and polymer matrix (Lu *et al.* 2005).

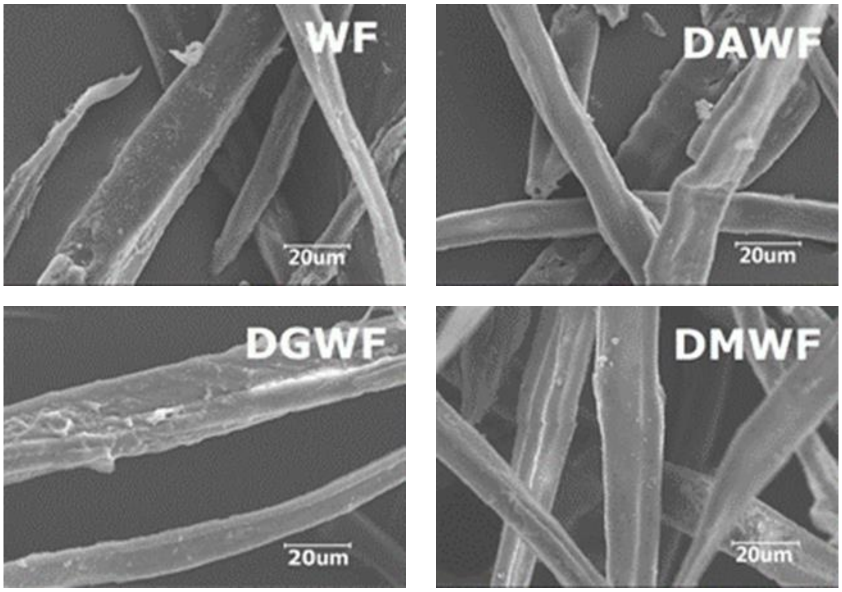


Fig. 5. SEM micrographs (1000×) of wood fiber

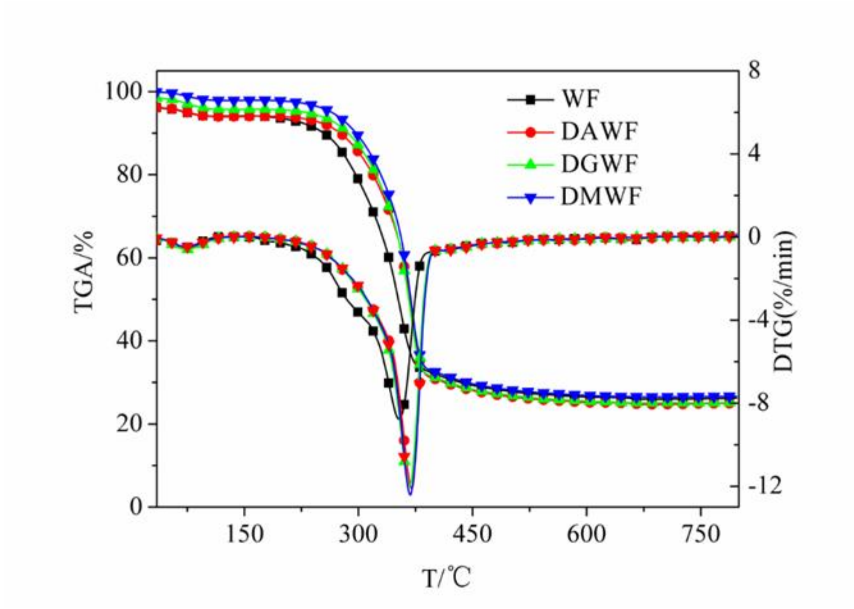


Fig. 6. TG and DTG of wood fibers

Table 3. Data from TG and DTG Curves of Wood Fibers

No.	$T_{5\%}$ (°C)	T_i (°C)	T_p (°C)	Residue (800°C) (%)
WF	244.7	303	333.8	30.37
DAWF	266.6	331.3	369.9	28.75
DGWF	259.3	329.6	367.0	26.72
DMWF	265.5	332.3	368.0	26.71

