

# Fluorine-free and Durable Hydrophobic Coating Made with Corn Straw-derived Silane Modified Epoxy Resin

Wenlong Liu,<sup>a,b</sup> Xingwen Zhang,<sup>b,\*</sup> Hongyu Ren,<sup>c,\*</sup> Xingcheng Hu,<sup>b</sup> Xinyu Yang,<sup>b</sup> and Hui Liu<sup>a</sup>

Hydrophobic materials have promising applications. However, fluorine present in hydrophobic materials can lead to health risks and environmental pollution. This study investigated an environmentally friendly route to produce fluorine-free hydrophobic coatings with good wear resistance. Wear-resistant hydrophobic coatings were prepared by introducing different ratios of spirocyclic alkoxy silane into the epoxy resin. Characterization by Fourier transform infrared spectroscopy, water contact angle measurement, scanning electron microscope, tape adhesion test, and abrasion testing showed that the multi-methyl group and double-ring rigid skeleton structure of spirocyclic alkoxy silane can remarkably improve the hydrophobic performance and wear resistance of the epoxy resin. The modified hydrophobic coatings can withstand more than 1600 instances of controlled rubbing. Furthermore, the maximum water contact angle can reach 110° after substantial abrasion. The novelty of the work is that the authors successfully synthesized spirocyclic alkoxy silane for the first-time using corn straw ash. The prepared spirocyclic alkoxy silane was then used as a modifier to prepare hydrophobic epoxy resin coating. This approach can broaden the utilization of corn straw ash. Therefore, this method can achieve a green and low-cost preparation of wear-resistant hydrophobic coatings without the introduction of fluorine.

DOI: 10.15376/biores.18.1.2011-2023

Keywords: Plant biomass; Corn straw ash; Hydrophobic Coating; Biosilica; Fluorine-free

Contact information: a: School of Energy Science and Engineering, Harbin Institute of Technology, No. 92, West Dazhi Street, Harbin 150001, China; b: School of Chemistry and Chemical Engineering, Harbin Institute of Technology, No. 92, West Dazhi Street, Harbin 150001, China; c: College of Resources and Environment, Northeast Agriculture University, No. 600, Changjiang Street, Harbin 150001, China;

\* Corresponding authors: zhangxingwen@hit.edu.cn; renhongyu@163.com

## INTRODUCTION

Hydrophobic materials have become a popular research topic in recent years because of their promising applications in self-cleaning (Ganesh *et al.* 2011), anti-fogging (Lai *et al.* 2012), hydrophobic (Liu *et al.* 2022), and anti-fingerprint (An *et al.* 2018) applications. The static water contact angle (WCA) of hydrophobic surfaces is greater than 90°. Because of the small atomic radius and high electronegativity of fluorine, materials containing it are often used to prepare hydrophobic materials (Nishino *et al.* 1999). However, fluorine-containing materials are expensive; they also can accumulate in living organisms and pollute the environment (Li *et al.* 2015). Dental fluorosis has been linked to fluoride levels between 1.5 and 4 mg L<sup>-1</sup> (Salah and Arab 2007). Skeletal fluorosis develops with sustained exposure to greater concentrations of fluorine sewage (4 to 10 mg L<sup>-1</sup>) (Raja

Reddy 2009; Dhorge *et al.* 2017). Thus, eliminating F-containing materials to reduce environmental concerns and using silicon-containing materials incorporated into alkyl-based polymer materials to promote hydrophobicity have become a research hotspot in recent years (Tang *et al.* 2015, 2016; Lin *et al.* 2019). The synthesis of silanes containing polymethyl structure from agricultural waste corn straw ash can significantly reduce the synthesis cost and environmental pollution. Moreover, there are few studies on the use of these silanes as modifiers to modify the hydrophobicity of epoxy resins. In addition, the surface of the hydrophobic coating is often damaged by wear and tear, resulting in the reduction or even loss of the hydrophobic effect of the coating. Therefore, it is of great importance to develop low-cost, fluorine-free, environmentally friendly, and wear-resistant hydrophobic coating preparation methods.

Here, the authors used corn straw ash as a reactant to synthesize the spirocyclic alkoxy silane by utilizing an environmentally friendly method (Laine *et al.* 2016; Putro *et al.* 2021) for the first time. Then, the prepared spirocyclic alkoxy silane was used, for the first time, as a modifier to fabricate an epoxy hydrophobic coating. The structure and properties of the material were characterized by Fourier transform infrared spectroscopy, WCA measurement, scanning electron microscopy (SEM), tape adhesion test, and abrasion testing. Furthermore, the effects of modifier addition and its mechanisms were investigated. Low-cost, fluorine-free, environmentally friendly, and wear-resistant hydrophobic coatings were successfully prepared in this study, which has broadened the application of corn straw ash.

## EXPERIMENTAL

### Materials

Methanol (CH<sub>3</sub>OH, 99.8%), ethanol (C<sub>2</sub>H<sub>5</sub>OH, 99.5%), hexane (C<sub>6</sub>H<sub>14</sub>, 99.5%), and 2-methyl-2,4-pentanediol (C<sub>6</sub>H<sub>14</sub>O<sub>2</sub>, 99%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Corn straw ash was received from the Xing Fu Farm (Qiqihar, China). Low molecular polyamide (99%) was purchased from Beijing Xiangshan Lianhe Auxillary Factory (Beijing, China). Epoxy resin (98%) was purchased from Nantong Xingchen Synthetic Material Co., Ltd. (Nantong, China). Glass substrates (76.2 mm × 25.4 mm × 1.2 mm) were purchased from Yancheng Fei Zhou Glass & Plastic Co., Ltd. (Yancheng, China). All reagents were used as received.

