

Advances in water-resistant modification of aqueous acrylic resins: modification methods, mechanism of action

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Abstract. Waterborne acrylic resin is widely available in architectural coatings, road adhesives, etc. Its non-toxicity, non-irritating odour, and low cost are characteristics that have received increasing attention in recent years. Concerning the water-resistance of the resin, this review introduces the effect of inorganic materials like silane coupling agents, fluorine silicone, and copolymers on the hydrophobic properties of aqueous acrylic resins, analyses and discusses the mechanism of action of various methods and their factors affecting hydrophobic properties, such as the formation of cross-linked structures and micro-convex structures on the surface, also points out the problems and challenges in the water-resistance modification of aqueous acrylic resins.

1. Introduction

Water-based resin is a resin system with water as a dispersion medium. Low volatile organic compounds (VOC) and good film-forming properties are outstanding advantages as functional materials cite coatings, adhesives, and sealants. [1-3]. Many water-based resins serve as epoxy resin, polyurethane, alkyd resin, acrylic resin, etc. [4-8]. In specific industrial applications, the cost needs to be comprehensively considered. And performance advantages to choose from. Waterborne acrylic resin is one of the fastest-growing resins. It is synthesized with acrylate or methacrylate as the main monomer [9]. It has intense light, thermal and chemical stability [10]. It is used as coatings for interior and exterior walls in the construction industry, adhesives for colored pavements in the road industry, etc. However, we found that water-based acrylic resins have defects from specific applications, including low water resistance, high film-forming temperature, and inadequate corrosion resistance. [9, 11, 12], which are limited in specific applications. Water-resistance refers to the resistance of the paint film to water. However, whether in the construction or road industry, water damage is a significant problem for water-based acrylic resins when used as coatings and adhesives. It is determined by the chemical structure of the resin, as proof of weak molecular polarity in the resin structure, the high surface energy of the film after film formation, insufficient self-crosslinking, etc. These factors will make it easier for water molecules to attack the resin coating. It increases its water absorption rate, thereby affecting its water resistance.

The water resistance of water-based acrylic resins is improved by two commonly used modification methods: physical modification and chemical modification. Physical transformation is to mechanically and physically

blend two or more inorganic/organic substances with acrylic resin. It is described as convenient and straightforward, but the modification effect of resin is generally inadequate. Due to the system's poor compatibility to single physical blending, remarkable substances undergo nucleation and growth phase separation, showing an "island structure," which affects the modification effect. However, the chemical method achieves molecular level compatibility between various substances through copolymerization or cross-linking between the modified importance and the acrylic resin by illustrating the formation of covalent bonds, grafting points, etc. The resin has outstanding advantages in performance, thus showing ethical application value in the follow-up.

This paper reviews different modifiers for water resistance modification of waterborne acrylic resins, namely silane coupling agents, fluorine and silicone substances, resin copolymerization, and analyses. It discusses the effects and characteristics of the different modification methods.

2. Water-based resin modification methods

2.1 Physical modification

Modification of aqueous resins is a standard modification method achieved by simple physical blending. To obtain a matte surface for acrylic resins, Ou et al. [13] prepared acrylic resin/micro-SiO₂/polymethylurea (AC/SiO₂/PMU) composites by physically blending acrylic resin emulsions (AC), polymethylurea resins (PMU) and modified silica (SiO₂). This blended composite has increased interfacial tension between polymer and inorganic, committing phase separation in the AC/SiO₂/PMU composite system,

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e.g., nucleation of SiO₂ particles on account of aggregation of particles through weak compatibility with the polymer. Aqueous acrylic coatings with a matte surface are obtained.

It is possible to see that physical modification has its unique advantages in obtaining certain specific properties of aqueous resins and can be used in synergy with chemical modification methods to achieve maximum transformation of the properties of aqueous resins.

2.2 Chemical modification

The chemical approach is to achieve molecular compatibility between the various substances utilizing copolymerization between the modifier and the aqueous resin, etc. Pablo J. Peruzzo et al. [14] We have synthesized polyurethane/acrylic resin composites with a cross-linked structure by emulsion polymerization of acrylic monomers with preformed polyurethane chains with polymerizable terminal vinyl—a polyurethane-acrylic resin blend dose preparation. The polyurethane/acrylic resin composite with a cross-linked structure performed significantly better than the polyurethane-acrylic resin blend. Physical or chemical modifications of aqueous resins have benefits and shortcomings.

