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**Waterborne acrylic resin co-modified by itaconic acid and  $\gamma$ -methacryloxypropyl triisopropoxidesilane for improved mechanical properties, thermal stability, and corrosion resistance**

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## Abstract

The waterborne acrylic resin modified by both itaconic acid (IA) and  $\gamma$ -methacryloxypropyl triisopropoxidesilane (KH571) was successfully synthesized by the seeded emulsion polymerization. The effects of IA and KH571 on the properties of waterborne acrylic resin, including mechanical properties, water resistance, thermal stability, storage stability and corrosion resistance, were studied. Fourier transform infrared spectroscopy analysis showed that IA and KH571 were successfully copolymerized with acrylic monomers. Compared with the unmodified resin, the introduction of IA and KH571 greatly improved the water resistance of the resin coating. When 2 wt.% IA and 4 wt.% KH571 were added, the contact angle of the resin coating increased from 78.91° to 90.49°. The water resistance time of the resin coating was improved from one day to 17 days. Additionally, the modified resin showed better mechanical properties, thermal stability, storage stability and corrosion resistance. The waterborne acrylic resin modified with IA and KH571 has a potential application prospect in the fields of waterproof and anticorrosive coating.

**Keywords:** Waterborne acrylic resin; Modified; Itaconic acid; Silane coupling agent; Performance

# 1 Introduction

With the strict restrictions on volatile organic compounds and toxic substances of resins in countries around the world [1-3], the market share of waterborne resins with the characteristics of green, health, and safety has been increasing, gradually occupying the market of solvent-based resins [4-6]. Waterborne acrylic resins, among the types of water resins, play an important role because of low price, safety and environmental protection, excellent weather resistance and other advantages [7, 8]. However, the shortcomings such as poor water resistance, high curing temperature, sticky when heated and fragile when cooled seriously restrict the application of waterborne acrylic resins [9].

The addition of modified monomer was reported to improve the performance of waterborne acrylic resins [10-16]. For example, Jiao *et al.* [7] studied the effects of silicone crosslinker 2-(3,4-epoxy) ethyltriethoxysilane on the properties of waterborne acrylic resin. The contact angle and water resistance of the resin film were improved remarkably. Glycidyl methacrylate (GMA) was introduced into acrylic polymer chain by Guo *et al.* [17]. The curing temperature of the resins has been significantly reduced and the mechanical properties have been improved with the addition of GMA.

Itaconic acid (IA) is an unsaturated binary organic acid, which can be produced by *aspergillus terreus* fermenting starch, sucrose and other carbohydrates [18-20]. It contains two carboxyl groups and a carbon-carbon double bond. The carboxyl group is conjugated with the

carbon-carbon double bond, which makes IA have active chemical properties and can be copolymerized with other monomers. Shivarkar *et al.* [21] designed IA modified polyester, which showed excellent mechanical properties and weather resistance. Liu *et al.* [22] prepared IA modified polyacrylate, which exhibited excellent mechanical properties and biocompatibility. In addition, silane coupling agents have also received extensive attention. Silane coupling agent shows a great crosslink effect due to the organic-inorganic functional groups. The silane coupling agent not only can react with the resin to improve the crosslinking density of the resin, but also can react with the polar group on the substrate to improve the adhesion of the resin. The commonly used silane coupling agents are  $\gamma$ -aminopropyl triethoxysilane [23],  $\gamma$ -glycidoxypropyl trimethoxysilane [24],  $\gamma$ -methacryloxypropyl trimethoxysilane (KH570) [25],  $\gamma$ -methacryloxypropyl triisopropoxidesilane (KH571) and so on. Both KH570 and KH571 contain a carbon-carbon double bond and can be used as comonomers to modify waterborne acrylic resin. Because of the high activity of silanol groups of alkoxysilane, premature hydrolysis and crosslinking reactions must be avoided to obtain stable latexes. KH571 is a better choice as a comonomer, its end group is isopropoxy, which gives KH571 a greater steric hindrance and results in a lower degree of premature hydrolysis and crosslinking [26]. Liu *et al.* [27] prepared core-shell acrylic emulsions using KH571 and acrylic monomers. Experiments showed that KH571 can greatly improve the hydrophobic and oleophobic properties of the resin. However, waterborne acrylic resins modified by itaconic acid (IA) and  $\gamma$ -methacryloxypropyl

triisopropoxidesilane (KH571) have not been reported yet.

In this study, waterborne acrylic resins modified by itaconic acid (IA) and  $\gamma$ -methacryloxypropyl triisopropoxidesilane (KH571) were synthesized by the seeded emulsion polymerization. Compared with the unmodified resin, the introduction of IA improved the mechanical properties, water resistance and storage stability. Then KH571 was introduced to modify the resin to further improve the water resistance and mechanical properties of the resin. Meanwhile, the effects of IA and KH571 amounts on resin properties were systematically investigated. The reaction mechanism was also analyzed by Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), X-ray photoelectron spectroscopy (XPS).

## **2 Experimental**

### **2.1. Materials**

Methyl methacrylate (MMA), styrene (St), butyl acrylate (BA) and 2-ethylhexyl acrylate (2-EHA) were all analytical reagents and supplied by Aladdin Reagent Co., Ltd. Glycidyl methacrylate (GMA) and IA were all analytical reagents and gained from Shanghai McLean Biochemical Technology Co., Ltd. KH571 (analytical reagents) were gained from Hangzhou Jessica Chemical Co., Ltd. Ammonium persulfate (APS, analytical reagents) and allyloxydecyl polyoxyethylene ether (10) ammonium sulfate (kl-100, analytical reagents) was obtained from Tianjin DW Chemical Co., Ltd. All reagents were used normally without further purification.

## 2.2. Synthesis of modified waterborne acrylic resin

Waterborne acrylic resins were prepared by semi-continuous seeded emulsion polymerization. The experiments were performed in a 250 mL four-necked flask equipped with a condenser, thermometer, constant pressure funnel and mechanical stirring shaft. A water bath heater was used to provide the required temperature for the reaction. MMA, BA, St, 2-EHA and GMA were used as copolymer monomers, which amounts are shown in Table 1.