### Methods

#### *Synthesis of spirocyclic alkoxy silane*

First, 500 g of corn straw ash was filled into a 2-L three-necked flask, and later 1.2 L of 2-methyl-2,4-pentanediol was added to the three-necked flask. Then, the reactants were stirred for 0.5 h, to make corn straw ash homogeneously disperse in the 2-methyl-2,4-pentanediol. Afterward, the reaction was completed at 180 °C under nitrogen and stirred for 48 h. The mixed solution of spirocyclic alkoxy silane and 2-methyl-2,4-pentanediol was collected by distillation. Later, the mixed solution was washed with hexane (1.2 L) and water (3 × 1.2 L), and then the hexane layer was collected and dried with sodium sulfate. Next, the sodium sulfate was removed by filtration. After that, the filtrate was placed in a rotary evaporator to remove hexane. Finally, the product spirocyclic alkoxy silane was collected and obtained. 0.67 g of spirocyclic alkoxy silane was synthesized from 1 g of corn straw ash as a reactant.

### *Preparation procedure for coatings*

Firstly, the epoxy resin (30 g) and curing agent (Low molecular weight polyamid 10 g) were weighed in beakers according to the mass ratio of 3:1. Then, 30 g and 10 g of epoxy resin and curing agent, respectively, were added to the beakers with 60 g and 20 g ethanol. The beakers were sealed and placed in an oven at 60 °C for 30 min. After that, the epoxy resin and curing agent were mixed well. Spirocyclic silane with mass percentages of 10%, 20%, 30%, and 40% was added. The epoxy resin coating solutions with 10 wt%, 20 wt%, 30 wt%, and 40 wt% of spirocyclic alkoxy silane and a control group (epoxy resin without added spirocyclic silane) were prepared. Glass substrates were ultrasonically cleaned with deionized water for 5 min. Then, glass substrates were ultrasonically cleaned with ethanol for 5 min. Finally, glass substrates were ultrasonically cleaned with acetone for 5 min. Glass substrates were thoroughly dried before spin coating. A KW-4A (Spin Coater, Beijing, China) spin coater was used to spin film at 2000 revolutions per minute for 15 s. Then, the film was cured at 80 °C for 16 h and 120 °C for 4 h.

### *Characterization*

Fourier transform infrared spectroscopy (NICOLET IS50, Waltham, MA, USA) was used to analyze the chemical groups of the samples by the KBr squash method. A SEM (Quanta 200FEG, Thermo Fisher Scientific, Waltham, USA) was adopted to observe the morphologies of the coatings with an acceleration voltage of 20 kV. Morphologic photographs were taken at a magnification of 200×. Nuclear magnetic resonance (NMR, Bruker Avance NEO 600, Bruker Corporation, Karlsruhe, Germany) and mass spectrometry (MS, Waters Quattro Premier XE, Milford, MA, USA) were used to analyze the chemical structure of the as-obtained spirocyclic alkoxy silane.

The WCA of the coating was measured by a contact angle meter (FCA2000A, Shanghai Aifis Precision Instruments Co., Shanghai, China). Three different areas in each coating were selected to repeat the WCA measurements. The average of the three tests was taken as the WCA for each coating. The error bars represent the standard deviation of the three tests for each coating.

An H-18 device purchased from Taber (North Tonawanda, NY, USA) was used to test the wear resistance of coatings. The coating was subjected to a pressure of 2 kPa. The rubbing speed was 50 mm/s. The numbers of rubbing actions were 400, 800, 1200, 1600, and 2000. Three different areas in each coating were selected to repeat the wear resistance test. The average of the three tests is taken as the WCA for each coating. The error bars represent the standard deviation of the three tests for each coating. In a review of the durability of hydrophobic coatings, Milionis suggests that this method may become a universal standard for evaluating the durability of hydrophobic coatings in the future (Milionis *et al.* 2016). Coating adhesion was evaluated according to ASTM D3359 (2009) (Krug *et al.* 2019).

## RESULTS AND DISCUSSION

### **Synthesis of Spirocyclic Alkoxy silane**

Figure 1 shows the infrared spectrum of the corn straw ash. The peak located at  $\sim 1100\text{ cm}^{-1}$  corresponds to the absorption peak of Si-O stretching vibration. In addition, the peak at  $\sim 3100\text{ cm}^{-1}$  corresponds to the stretching vibration absorption peak of OH.

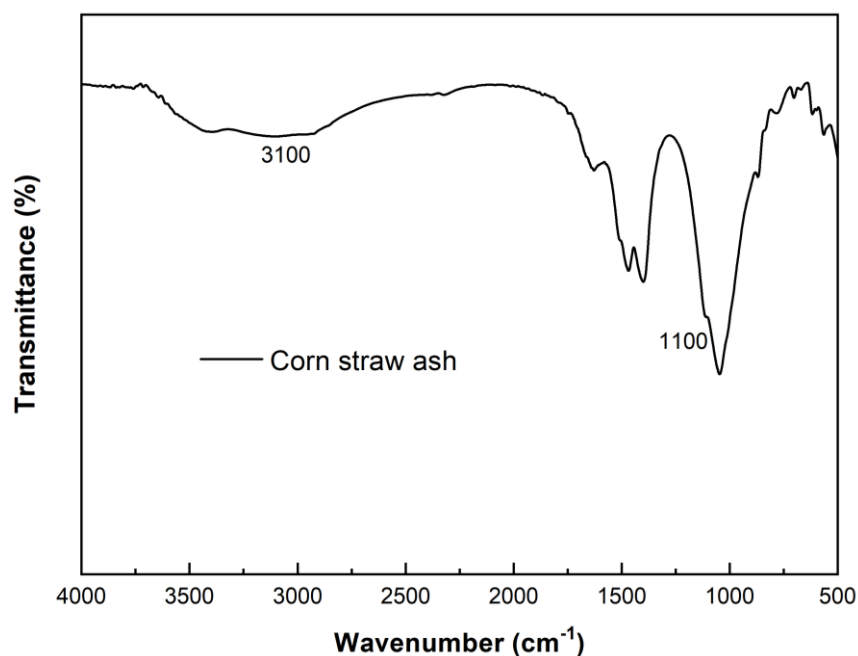


Fig. 1. Infrared spectroscopy of corn straw ash

The infrared spectrum of the product is shown in Fig. 2(a), in which the peak at  $961\text{ cm}^{-1}$  was ascribed to the stretching vibration of Si-O-C; the peaks at  $996\text{ cm}^{-1}$  and  $1054\text{ cm}^{-1}$  were attributed to the stretching vibration of Si-O (Liu *et al.* 2022). The mass spectrum of the product is shown in Fig. 2(b), from which it can be seen that the signals at  $m/z = 283.3$  and  $278.3$  were respectively assigned to the molecular weight of spirocyclic alkoxy silane ( $\text{Na}^+$  adduct) and spirocyclic alkoxy silane ( $\text{NH}_4^+$  adduct).