Physical blending is convenient and straightforward. Chemical changes are stable and long-lasting and provide more significant performance improvements. In addition, waterborne resins have high water resistance requirements for coating applications, so it is crucial to prepare waterborne resins with high hydrophobicity by chemical modification. At the same time, it has excellent application value.

3. Water-resistant modification of water-based acrylic resins

3.1 Water-resistance modification of aqueous acrylic resins by silane coupling agents

Silane coupling agents can cross-link with aqueous acrylic resins or other substances to amend the chemical structure of the resin, thereby improving its water resistance. Jiao et al. [15] operate 2-(3,4-epoxy)ethyltriethoxysilane (KH567) to modify aqueous acrylic resins, and KH567 underwent a grafting reaction with the acrylic resin, changing the molecular chain structure of the resin. The migration of the KH567 side-chain structure in the aqueous acrylic resin to the film surface resulted in a reduction in the surface energy of the resin film [16], consequently improving its water resistance. However, excessive amounts of silane coupling agent can introduce more -OH groups, which worsens the water resistance, and the dose should generally control between 10-15 wt%. Zheng et al. [17] utilized 2-butoxyethanol, cellulose acetate butyrate, and acrylic acid monomer as raw materials, N, N - dimethylethanolamine as a neutralizing agent, and γ -aminopropyltriethoxysilane (KH-550) as curing agent to prepare a new waterborne acrylic resin modified with cellulose acetate by homogeneous solution polymerization. A three-dimensional network structure

was formed between KH-550 and the resin. Increased crosslink density and the addition of the curing agent reduced the surface tension, lowered the surface energy, and enlarged the contact angle [18].

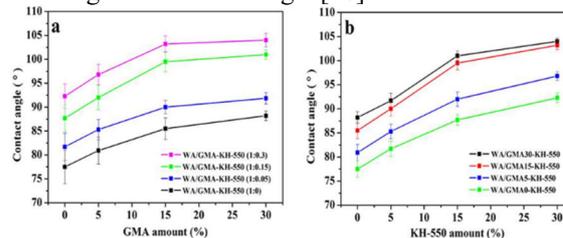


Figure 1. (a) Influence of the GMA amount on the contact angle for different amount of KH-550. (b) Influence of the KH-550 amount on the contact angle for different amount of GMA.

Guo et al. [19] applied aminopropyltriethoxysilane (KH-550) as a curing agent to cure the GMA-modified resin and then modified the aqueous acrylic resin with the GMA-modified resin. The data in Fig. 1 showed that the increase in both GMA and KH550 content brought forth a more extensive water contact angle of the resin film, which resulted from the cross-linking reaction between KH550 and the system, altering the physicochemical properties of the coating [20, 21]. Wu et al. [22] synthesized multi-walled carbon nanotubes (CNTs)/waterborne acrylic resin nanocomposite coatings using 3-aminopropyltriethoxysilane (KH-550) coupling agent as a curing agent by a solution mixing method. The synthesis mechanism in Fig. 2 and the contact angles with the CNTs/WA nanocomposite coatings with different CNTs loadings and water droplets in Fig. 3. As a result of the small particle size and large specific surface area of CNTs, they are not compatible with water droplets. The resin changes its internal structure after mixing [23]. And the surface energy of the coating of the water-based wax decreases. Hence, the contact angle of the coating shows an increasing trend with the increase of the CNTs content, but when the carbon nanotube content increases from 6wt% to 10wt%, The ordered dispersion state results in a slow rise in the contact angle. It can be deduced that when the carbon nanotube content continues to increase, the effect on the contact angle will tend to a stable value.