**Table 1.** Ingredient for the preparation of waterborne acrylic resin.

Component	Chemicals	Mass (g)
Monomer	MMA	8
	BA	8
	St	12
	2-EHA	6
	GMA	5
Emulsifier	kl-100	0.75
Initiator	APS	0.4
Solvent	H <sub>2</sub> O	65

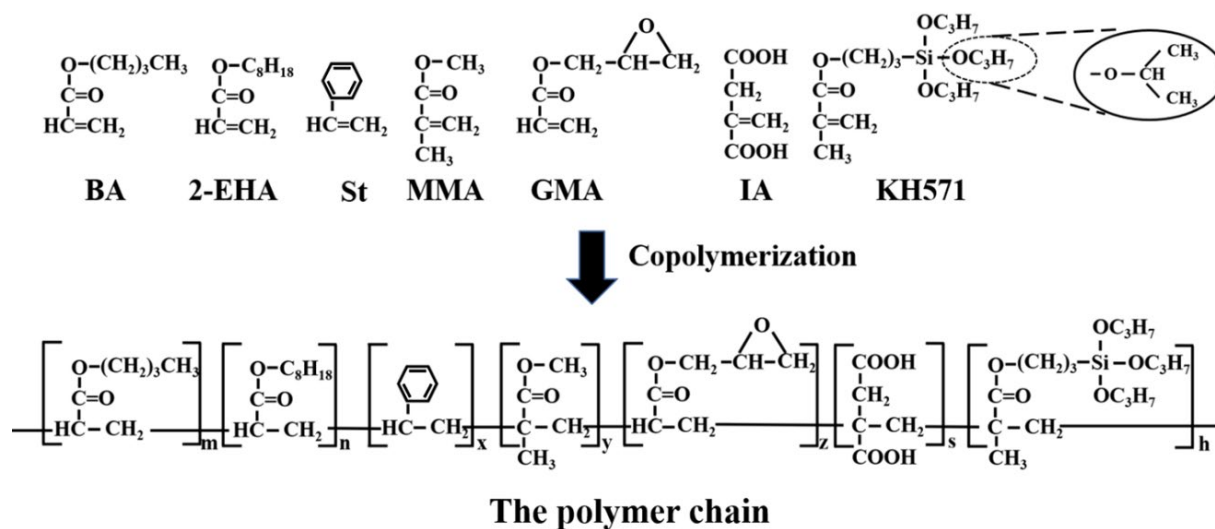
The synthesis of resin was divided into three stages. The first stage was the pre-emulsification, half of the emulsifier and water were added to a four-necked flask and the reaction system was stirred at a speed of about 300 rad/min with a mechanical stirring shaft at a temperature of 30 °C. All monomers were slowly added to the four-necked flask and stirred for 30 minutes to obtain a milky white homogeneous pre-emulsion. In the second stage of polymerization, the pre-emulsion was transferred to a constant pressure funnel, and the

four-necked flask was filled with the remaining water and emulsifier and 1/3 of the pre-emulsion and heated in an 80 °C water bath with a stirring shaft speed of about 120 rad/min. When the temperature of the reaction system reached 80 °C, 1 ml of initiator solution (the concentration of the initiator aqueous solution was 3 wt.%) was added. After the emulsion changed from milky white to blue, the remaining pre-emulsion was added dropwise with a constant pressure funnel, while 1 ml of initiator solution was added every 15 min. The dropping time was controlled to 120 min. Finally, in the insulation stage, the system was warmed up to 88 °C for 60 min.

After completion, the emulsion was cooled to room temperature and filtered to obtain waterborne acrylic resin (named as WA).

The preparation process of IA modified waterborne acrylic resin was similar to that of WA. IA was added in the pre-emulsification stage. In order to investigate the effect of IA amount on resin properties, a series of IA amount gradient experiments were designed. The amount of IA was 1wt.%-4wt.% (for the total monomers) and the synthesized samples of modified waterborne acrylic resins were named as WAIAn, here n presents wt.% of total monomer by IA.



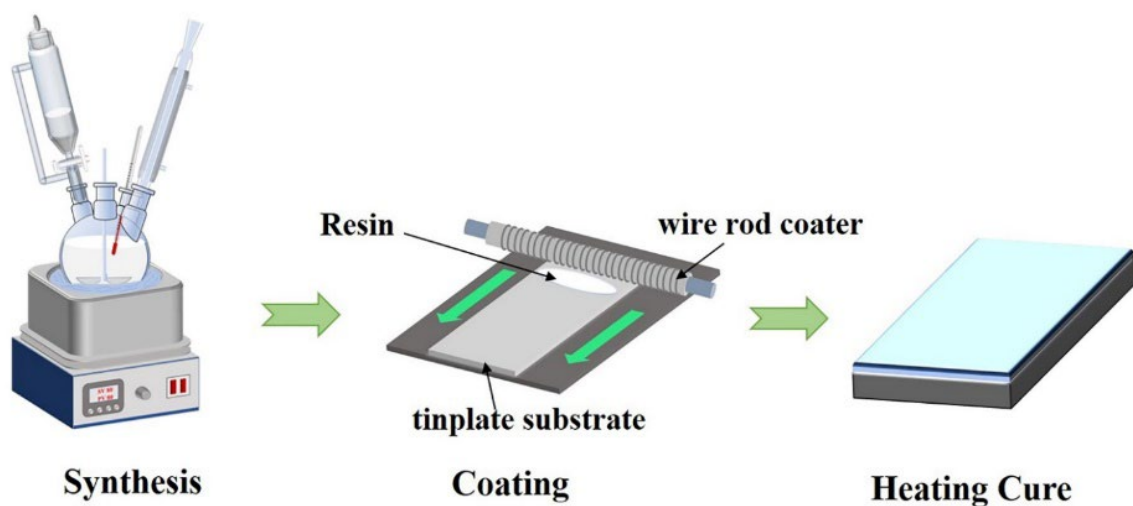


**Scheme 1.** Diagram of WAIAn/Sim copolymerization reaction.

After determining the optimal amount of IA, KH571 together with other acrylic monomers and the optimal amount of IA were added to the copolymerization system to synthesize IA and KH571 modified acrylic resins. Diagram of WAIAn/Sim copolymerization reaction is shown in Scheme 1. The obtained series of samples were named as WAIAn/Sim, where n and m present the weight percent of IA and KH571, respectively. For example, when the amount of modified monomer IA and KH571 was 2 wt.% and 4 wt.%, respectively, the sample was named WAIAn/Si4.