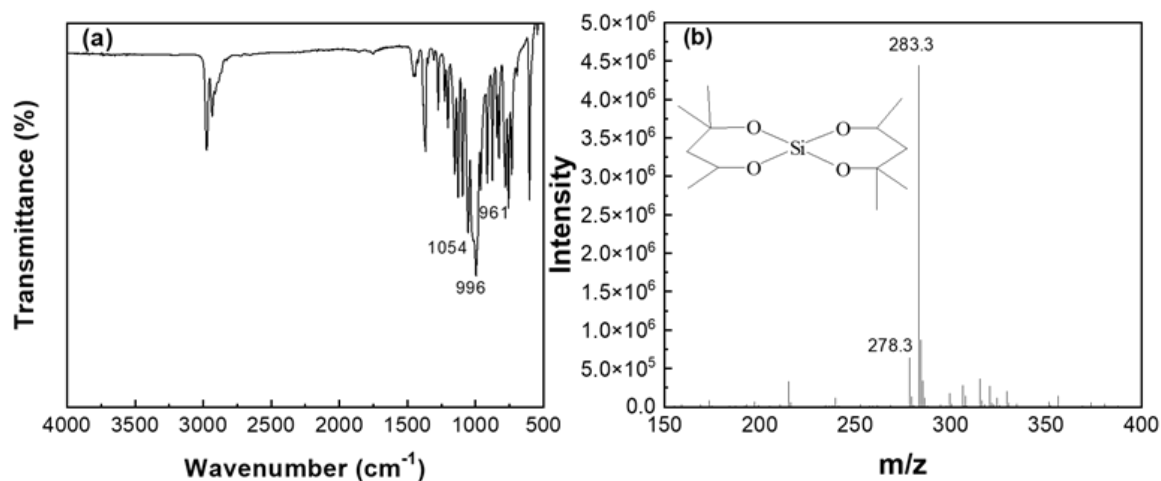


Fig. 2. Spirocyclic alkoxy silane (a) Infrared spectrum, (b) mass spectrum

The  $^1\text{H}$  NMR spectrum of spirocyclic alkoxy silane is shown in Fig. 3(a), from which it can be seen that the signals at 1.33 ppm and 1.22 ppm can be attributed to  $-\text{CH}_3$ ; the signals at 1.62 ppm and 1.47 ppm were assigned to  $-\text{CH}_2-$ . The  $^{29}\text{Si}$  NMR spectrum of spirocyclic alkoxy silane is shown in Fig. 3(b), and a sharp signal at  $-81.65\text{ ppm}$  can be seen in the spectrum, whose chemical shift was the same as that of Q-type siloxane. The  $^{13}\text{C}$

NMR spectrum of spirocyclic alkoxy silane is shown in Fig. 3(c). In the  $^{13}\text{C}$  NMR spectrum, the peak at 23.93 ppm was attributed to  $-\text{CH}_3$ ; the peaks at 32.04 ppm and 27.79 ppm were attributed to  $(\text{CH}_3)_2$ ; the peaks at 49.29 ppm and 48.10 ppm corresponded to  $-\text{CH}_2-$ ; the peak at 67.34 ppm corresponded to  $-\text{CHMeO}$ ; the peak at 74.12 ppm was assigned to  $-\text{CMe}_2\text{O}$ . The above results combined with the IR and MS results indicate that the spirocyclic alkoxy silane structure was successfully synthesized (Laine *et al.* 2016).

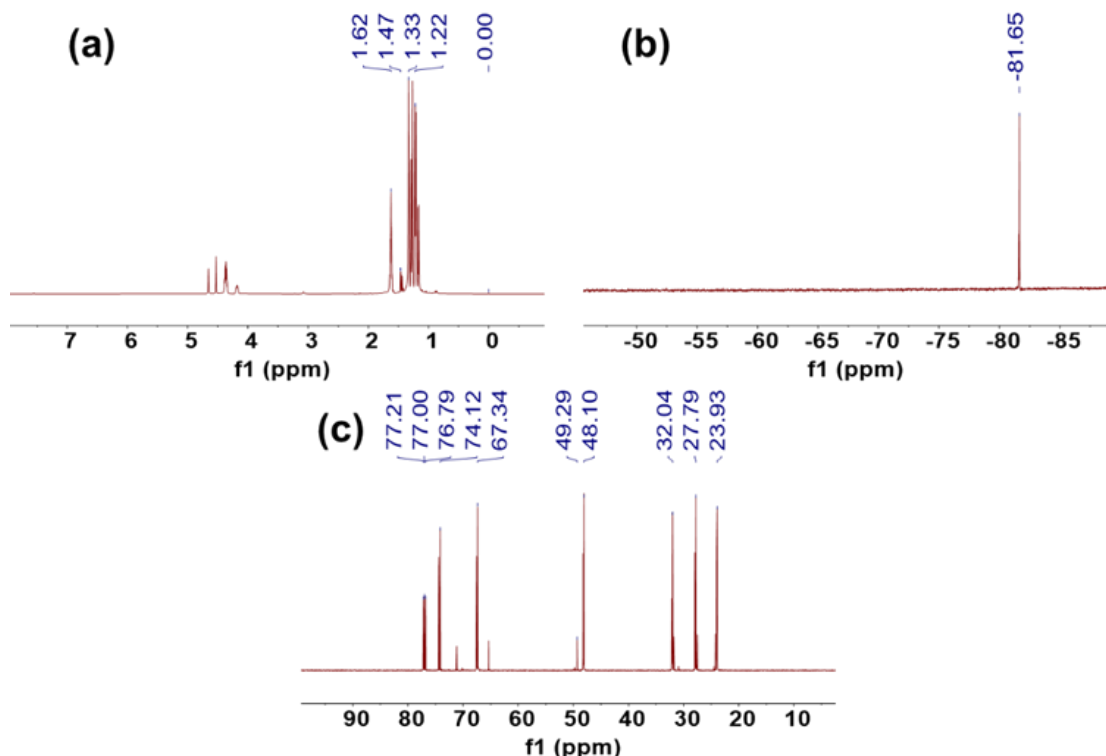


Fig. 3. NMRs of spirocyclic alkoxy silane (a)  $^1\text{H}$  NMR, (b)  $^{29}\text{Si}$  NMR, and (c)  $^{13}\text{C}$  NMR