Thermal stability

The thermal stability of the wood fibers was evaluated by thermogravimetric analysis (TGA) in N_2, as shown in Fig. 6. The related data, including $T_{5\%}$, T_i, and T_P (the temperature of 5% weight loss, initial, and peak degradation temperatures, respectively) are summarized in Table 3. Compared with WF, the thermal stability of DAWF, DGWF, and DMWF were increased. $T_{5\%}$ increased by 8.95%, 5.97%, and 8.50%, respectively. T_i increased by 9.34%, 8.78%, and 9.67%, respectively. T_P increased by 10.81%, 9.95%, and 10.25%, respectively. The residues (800 °C) were slightly reduced. These results could be explained by the molecular structures of DAWF, DGWF, and DMWF, which contained high thermal stability materials including heterocyclic ring, phosphorous, and silicon. Therefore, the thermal stability of DAWF, DGWF, and DMWF were improved. In addition, during the process of pretreatment, some of the small and soluble molecule impurities present on the surface of the wood fiber were dissolved and removed by suction filtration, which was one possible reason for the reduction in residual carbon (800 °C).

The Properties of PFs

Compression and bending strength

The compression and bending strengths of PFs are shown in Fig. 7. Compression strengths of WFCPF were the largest in all the samples. Compared with PF, DAWFCPF had about the same compression strength as PF, while others were less than that of PF. However bending strengths of DAWFCPF and DGWFCPF were greater than that of PF and WFCPF. Bending strengths of DAWFCPF was the largest of all the samples. The results showed that the hardness of WFCPF was greater, but the toughness was poor. In contrast, DAWFCPF and DGWFCPF were softer, and the toughness was good. These results could be explained by the interfacial compatibility being improved between DAWF or DGWF and phenolic resin. As a result, the toughening effect of composite foam was more significant, and the toughening effects of DAWF on composite foam were excellent.