### 2.3. Film preparation

The as-prepared liquid resin was evenly coated on the tinplate substrate with a 60  $\mu\text{m}$  applicator, and the thickness of the coatings was 60  $\mu\text{m}$ . The resin-coated tinplate substrate is placed in an oven at 140  $^{\circ}\text{C}$  to cure the resin film for 10 minutes. The synthesis, coating and curing process of the resin is shown in Fig. 1.



**Fig. 1.** Process of resin synthesis, coating and curing.

## 2.4. Characterizations

The chemical structure of resin was determined by FTIR (Nicolet iS50, Thermo Fisher Scientific Co., USA). The thermal stability of the coating was evaluated by the thermogravimetric analyzer (Mettler Toledo Co. Swiss Confederation). Under the experimental conditions of nitrogen flow rate of 70 ml/min and heating rate of 20 °C/min, the weight loss of about 10 mg solid samples was measured in the range of 30 °C to 700 °C. The XPS (ESCALAB XI+, Thermo Fisher Scientific, USA) with an Al K $\alpha$  X-ray radiation was used for measuring the chemical composition of waterborne acrylic resin films.

The mechanical properties of resin samples were tested by tensile testing machine (AI-7000-LA3, Gotech Testing Machines). According to ASTM-D638, the sample was stretched by crosshead at a rate of 6 mm/min at room temperature with 100×10×1 mm as the standard size

of the sample. Make three tensile samples for each resin sample and take the average value. After the tensile test, the fracture samples were collected and the fracture morphology was observed by SEM. SEM was conducted on a Thermo Scientific Apreo S with an accelerating voltage of 2.0 kV and a beam current of 0.2 nA.

The hydrophobicity of the coating was tested by contact angle meter (DSA30, Germany). The average value obtained from five measurements of the same sample at different locations was determined as the contact angle of the sample.

The particle size of the emulsion was measured by (Malvern ZEN1690, Malvern Instrument Ltd., UK). Each sample was measured three times and averaged to obtain the average particle size. The Zeta potential values were tested by a Zetasiser Nano instrument (Malvern Instruments, UK). Samples were diluted with deionized water and were measured thrice.

Swelling test was performed by immersing the resin film in acetone at room temperature for 12 h. The swelling ratio (Q) was calculated by the Equation (1):

$$Q = \left[ \frac{m_2 - m_1}{m_1} \right] \times 100\% \quad (1)$$

where  $m_1$  and  $m_2$  are the weights of resin film before and after being soaked in acetone, respectively.

Other physical properties of the waterborne acrylic resin film were tested by national standard testing methods. The test methods for the water resistance, corrosion resistance and

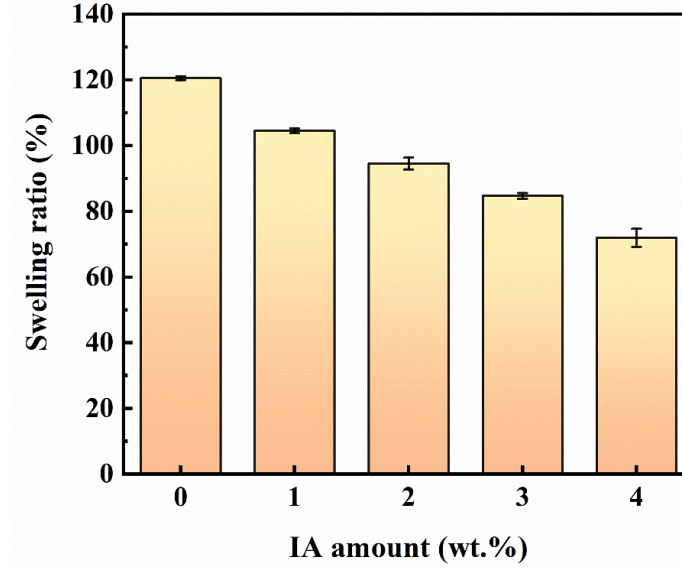
water absorption of resin films are according to, GB/T 1733-1993, GB/T 35858-2018, GB/T 1034-2008.

### **3. Results and discussion**

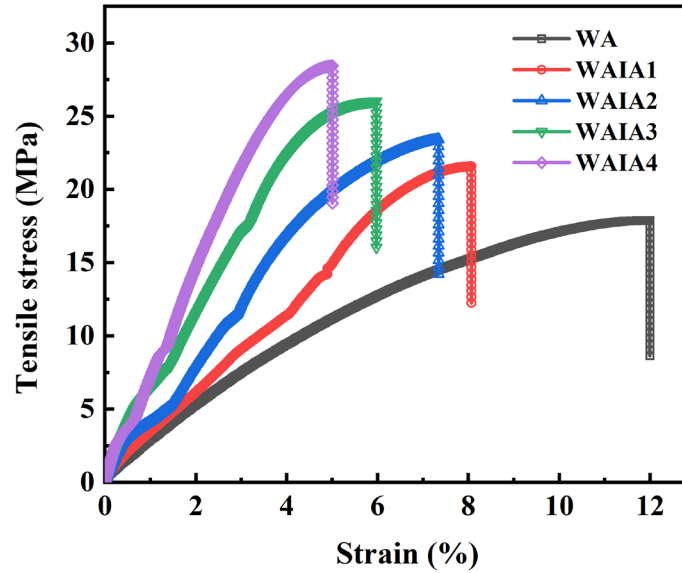
#### **3.1 Synthesis of modified resin**

##### **3.1.1 The influence of IA amount on resin properties**

The effect of IA amount on the swelling capacity, mechanical properties and water resistance of the resin were studied. The swelling ratio is an important index to evaluate the crosslinking level of resin [28, 29]. When the crosslinking level of resin is high, the dense structure formed by polymer chain can effectively prevent the penetration of solvent molecules, thus showing a low swelling ratio. As shown in Fig. 2, the swelling ratio of the resin film gradually decreases with the increase of IA amount. This indicates that the introduction of IA increases the crosslinking density of the resin system.