### Synthesis of Coatings

Figure 4 shows the infrared spectra of epoxy resin (EP), spirocyclic alkoxy silanes (SP), and spirocyclic alkoxy silane modified epoxy resin (EP-SP). In the spectrum of epoxy resin, which is shown in black, the peak at  $826\text{ cm}^{-1}$  is the absorbance peak of p-disubstituted benzene. The peak at  $1235\text{ cm}^{-1}$  is the stretching vibration absorbance peak of Ar-O-R. The peak at  $1180\text{ cm}^{-1}$  is the absorbance peak of C-N formed by ring-opening polymerization after the reaction between the epoxy resin and curing agent, and additionally, there is no obvious infrared absorption peak of the epoxy group in the infrared spectra, indicating that the curing of epoxy resin is relatively complete. The peaks at  $1507\text{ cm}^{-1}$  and  $1606\text{ cm}^{-1}$  are absorbance peaks of the benzene ring. The peak at  $2924\text{ cm}^{-1}$  is the absorbance peak of  $-\text{CH}_2$ . The broad absorption peak at  $3362\text{ cm}^{-1}$  is the absorbance peak of the stretching vibration of the hydroxyl group. In the red spectrum of spirocyclic alkoxy silanes, the peak at  $961\text{ cm}^{-1}$  is the absorbance peak of Si-O-C. The peaks at  $996$  and  $1054\text{ cm}^{-1}$  are the absorbance peaks of Si-O. There is no absorbance peak near  $3300\text{ cm}^{-1}$ . In the spectrum of EP-SP, the peak at  $825\text{ cm}^{-1}$  is the absorbance peak of the p-disubstituted benzene structure. The broad peak at  $1081\text{ cm}^{-1}$  is the absorbance peak of Si-O. The peak at  $1245\text{ cm}^{-1}$  is the stretching vibration absorbance peak of Ar-O-R. The peaks at  $1508$  and  $1606\text{ cm}^{-1}$  are the absorbance peaks of the benzene ring. The peak at  $1181\text{ cm}^{-1}$  is the

absorbance peak of the C-N bond formed by ring-opening polymerization after the reaction between the epoxy resin and curing agent, and in addition, no obvious infrared absorbance peak of the epoxy group can be seen in the infrared spectrum, which indicates that the addition of spirocyclic alkoxy silane did not influence the curing effect of the curing agent in the original system of the epoxy resin. The curing of epoxy resin remained relatively complete after modification. The peak at  $2920\text{ cm}^{-1}$  is the absorbance peak of  $-\text{CH}_2$ . Compared with the IR spectrum of the pure epoxy resin, the IR spectrum of the spirocyclic alkoxy silane modified epoxy resin showed a broader peak near  $1081\text{ cm}^{-1}$ , indicating that spirocyclic alkoxy silane had been successfully introduced into the epoxy resin. Further supporting this finding, the other peaks in the IR spectrum and the main absorbance peaks of the pure epoxy resin have similar positions and shapes, indicating that the addition of spirocyclic alkoxy silane does not destroy the main structure of the epoxy resin. Compared with the pure epoxy resin, the hydroxyl absorbance peak near  $3300\text{ cm}^{-1}$  of the spirocyclic alkoxy silane modified epoxy resin is remarkably reduced, indicating that the hydroxyl content in the cured epoxy resin film layer is relatively low, which is beneficial to enhancing the WCA and reducing the contact angle hysteresis for the epoxy resin coating.

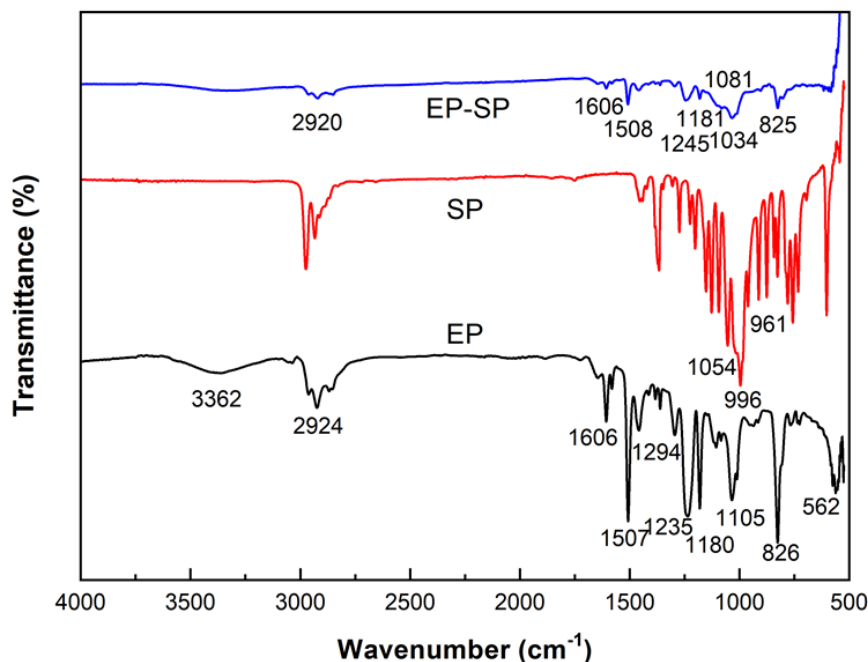
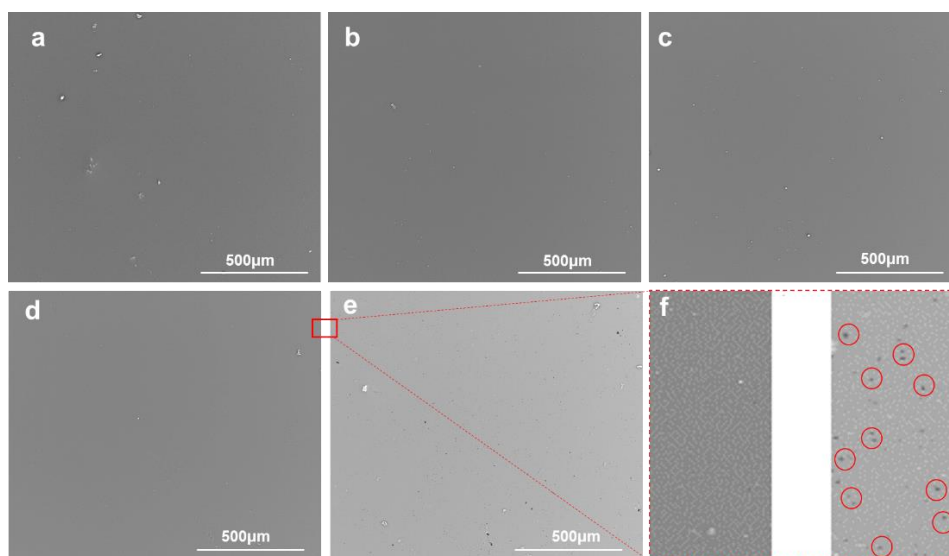