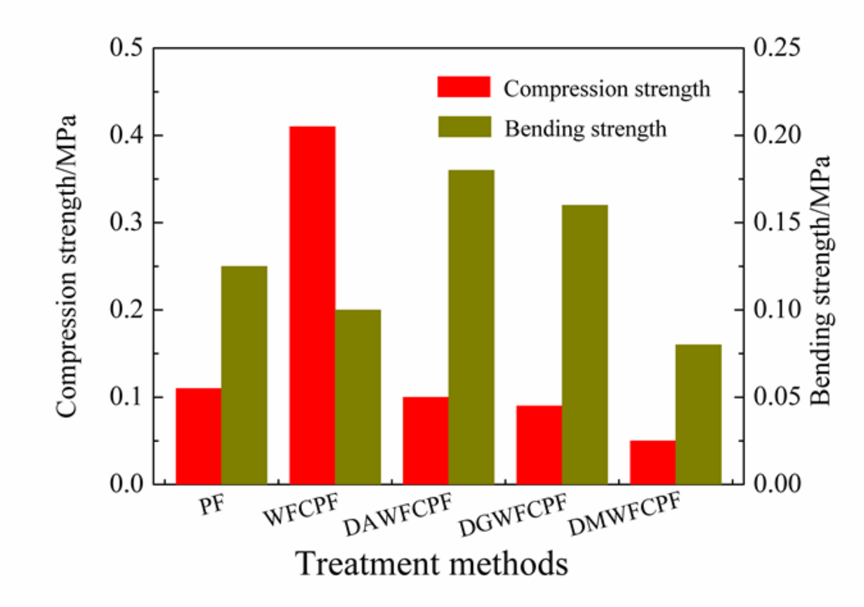


Fig. 7. Compression and bending strength of PFs

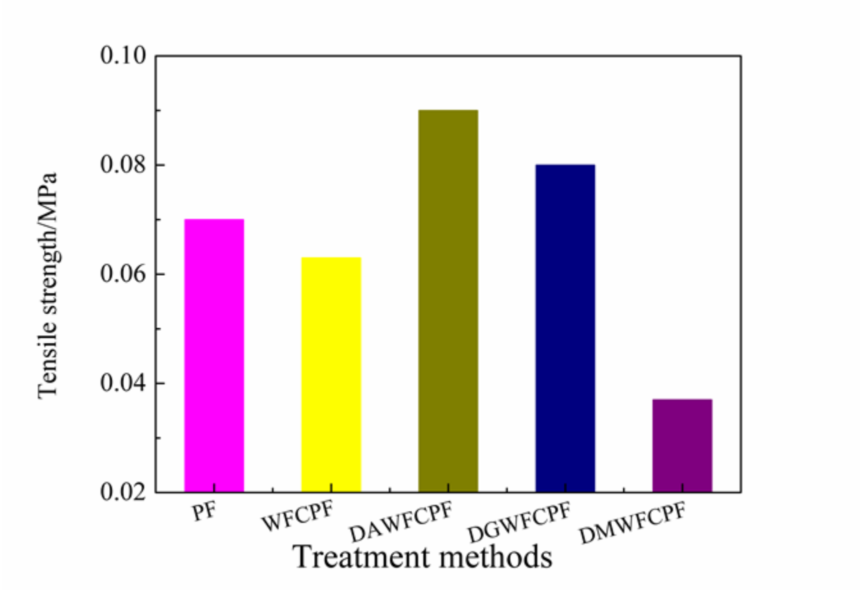


Fig. 8. Tensile strength of PFs

Tensile strength

Figure 8 shows the tensile strength of PFs. Compared with WFCPF, tensile strengths of DAWFCPF and DGWFCPF were dramatically improved and were greater than that of PF. The tensile strength of DAWFCPF was the largest in all the samples. These results proved again that the interfacial compatibility was improved between DAWF or DGWF and phenolic resin. Therefore the ability of resistance tensile deformation improved significantly. Nevertheless, tensile strength of DMWFCPF was the least in all the samples and was less than that of PF and WFCPF. This explained that the interfacial compatibility was poor, and it was even lower than WF.