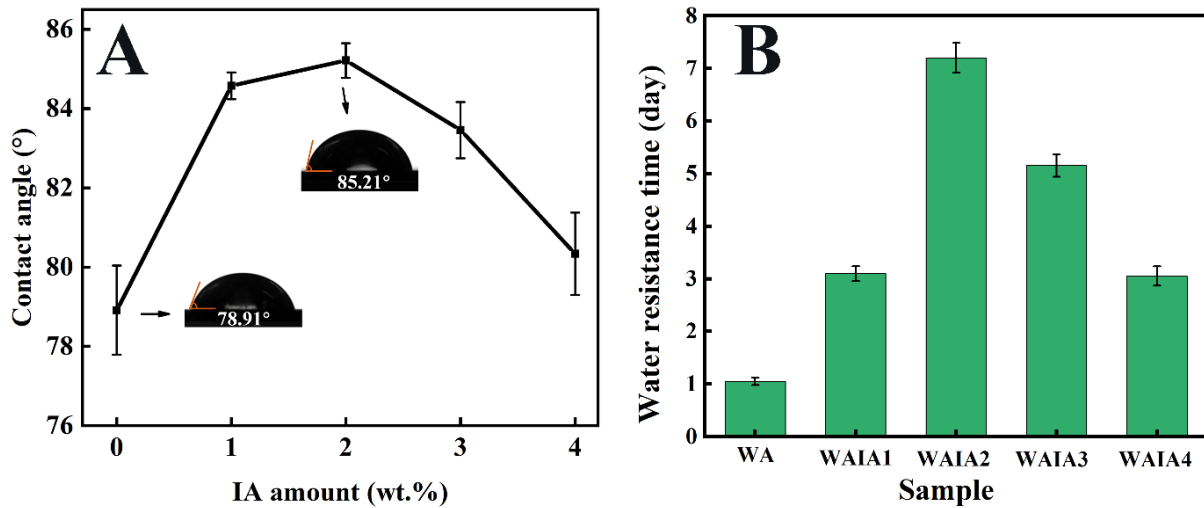
**Fig. 2.** Swelling ratio of samples WAIAn.



**Fig. 3.** The stress-strain curves of samples with different amount of IA.

The stress-strain curves of samples with different amount of IA are showed in Fig. 3. It can be seen that IA amount has a significant effect on the tensile properties of the resin. With the increasement of IA, the tensile strength of the resin increases and Young's modulus increases as

well, but the elongation at break decreases (as shown in Table S1).



**Fig. 4.** (A) Comparison of the contact angles and (B) Water resistance time of different samples.

The wettability of resin surface is determined by the chemical composition and microstructure of the surface [30], which can be measured by the contact angle. The water resistance was evaluated by testing the contact angle and water resistance time of the resin coatings. As can be seen from Fig. 4A, the contact angle of the sample without IA (sample WA) is 78.91°. When the amount of IA is less than 2 wt.%, the contact angle increases significantly with the increase of IA, and the contact angle of WAIA2 reaches 85.21°. The increase in contact angle may be due to reduction of the surface energy caused by the crosslinking reaction between the carboxyl groups of IA and other groups [17]. However, further increase of IA does not make any contribution to increase the contact angle, but rather lead to a sharp decrease. This is probably caused by a higher amount of unreacted hydrophilic carboxyl groups from IA in the resin, resulting in an increase in surface energy [31]. The water resistance time of the resin

coatings (Fig. 4B) shows that sample WAIA2 remains excellent performance with no blistering, rusting, peeling and other damage phenomena after 7 days.

To sum up, when the amount of IA is 2 wt.%, the resin modified only by IA shows better performances, and thus the proper amount of IA is selected as 2 wt.% for further studies.

### 3.1.2 The influence of KH571 amount on resin properties

In order to further improve the resin properties, the influence of KH571 on the resin properties was investigated on the basis of sample WAIA2. Fig. 5 shows the swelling capacity of the resin with different amount of KH571. According to the figure, when the resin is not modified by KH571, the swelling ratio of WAIA2 is 94.5%, and the swelling ratio of the resin film gradually decreases with the increase of KH571 amount. It may be due to the fact that the introduction of KH571 makes the resin produce a denser three-dimensional network crosslinking structure [32].

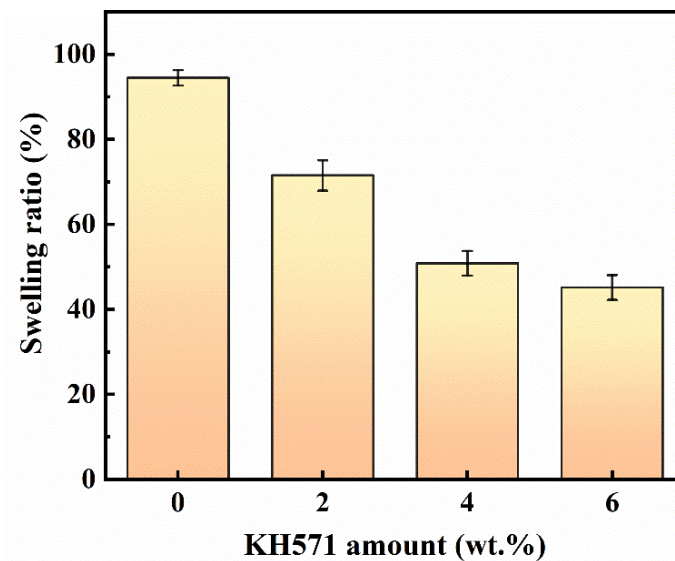
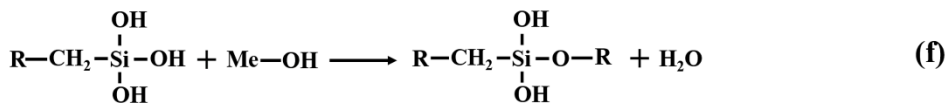
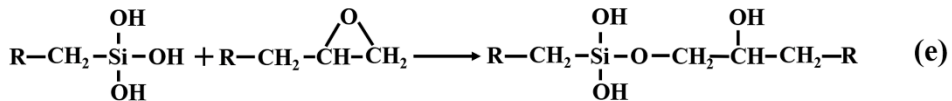
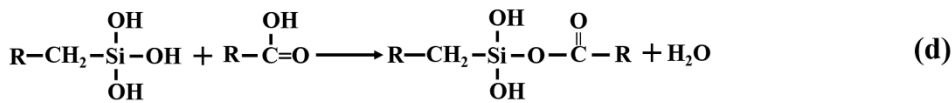
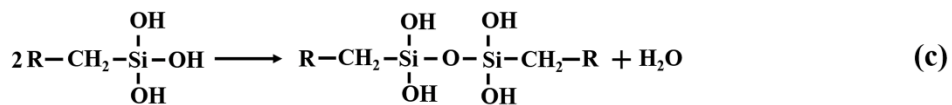
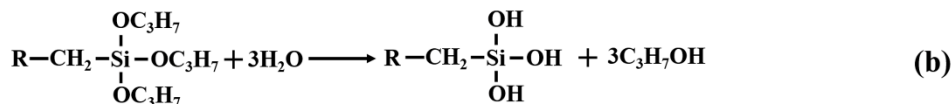
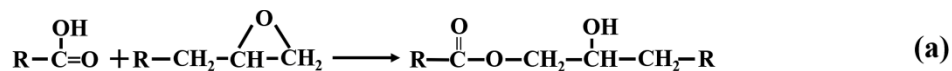