Fig. 4. IR spectra of the EP, SP, and EP-SP

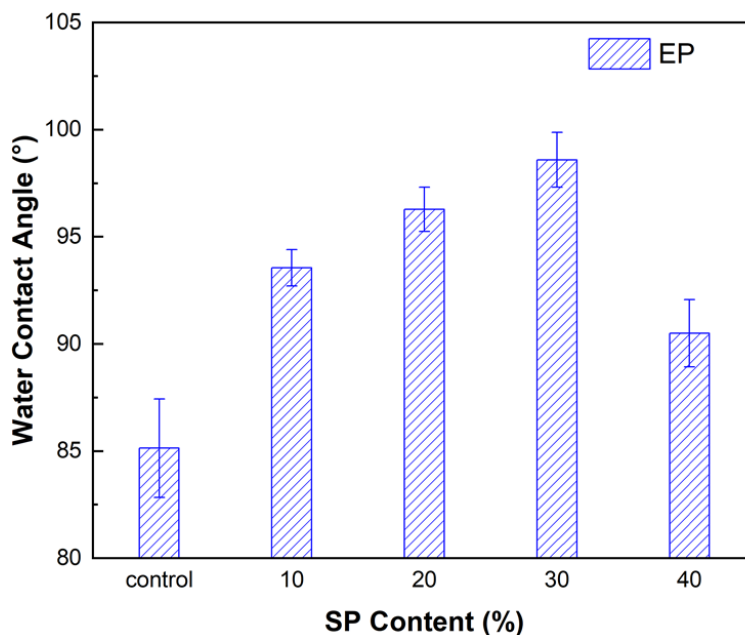
Figure 5 shows the SEM image of the spirocyclic alkoxy silane modified epoxy resin. It can be seen that the surfaces of the control group, 10%, 20%, and 30% spirocyclic alkoxy silane modified epoxy resin film layers were flat, dense, and homogeneous, supposing that the curing effect of epoxy resin is pretty good at this time and showing great compatibility between spirocyclic alkoxy silane and epoxy resin. The surface of the epoxy resin layer modified by 40% spirocyclic alkoxy silane showed more small black defects. The main reason for this is that the spirocyclic alkoxy silane does not contain active groups, and the epoxy resin was mainly modified by physical doping. When the addition ratio of spirocyclic alkoxy silane reached 40%, partial spirocyclic alkoxy silane agglomerated in the epoxy resin and formed defects.



**Fig. 5.** SEM images of coatings: (a) control, (b) 10%, (c) 20%, (d) 30%, (e) 40%, and (f) detail view; Magnification 200x, scale bar 500 μm

### Hydrophobic Performance

Figure 6 shows the hydrophobic performance of the modified epoxy resin.



**Fig. 6.** Hydrophobic performance of modified epoxy resin

It can be observed that with an increased spirocyclic alkoxy silane doping ratio, the WCA initially showed an upward trend. When the doping ratio of spirocyclic alkoxy silane was 30%, the WCA of the modified epoxy resin reaches its maximum value. This value was higher than the WCA of resin film previously reported in the literature (Liu *et al.* 2022). The possible reasons why the WCA of the modified epoxy resin was noticeably higher are as follows: Firstly, spirocyclic alkoxy silane contains 6 methyl groups per

molecule. As it is introduced into the epoxy resin, the proportion of methyl groups in the epoxy resin remarkably increases. Due to the multi-methyl group structure of spirocyclic alkoxy silane, with an increased doping ratio of spirocyclic alkoxy silane, the WCA of the modified resin gradually increases within a certain range. Secondly, the unique silica-oxygen bond core of spirocyclic alkoxy silane and the rigid skeleton structure of the double ring contribute to an enhancement of the hydrophobicity of the epoxy resin in both composition and structure. As a result, spirocyclic alkoxy silane does not contain reactive groups, and it predominantly modifies the epoxy resin by physical doping. When the spirocyclic alkoxy silane doping ratio exceeds 30%, the high amount may lead to agglomeration in the resin, resulting in a change of the surface micro-nano structure of the modified epoxy resin. Thus, the hydrophobicity of the coating decreases.

Figure 7 shows the contact angle hysteresis data of the epoxy resin film layer.