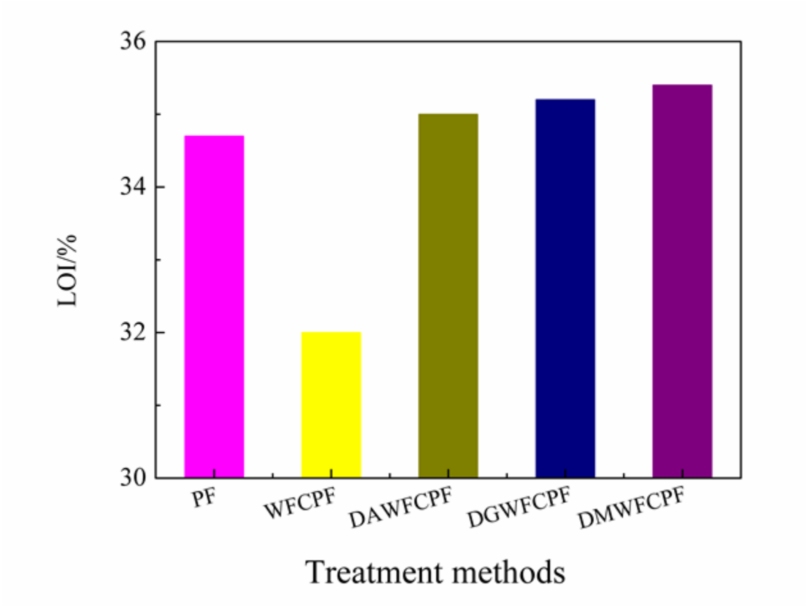


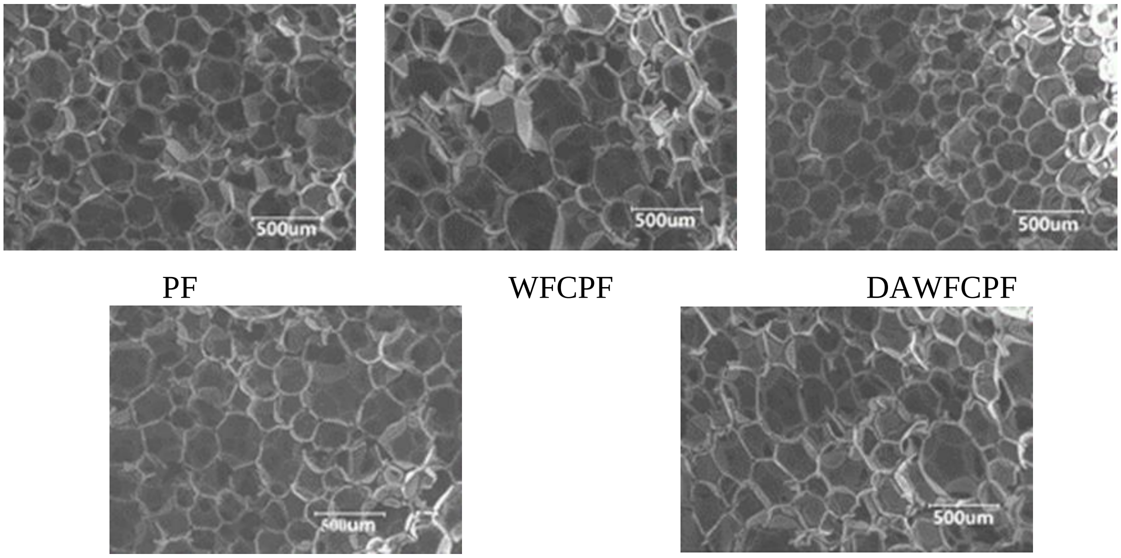
Fig. 9. LOI of PFs

Limited oxygen index (LOI)

As shown in Fig. 9, the LOI of PFs was more than 27%, and remained at 32% to 35.4%; therefore these foams were regarded as flame resistant materials (Wang and Xu 2010). The LOI of WFCPF was the least out of all the samples. This was because wood fiber is not a flame resistant material, and the introduction of wood fiber reduced the LOI of composite foams. In addition, LOI of DAWFCPF, DGWFCPF, and DMWFCPF were increased significantly and were slightly more than that of PF. The results showed that there was a positive effect of treated wood fiber on improving flame retardancy of composite foams. These could be explained by the introduction of the flame retardant (DOPO) and silicon (in coupling agents) on the surface of the treated wood fibers. The synergistic effect of phosphorus and silicon element markedly improved the flame retardancy properties of DAWFCPF, DGWFCPF, and DMWFCPF (Dong *et al.* 2013; Oktay and Emrah 2017). In consequence, LOIs of DAWFCPF, DGWFCPF, and DMWFCPF were significantly more than that of WFCPF, and were also more than that of PF.

SEM micrographs

SEM micrographs (×50) of PFs are shown in Fig. 10. Compared with PF, the cell distribution of WFCPF was more irregular, the size of cell was larger, and was about 200 μm to 500 μm. The cell size of DAWFCPF, DGWFCPF, and DMWFCPF was about at 150 μm to 300 μm, 200 μm to 300 μm, and 200 μm to 450 μm respectively. The results showed that the bubble cells of DAWFCPF were smallest, and the cells were the most uniformly distributed in all of samples. These confirmed that the influence of DAWF on the properties of composite foams was the least in all of the samples. It also confirmed that the interfacial adhesion was significantly improved between treated wood fibers (especially DAWF) and phenolic resin once again.



PF WFCPF DAWFCPF

DGWFCPF DMWFCPF

Fig. 10. SEM micrographs (50×) of PFs

CONCLUSIONS

1. The results revealed that the structures of DOPO-g-APS, DOPO-g-GPS, and DOPO-g-MPS were successfully synthesized and introduced on the surface of wood fibers. Compared with WF, the crystallinity of DAWF, DGWF, and DMWF were slightly increased, but the diffraction peak positions were basically unchanged. Thermal stabilities were increased slightly, but the residue (800 °C) was reduced slightly.
2. Compared with WFCPF and PF, the mechanical properties, flame retardancy, and microstructure of DAWFCPF was the best in all of samples. DGWFCPF had the second best properties. The modification effect of DMWF was worst, and the negative effect of DMWF on composite foam properties was largest.
3. These results indirectly confirmed that the interfacial compatibility was significantly improved between DAWF, DGWF, and phenolic resin, especially DAWF, and the properties of DAWFCPF were the best in all of the samples.

ACKNOWLEDGEMENTS

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