Fig. 5. Swelling ratio of samples WAIA2/Sim

The possible chemical reactions during the curing of the resin are shown in Scheme 2. The carboxyl group in IA reacts with the epoxy group in the resin system (Scheme 2a). Because the siloxane of KH571 can undergo hydrolysis reaction to change the terminal group of KH571 to a silicon hydroxyl groups (Scheme 2b), which have strong activity, condensation reaction occurs between silicon hydroxyl groups (Scheme 2c). Furthermore, they will react with the carboxyl groups and epoxy groups in the polymer chain (Scheme 2d and Scheme 2e). The silicon hydroxyl group may also react with the hydroxyl group on the metal surface [33] (Scheme 2f).



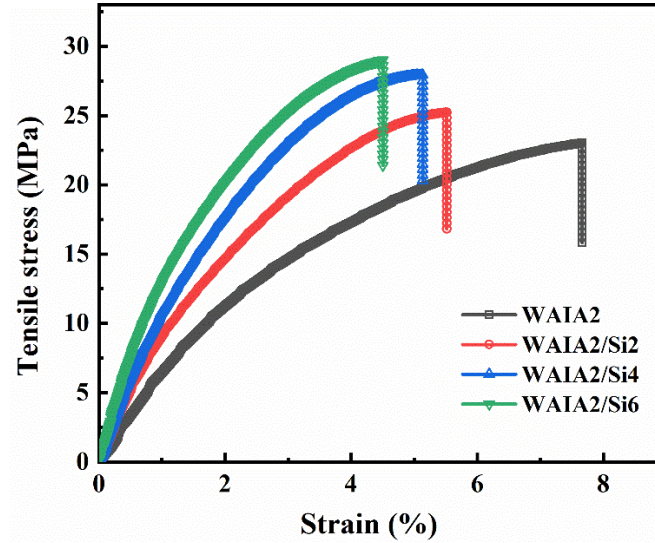
**R:** Polymer chain      **Me:** Metal surface

**Scheme 2.** Diagram of the reaction mechanism of resin polymer in the process of curing.

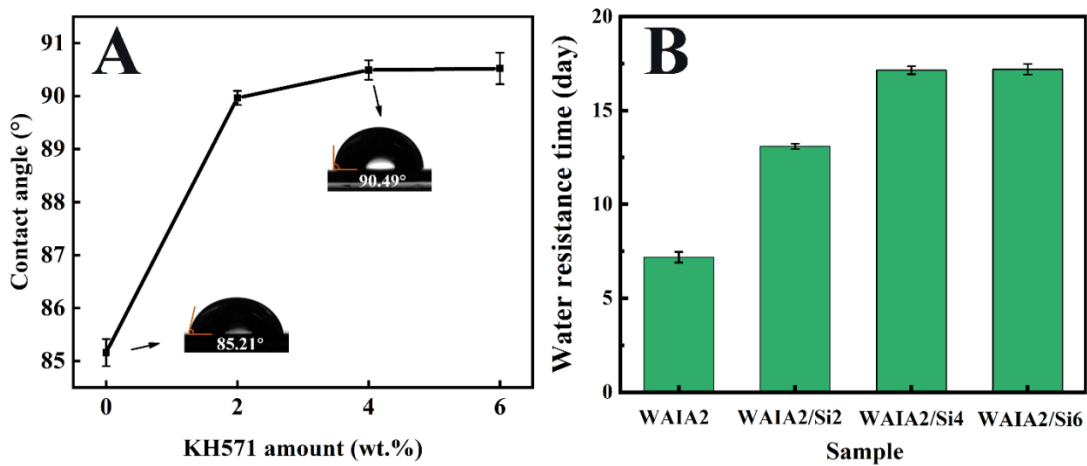
Fig. 6 shows the stress-strain curve of the resin samples with different KH571 amount. The data of tensile strength, Young's modulus and elongation at break of each resin sample are shown



in Table S2. It can be observed that the addition of KH571 further improves the mechanical properties of the resin. With the increase of KH571 amount, the tensile strength of the resin increases from 23.41 MPa to 29.00 MPa, the Young's modulus increases from 804.12 MPa to 1954.67 MPa, and the elongation at break decreases from 7.34% to 4.50%.



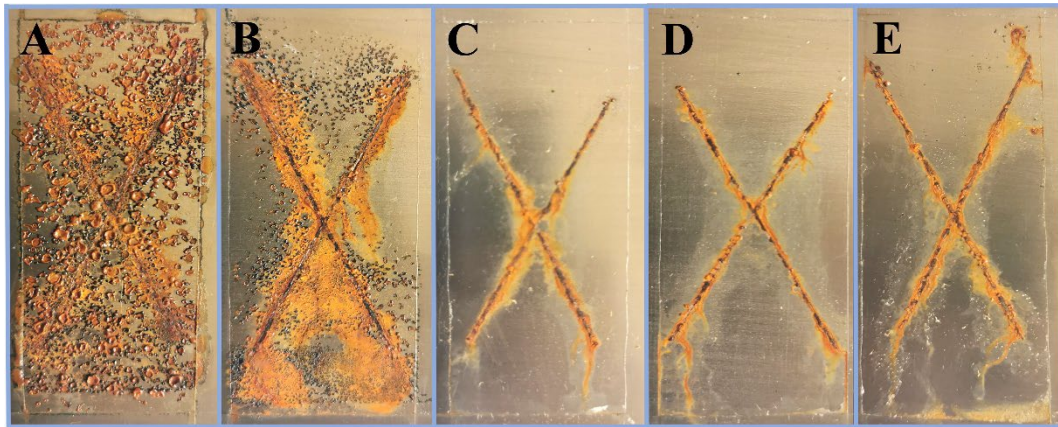
**Fig. 6.** The stress-strain curves for resin with different amount of KH571.