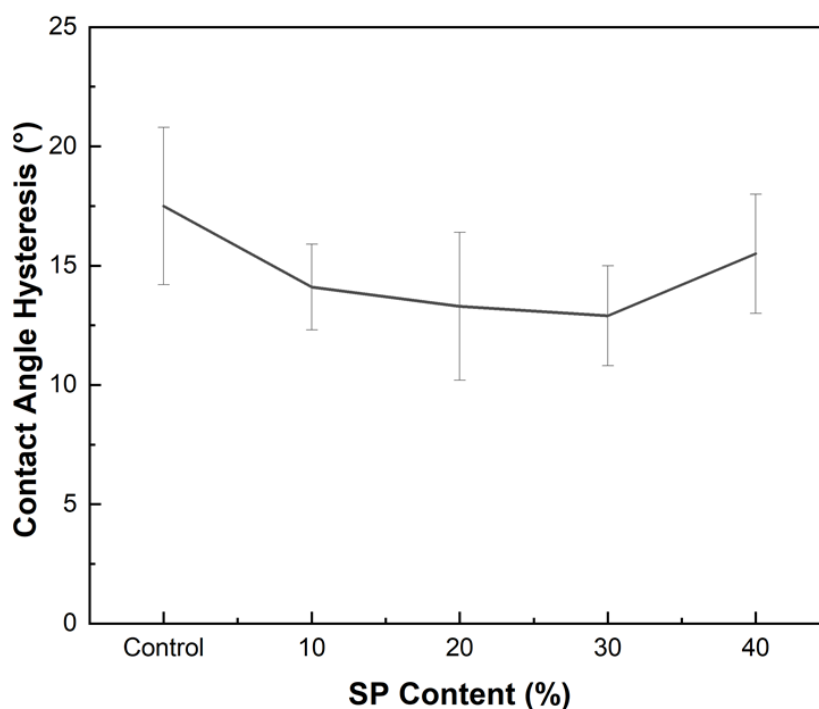


Fig. 7. Contact angle hysteresis of coatings

Figure 7 illustrates that as the addition ratio of spirocyclic alkoxy silane was gradually increased, the contact angle hysteresis of the film layer gradually decreased at first, it reached the minimum point when the addition ratio was 30%, and then it increased after that. The main reason is that spirocyclic alkoxy silane was not introduced in the control group. Further, the epoxy resin still contained a large quantity of hydroxyl and amino groups after curing. These hydroxyl and amino groups could combine with water and thus induce molecular rearrangement on the surface. As the addition ratio of spirocyclic alkoxy silane gradually increased, the proportion of hydroxyl groups in the cured film layer was relatively reduced. Thus, the polymer composition became more fixed, and the water-induced molecular rearrangement was greatly reduced (Lin *et al.* 1996). Therefore, the contact angle hysteresis of the modified epoxy resin film layer gradually decreased at first. When the addition ratio of spirocyclic alkoxy silane exceeded 30%, the surface morphology



and roughness of the film layer changed due to the agglomeration of spirocyclic alkoxy silane. As a result, the contact angle hysteresis of the film layer then increased.

### Wear Resistance

Figure 8 shows the wear resistance data of spirocyclic alkoxy silane modified epoxy resin.

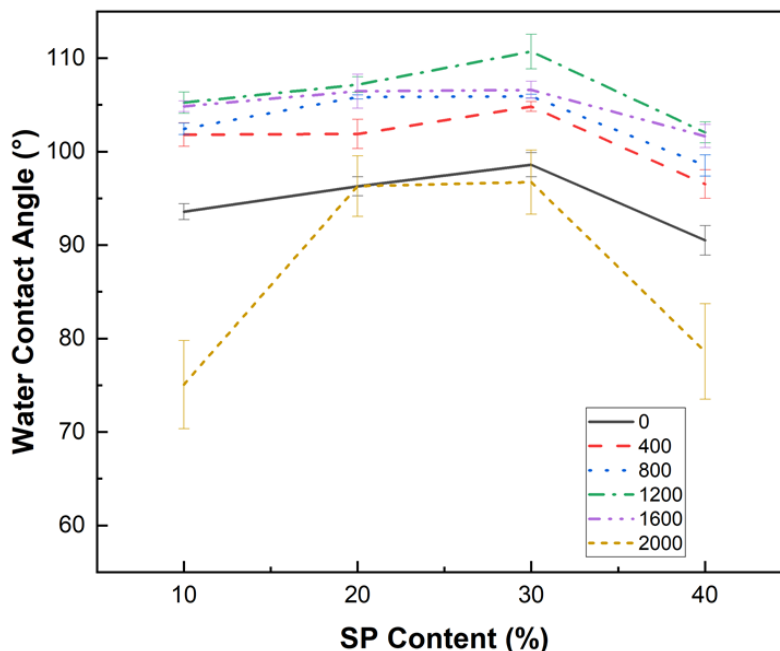


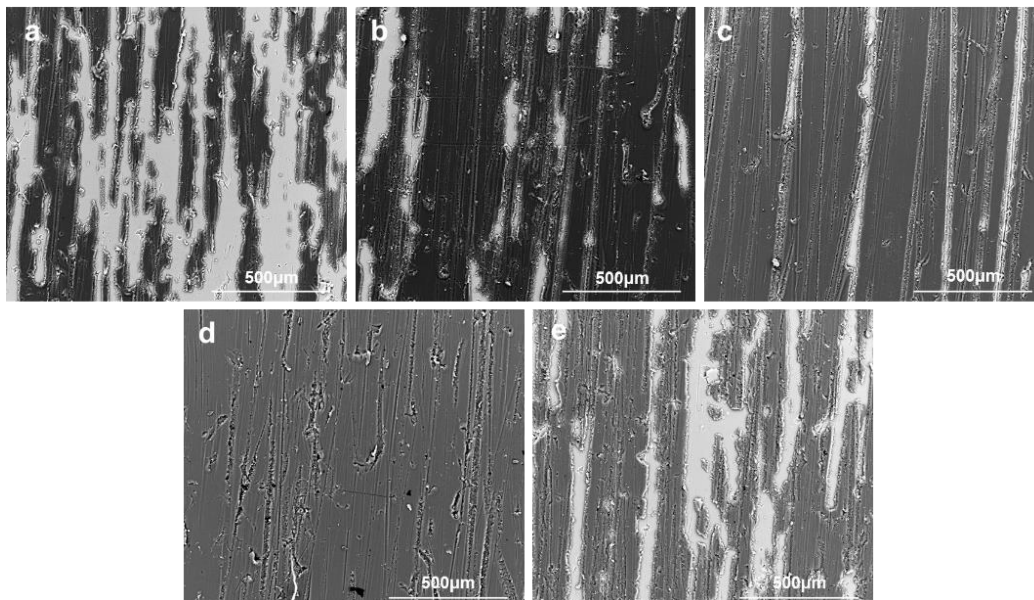
Fig. 8. Wear resistance of the modified epoxy resin

From Fig. 8, it can be seen that with increased exposure to bouts of abrasion, the WCA of each group of epoxy resin showed a gradually increasing trend. When the rounds of friction number were 1200, the WCA of each group of epoxy resin reached the corresponding maximum value. After that, with the times of friction increasing, the WCA of each group of epoxy resin gradually decreased. When the number of instances of friction was 2000, the WCA of each group of epoxy resin was smaller than the corresponding group without friction being applied, which indicates that the hydrophobic of the coating had been destroyed. The WCA of the epoxy resin coating without the addition of spirocyclic alkoxy silane gradually decreased with the increased exposure to bouts of friction, and a more obvious breakage occurred after 1200 applications of friction. From Fig. 8, it can be seen that the WCA of epoxy resin modified by 20% and 30% doping of spirocyclic alkoxy silane decreased remarkably less than other groups; those specimens were able to withstand more than 1600 applications of friction. This value is significantly better than the applications of friction of resin coating previously reported in the literature (Liu *et al.* 2022). Furthermore, the epoxy resin modified by 30% doping of spirocyclic alkoxy silane was able to reach the maximum WCA at more than 110° after 1200 applications of friction.

The main reasons for the improvement of the wear resistance of the modified epoxy resin are as follows: Firstly, in the modified epoxy resin system, silicon-oxygen bonds are introduced due to the addition of spirocyclic alkoxy silane. The bond energy of silicon-oxygen bonds is 422.5 kJ/mol, while the bond energy of carbon-carbon bonds is 334.7

kJ/mol. Therefore, the bond energy of silicon-oxygen bonds is much stronger than that of carbon-carbon bonds, resulting in the increase of wear resistance of the modified epoxy resin. Secondly, the unique double-ring rigid skeletal structure of spirocyclic alkoxy silane can play the role of “anchor point” (Grassie *et al.* 1980) in the epoxy resin system. Meanwhile, the infrared spectroscopy (Fig. 3) suggests that the solidification of epoxy resin has not been destroyed by the addition of spirocyclic alkoxy silane and the modified epoxy resin still maintains a high crosslink density.

Figure 9 shows the SEM of the spirocyclic alkoxy silane modified epoxy resin film layer after 2000 wear cycles.



**Fig. 9.** SEM images of coatings after 2000 wear cycles: (a) control, (b) 10%, (c) 20%, (d) 30%, and (e) 40%; magnification 200 $\times$ , scale bar 500  $\mu\text{m}$

It can be seen that the film layer of the control group was the most severely broken, with a large area of rupture and peeling of the film layer. With the increase of the addition ratio of spirocyclic alkoxy silane, the breakage of the epoxy resin layer was gradually discouraged. The lowest degree of breakage was reached when the addition ratio was 30%, indicating that this kind of film layer had the best wear resistance. When the addition ratio of spirocyclic alkoxy silane exceeded 30%, the breakage of the film layer was further aggravated. The possible reasons are given as follows: Firstly, the bond energy of the silicon-oxygen bond is higher than that of the carbon-oxygen bond. Secondly, the spirocyclic alkoxy silane has the rigid structure of a double-ring skeleton. When the addition ratio of spirocyclic alkoxy silane did not exceed 30%, the spirocyclic alkoxy silane was homogeneously dispersed in the epoxy resin film layer. In addition, the spirocyclic alkoxy silane could be used as an anchor point to remarkably improve the wear resistance of the film layer. When the addition ratio of spirocyclic alkoxy silane exceeded 30%, the spirocyclic alkoxy silane agglomerated in the film layer and formed defects, which led to a decrease of the wear resistance of the epoxy resin film layer.

Coating adhesion was evaluated according to ASTM D3359 (2009) (Krug *et al.* 2019). Table 1 shows the tape adhesion test of the epoxy resin film layer. It can be seen from the table that, when the doping ratio of spirocyclic alkoxy silane was lower than 30%,

the epoxy resin film layer showed good adhesion, and each test of the adhesion strength reached level 4B (excellent adhesion strength), which shows promising compatibility between spirocyclic alkoxy silane and epoxy resin. It was found that proper addition of spirocyclic alkoxy silane did not affect the adhesion of the layer. When the doping ratio exceeded 30%, the adhesion strength of the epoxy resin film was slightly reduced to 3B (good adhesion strength). The main reason for the above fact is that too much spirocyclic alkoxy silane was agglomerated in the epoxy resin film layer, which led to more defects and degraded the adhesion of the film. But the adhesion of the spirocyclic alkoxy silane modified epoxy resin film was significantly better than that of the resin film previously reported in the literature (Liu *et al.* 2022).

**Table 1.** Tape Adhesion Test of Coatings

	ISO 2409 (2013)	ASTM D3359 (2009)
Control	1	4B
10%	1	4B
20%	1	4B
30%	1	4B
40%	2	3B

## CONCLUSIONS

1. The novelty of this work is that spirocyclic alkoxy silane synthesized from corn straw ash was used for the first time to modify epoxy resin and prepare wear-resistant hydrophobic material.
2. The 30% spirocyclic alkoxy silane modified epoxy resin coating exhibited the best hydrophobic performance.
3. The coating was able to withstand more than 1600 applications of friction, and the maximum water contact angle (WCA) reached 110°.
4. The multi-methyl group and double-ring rigid skeleton structure of spirocyclic alkoxy silane can remarkably improve the hydrophobic performance and wear resistance of epoxy resin.

## ACKNOWLEDGMENTS

The authors are grateful for the support of the Major Project of the Ministry of Science and Technology of China, Grant No. 2017YFB0307700.