**Fig. 7.** (A) Comparison of the contact angles (B) Water resistance time of different samples.

Fig. 7 shows the influence of KH571 amount on the contact angle and water resistance time

of the resin coating. The contact angle of the samples shows an upward trend with the increase of KH571 amount (Fig. 7A). The contact angle of sample WAIA2/Si4 reaches  $90.49^\circ$ , which is increased by  $5.3^\circ$  compared with sample WAIA2. The increase of coating contact angle may be due to the increase of crosslinking degree and the migration of silane to the coating surface [34, 35]. As the amount of KH571 increases from 4 wt.% to 6 wt.%, there is no evident increment in contact angle. The saturation of silane side chain on the resin surface may explain the reason of this situation. The water resistance test of the resin coatings (Fig. 7B) shows that when the resin was co-modified by both IA and KH571, the water resistance can be further improved. When the amount of KH571 is 4 wt.%, (sample WAIA2/Si4), the water resistance time can reach 17 days. That means the introduction of KH571 can effectively improve the water resistance properties of the resins.



**Fig. 8.** The state of different coating samples after 24 hours of salt spray test: (A) WA, (B) WAIA2, (C) WAIA2/Si2, (D) WAIA2/Si4, (E) WAIA2/Si6.

To further evaluate the anticorrosion property of the modified resin coatings, scratch salt

spray test was used to accelerate corrosion of resin coatings[36-38]. Fig. 8 shows the corrosion behavior of samples after 24 hours of the salt spray test. It can be seen that severe corrosion occurred in WA sample without modification (Fig. 8A). As shown in Fig. 8B, compared with WA, the corrosion of WAIA2 coating modified only by IA was weakened, but the corrosion was still serious. The corrosion extended more than 5 mm from scratch, and serious pitting corrosion occurred on the metal substrate. After adding KH571 to the resin, the corrosion degree of the coating obviously decreased, and the rust was only scattered in the scratches. The reason for this phenomenon may be that, on the one hand, the introduction of KH571 enables the resin to produce denser crosslinking structure to prevent erosion of salt fog. On the other hand, the silicon hydroxyl group reacts with the hydroxyl group on the metal substrate to closely combine the resin with the metal substrate, which effectively prevents corrosion diffusion [39]. Based on the experimental results and the principle of cost saving, 4 wt.% KH571 is selected as the proper amount.

## **3.2 Characterization and performance of modified resins**

### **3.2.1 Chemical structure analysis**

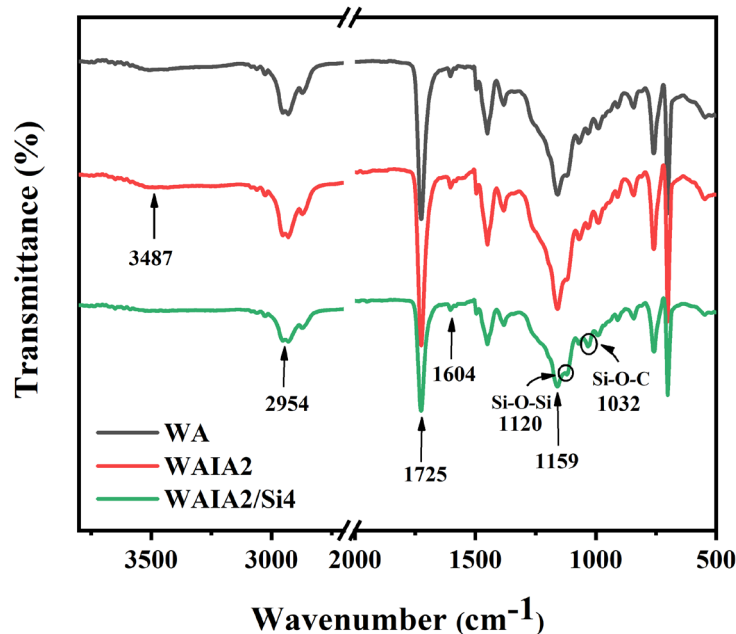
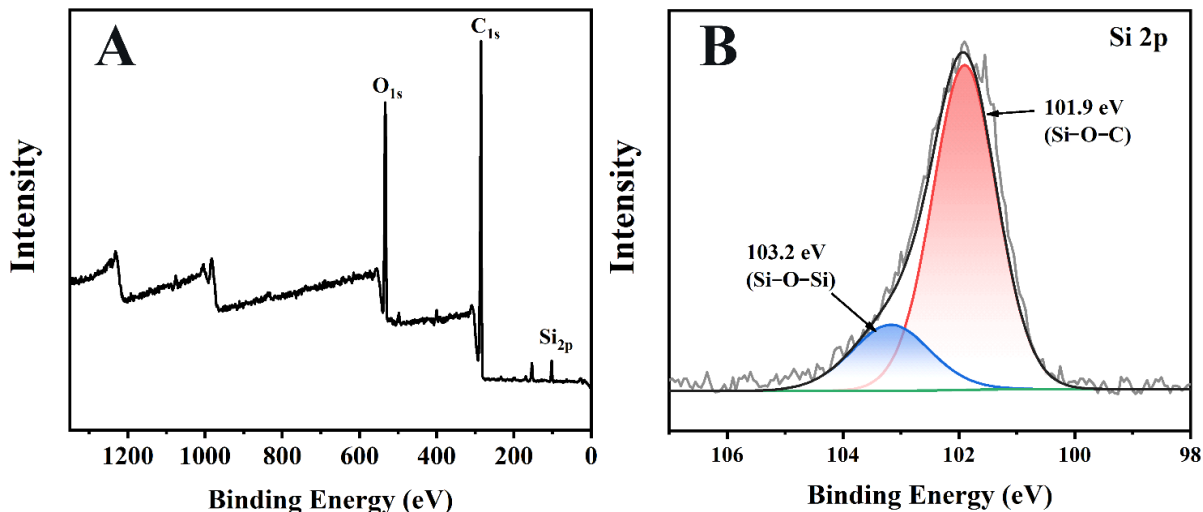


Fig. 9. Infrared spectra of WA, WAIA2, WAIA2/Si4 coatings.