## REFERENCES CITED

- An, Q., Lyu, Z., Shanguan, W., Qiao, B., and Qin, P. (2018). "The synthesis and morphology of a perfluoroalkyl oligosiloxane@ SiO<sub>2</sub> resin and its performance in anti-fingerprint coating," *Coatings* 8(3), article 100. DOI: 10.3390/coatings8030100
- ASTM D3359 (2009). "Standard test methods for measuring adhesion by tape test," ASTM International, West Conshohocken, PA, USA.
- Dhorge, P. S., Acharya, R., Rajurkar, N. S., Chahar, V., Tuli, V., Srivastava, A., and Pujari, P. K. (2017). "Quantification of trace fluorine concentrations in soil and food samples from fluoride affected region by in situ current normalized particle induced gamma-ray emission method," *Journal of Radioanalytical and Nuclear Chemistry* 311(3), 1803-1809. DOI: 10.1007/S10967-016-5118-5
- EN ISO 2409 (2013). "Paints and varnishes - Cross-cut test," European Committee for Standardization, Brussels, Belgium
- Ganesh, V. A., Raut, H. K., Nair, A. S., and Ramakrishna, S. (2011). "A review on self-cleaning coatings," *Journal of Materials Chemistry* 21(41), 16304-16322. DOI: 10.1039/C1JM12523K
- Grassie, N., Francey, K. F., and Macfarlane, I. G. (1980). "The thermal degradation of polysiloxanes—Part 4: Poly(dimethyl/diphenyl siloxane)," *Polymer Degradation and Stability* 2(1), 67-83. DOI: 10.1016/0141-3910(80)90016-6
- Krug, D. J., Asuncion, M. Z., and Laine, R. M. (2019). "Facile approach to recycling highly cross-linked thermoset silicone resins under ambient conditions," *ACS Omega* 4(2), 3782-3789. DOI: 10.1021/acsomega.8b02927
- Lai, Y., Tang, Y., Gong, J., Gong, D., Chi, L., Lin, C., and Chen, Z. (2012). "Transparent superhydrophobic/superhydrophilic TiO<sub>2</sub>-based coatings for self-cleaning and anti-fogging," *Journal of Materials Chemistry* 22(15), 7420-7426. DOI: 10.1039/C2JM16298A
- Laine, R. M., Furgal, J. C., Doan, P., Pan, D., Popova, V., and Zhang, X. (2016). "Avoiding carbothermal reduction: Distillation of alkoxy silanes from biogenic, green, and sustainable sources," *Angewandte Chemie International Edition* 55(3), 1065-1069. DOI: 10.1002/anie.201506838
- Li, S. H., Huang, J. Y., Ge, M. Z., Li, S. W., Xing, T. L., Chen, G. Q., Liu, Y. Q., Zhang, K. Q., Al-Deyab, S. S., and Lai, Y. K. (2015). "Controlled grafting superhydrophobic cellulose surface with environmentally-friendly short fluoroalkyl chains by ATRP," *Materials & Design* 85, 815-822. DOI: 10.1016/J.MATDES.2015.07.083
- Lin, H., Rosu, C., Jiang, L., Sundar, V. A., Breedveld, V., and Hess, D. W. (2019). "Nonfluorinated superhydrophobic chemical coatings on polyester fabric prepared with kinetically controlled hydrolyzed methyltrimethoxysilane," *Industrial and Engineering Chemistry Research* 58(33), 15368-15378. DOI: 10.1021/acs.iecr.9b02471
- Lin, J., Zhu, J., Swanson, D. R., and Milco, L. (1996). "Cross-linking and physical characteristics of a water-based nonstick hydrophobic coating," *Langmuir* 12(26), 6676-6680. DOI: 10.1021/la960563h
- Liu, W., Zhang, X., Ren, H., Hu, X., Li, J., and Liu, H. (2022). "Spirocyclic alkoxy silane synthesized from rice straw ash for preparation of eco-friendly hydrophobic silicone coatings," *BioResources* 17(3), 5065-5078. DOI: 10.15376/biores.17.3.5065-5078

- Milionis, A., Loth, E., and Bayer, I. S. (2016). "Recent advances in the mechanical durability of superhydrophobic materials," *Advances in Colloid and Interface Science* 229, 57-79. DOI: 10.1016/J.CIS.2015.12.007
- Nishino, T., Meguro, M., Nakamae, K., Matsushita, M., and Ueda, Y. (1999). "The lowest surface free energy based on –CF<sub>3</sub> alignment," *Langmuir* 15(13), 4321-4323. DOI: 10.1021/LA981727S
- Putro, W. S., Lee, V. Y., Sato, K., Choi, J.-C., and Fukaya, N. (2021). "From SiO<sub>2</sub> to alkoxysilanes for the synthesis of useful chemicals," *ACS Omega* 6(51), 35186-35195. DOI: 10.1021/acsomega.1c05138
- Raja Reddy, D. (2009). "Neurology of endemic skeletal fluorosis," *Neurology India*, 57(1), 7. DOI: 10.4103/0028-3886.48793
- Salah, H., and Arab, N. (2007). "Application of PIGE to determine fluorine concentration in human teeth: Contribution to fluorosis study," *Journal of Nuclear and Radiochemical Sciences* 8(1), 31-34. DOI: 10.14494/JNRS2000.8.31
- Tang, Z., Hess, D. W., and Breedveld, V. (2015). "Fabrication of oleophobic paper with tunable hydrophilicity by treatment with non-fluorinated chemicals," *Journal of Materials Chemistry A* 3(28), 14651-14660. DOI: 10.1039/C5TA03520A
- Tang, Z., Li, H., Hess, D. W., and Breedveld, V. (2016). "Effect of chain length on the wetting properties of alkyltrichlorosilane coated cellulose-based paper," *Cellulose*, 23(2), 1401-1413. DOI: 10.1007/S10570-016-0877-2

Article submitted: October 24, 2022; Peer review completed: December 31, 2022;  
Revised version received and accepted: January 19, 2023; Published: January 25, 2023.  
DOI: 10.15376/biores.18.1.2011-2023