FTIR spectra of sample WA, WAIA2, WAIA2/Si4 are shown in Fig. 9. The absorption peaks at 3487, 2945, 1725, and 1159  $\text{cm}^{-1}$  correspond to the stretching vibrations of -OH, C-H, C=O, and C-O-C, respectively [39, 40]. The peak at 1604  $\text{cm}^{-1}$  can be attributed to the C=C stretching vibration of benzene ring [41]. The peak near 1640  $\text{cm}^{-1}$  is the characteristic peak of C=C in olefins [42]. As can be seen in the figure, there is no obvious characteristic peak at 1640  $\text{cm}^{-1}$ , which indicated that all monomers containing double bonds in the emulsion participate in the reaction. This proves that the modified monomers IA and KH571 were successfully connected to the polymer chain through the copolymerization reaction of carbon-carbon double bond. Compared with the reference sample WA, the characteristic absorption peaks of C=O and -OH of WAIA2 are enhanced due to the introduction of carboxyl groups in the resin chain. In addition, the characteristic absorption peaks of WAIA/Si4 are also enhanced at 1120  $\text{cm}^{-1}$  and 1032  $\text{cm}^{-1}$ ,

which can be assigned to the Si-O-Si and Si-O-C structure, and demonstrates that hydrolysis and crosslinking of KH571 had occurred [43, 44].



**Fig. 10.** XPS spectra for WAlA2/Si4 (A) and high-resolution XPS spectra of the Si 2p (B).

In order to further certify that KH571 had participated in the polymerization, the XPS analysis to the modified resin coatings was applied and the XPS spectra of WAlA2/Si4 is illustrated in Fig. 10. It can be observed the appearance of characteristic signals at around 285 eV, 533 eV and 102 eV, which belonging to C 1s, O 1s and Si 2p, respectively. In the Si2p spectrum (Fig. 10B), there are obvious characteristic peaks at 103.2 eV and 101.9 eV, which represent Si-O-Si bond and Si-O-C bond [45]. This also demonstrates once again that KH571 hydrolyzes to produce silicon hydroxyl groups, so that dehydration condensation reaction can occur between different silicon hydroxyl groups, which can react with other active groups in the resin.

### 3.2.2 Mechanical properties

By observing the stress-strain curves of WA, WAlA2 and WAlA2/Si4 samples in Fig. 3 and

Fig. 6 and Table S1 and S2 respectively, it is found that the tensile strength and Young's modulus of the resin are significantly improved after modification by IA and KH571. The incorporation of 2 wt.% IA and 4 wt.% KH571 in WA enhances the tensile strength by 56% (from 17.86 MPa to 27.92 MPa), increases Young's modulus by 193% (from 458.28 MPa to 1343.85 MPa, as shown in Table S1 and S2). Studies have shown that crosslink density is an important factor affecting the tensile strength of the resin [46]. The carboxyl groups in IA and the silicon hydroxyl groups formed by hydrolysis of KH571 increase the crosslinking sites between polymer chains and allow more polymeric chains to bind together [47, 48]. This results in a higher crosslink density and makes the resin more difficult to be broken [49]. However, the increase of crosslinking density inevitably restricts the mobility between chain segments, which reduces the elongation at break of the resin. The elongation at break is decreased from 11.98% to 5.13% sharply. Fig. S1 shows the SEM images of the fracture surfaces of WA, WAIA2 and WAIA2/Si4 tensile samples. Compared with WA, the fracture surfaces of WAIA2 and WAIA2/Si4 show rougher appearance, which proves that the crosslinking density of the modified resin is improved.

### **3.2.3 Water resistance properties**

It is found in 3.1.1 and 3.1.2 that IA and KH571 significantly improve the water resistance of the resin. The introduction of IA and KH571 change the chemical composition and microstructure of the resin coating surface, which improves the hydrophobicity of the coating. Moreover, the dense crosslinking structure in the coating can effectively resist the erosion of water

molecules and improve the water resistance time. The test results show that the introduction of 2 wt.% IA and 4 wt.% KH571 increased the water resistance time from 1 day to 17 days and increased the contact angle from 78.91° to 90.49° [31, 50].

When the surface tension of liquid is known ( $\gamma_{(H_2O)} = 72.75 \text{ (mN/m)}$ ) and the contact angle has been measured, the solid surface energy of specific liquid can be calculated by Neumann's equation of state [33, 51] as shown by Equation (2):

$$\cos \theta = 2 \cdot \sqrt{\frac{\gamma_s}{\gamma_l}} \cdot e^{-\beta(\gamma_l - \gamma_s)^2} - 1 \quad (2)$$

where  $\beta$  is a constant, which is determined by the experimental contact angle of different kinds of solid surfaces, and its average value is  $0.0001247 \text{ (m}^2/\text{mJ)}^2$ . The surface energy of different resin samples is shown in Table 2, it can be seen that the contact angle is negatively correlated with the surface energy. The addition of 2 wt.% IA reduces the surface energy by 3.94 mN/m (from 36.13 mN/m to 32.19 mN/m). When the resin was co-modified by IA and KH571, the surface energy of the resin coatings decreased by 7.24 mN/m (from 36.13 mN/m to 28.89 mN/m). The introduction of modified monomer reduces the surface energy of the resin coatings and enhances the hydrophobicity of the resin coatings.

**Table 2.** The relationship between contact angle and surface energy.

Sample	contact angle (°)	surface energy (mN/m)
WA	78.91	36.13
WAIA2	85.21	32.19
WAIA2/Si4	90.49	28.89

### 3.2.4 Thermal properties

To analyze the effect of IA and KH571 on thermal properties of modified resins, TG analysis was conducted for WA, WAIA2 and WAIA2/Si4. The thermal stability of the material was evaluated based on the onset temperature of decomposition ( $T_{\text{onset}}$ ) and the mass residue at 700 °C (char yield). Fig. S2 shows the thermal degradation behavior of resin samples. In the temperature range of 30-200 °C, the weight loss of resin materials is related to the elimination of free water and bound water in the resin [31]. The weight loss at 300-450°C is mainly due to the decomposition of macromolecular chains [7]. Meanwhile, it can be seen that the addition of IA and KH571 improve the  $T_{\text{onset}}$  and char yield of the resin samples. Compared with the reference sample WA,  $T_{\text{onset}}$  and char yield of WAIA2 increased by 6.3 °C (from 353.2 °C to 359.5 °C) and 0.66% (from 0.27 % to 0.93 %), respectively, while that of WAIA2/Si4 are increased to 361.8 °C and 2.01%, respectively. This is because the addition of crosslinking monomers IA and KH571 reinforce the spatial structure of the polymer system, and a three-dimensional network structure is formed inside the resin, which hinders the rotation, translation and movement of molecular chains



and the escape of small molecules, thus requiring more energy to disrupt the structure [46].

### 3.2.5 Storage stability

The emulsion samples were sealed and stored at room temperature. The storage stability of the sample is judged by observing whether appears gel or agglomerate. The storage stability of samples WA, WAIA2 and WAIA2/Si4 is shown in Table 3. It can be found that the storage stability of the samples is observably affected by IA. The addition of 2 wt.% IA in WA improved the storage stability from 60 days to 105 days. The stability of the emulsion modified by KH571 also increased storage slightly but not significantly.

**Table 3.** Storage stability of different resin samples.

Sample	WA	WAIA2	WAIA2/Si4
Storage stability (day)	60	105	110

In order to determine the role of IA on the polymerization and storage of emulsion. The particle size and Zeta potential of samples with different IA amount were tested and the results are shown in Fig. 11. It can be seen that with the increase of IA, the particle size of emulsion decreases significantly with a near linear relationship. This maybe because the introduction of the polar group carboxyl group into the resin by IA. The hydrophilic carboxyl groups tend to distribute on the surface of the emulsion particles, which can play a similar role as an emulsifier. The increase of carboxyl group leads to smaller particle size and better stability of the emulsion [52, 53]. In addition, the increase of latex particles due to the homogeneous nucleation mechanism of IA may also be an important reason for the reduction of particle size [54].

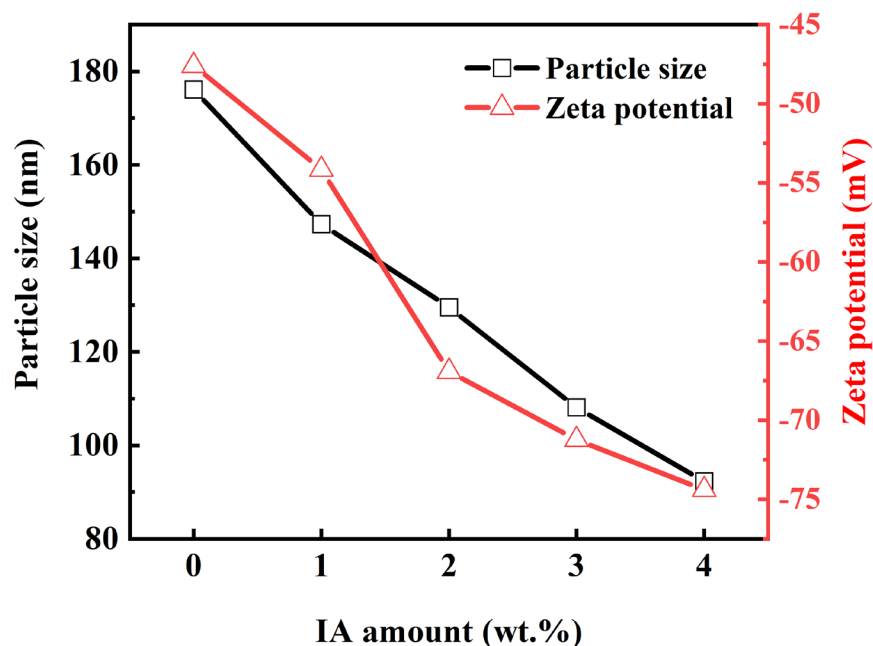


Fig. 11. The particle size and Zeta potential with different amount of IA.

Emulsion stability can also be evaluated by Zeta potential [55]. Generally, the emulsion with high Zeta potential (the absolute value of Zeta potential is more than 30 mV) is stable. As shown in Fig. 11, the Zeta potential of all emulsion samples is smaller than -30 mV, suggesting the excellent emulsion stability. In addition, the Zeta potential of emulsion samples decreased with the increase of IA amounts. This is because the negative charge on the surface of latex particles is provided by carboxyl groups in IA, anions in emulsifiers, and sulfate ions in initiators. The negative charge on the surface of the latex particles increases with the increase of the amount of IA, which enhances the electrostatic repulsion between latex particles. Strong electrostatic repulsion can slow down the condensation of latex particles, so the emulsion prepared is more stable [22, 56].

The Zeta potential of emulsions with different amounts of KH571 is shown in Fig. S3. The introduction of KH571 does not affect the Zeta potential of the emulsion, which indicates that the

crosslinking reaction between KH571 and IA occurs mainly in the curing stage.

## **4. Conclusion**

Waterborne acrylic resin modified by IA and KH571 was synthesized by seeded emulsion polymerization. The effects of IA and KH571 amounts on the resin properties were investigated. The results of FTIR and XPS showed that the modified monomers IA and KH571 were successfully connected to the main chain of the polymer, and the active functional groups (such as carboxyl groups and silicon hydroxyl groups) in the resin were crosslinking reacted. IA is not only a functional monomer that introduces hydrophilic carboxyl groups in the system to improve the stability of the emulsion, but also a crosslinking monomer that increases the crosslinking density of the resin and improves the resin properties. KH571 is used as crosslinked monomer to enhance the performance of the coating by introducing Si-O-C and Si-O-Si into the coating. The performance of the resins co-modified with IA and KH571 is greatly improved, with the contact angle increasing from  $78.91^{\circ}$  to  $90.49^{\circ}$ , the water resistance time improving from 1 day to 17 days and the increase in tensile strength and Young's modulus reaching 56% and 193%, respectively. In addition, the stability of the emulsion, corrosion resistance and thermal stability of the resin coating are significantly enhanced. With the significant applications of metals and alloys [57-66] and the awareness of corrosion [67-70], the modified waterborne acrylic resin with its excellent water resistance will have a potential application prospect in the fields of waterproof and anticorrosive coating of metals.

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