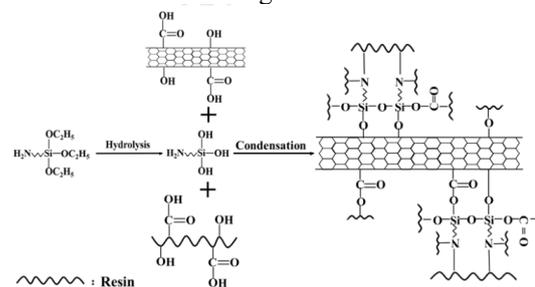


Figure 2. Mechanism of CNTs/WA nanocomposite synthesis.

The relationship between the contact angle and the equilibrium of the three-phase boundary forces does investigate by utilizing Young's equation [24]. Where γ_{sv} , γ_{sl} , γ_{lv} and θ represent the surface free energy, solid-liquid interfacial tension, liquid-vapor interfacial

tension, and contact angle of the solid-vapor interface, respectively.

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cos\theta \quad (1)$$

The Newman equation of state can yield the surface energy [25]:

$$\gamma_{sl} = \gamma_{lv} + \gamma_{sv} - 2\sqrt{\gamma_{lv}\gamma_{sv}}e^{-\beta(\gamma_{lv}-\gamma_{sv})^2} \quad (2)$$

Simultaneous (1) and (2):

$$\cos\theta = -1 + 2\sqrt{\gamma_{sv}/\gamma_{lv}}e^{-\beta(\gamma_{lv}-\gamma_{sv})^2} \quad (3)$$

Combined with the equations and the analysis of the test results, it is clear that the surface energy tends to decrease, and the hydrophobicity improves as the loading of carbon nanotubes increases. Nanocomposites containing 10wt% carbon nanotubes have the lowest surface energy (28 mN·m⁻¹), much lower than some other resins [26-28]. Low surface energy coatings are widely used for antifouling based on their hydrophobicity and have potential applications for non-toxic antifouling coatings.

Aiming at the water resistance modification of water-based acrylic resin by different silane coupling agents and other modifiers, the change law of its water contact angle makes the comparison, as shown in Table 1. By comparing the three groups of KH567, KH550/GMA, and KH550/CNTs, It can be seen from the water contact angle data of the pure WA resin coating that the contact angle of the pure WA resin coating is above 80 before the modification and the contact angle increases after the conversion. The KH550/GMA and KH550/CNTs modified WA resins. The rise in the contact angle of the coating film is above 10, while that of KH567 is relatively weak. In addition, the KH550/CAB modified system has a relatively significant change in the contact angle of the WA resin coating film, with a growth rate of 21.4%. Still, the water contact angle itself is relatively low, 65.1° and 78.1° before and after modification, respectively, indicating that the system Compared with the other three scenarios, the hydrophobicity of the WA resin coating film is relatively weak. The hydrophobic type of the KH550/GMA modified system is the greatest.

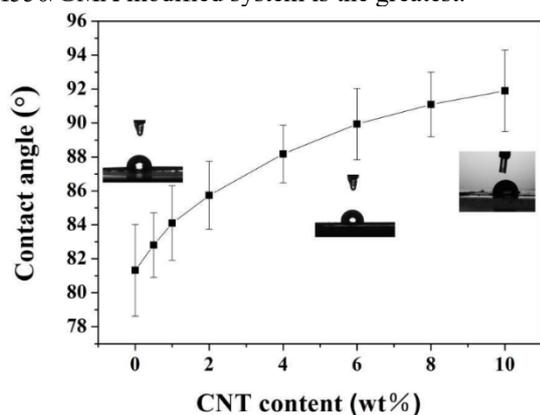


Figure 3. Influence of the CNT amount on the contact angle.

Table 1. The change of WA water contact angle

| | KH567 | KH550/CAB | KH550/GMA | KH550/CNTs |
|--------------------------------------|-------|-----------|-----------|------------|
| Contact angle before modification(°) | 84.7 | 65.1 | 87.7 | 81.32 |
| Contact angle after modification(°) | 90.4 | 79.1 | 99.5 | 90.0 |
| Rate of change(%) | 6.7 | 21.4 | 13.4 | 10.7 |

In summary, silane coupling agents ameliorate the water-resistance of waterborne acrylic resins can be summarized. Silane coupling agents can cross-link with the resin to form a stable three-dimensional network structure, thereby increasing the cross-link density and reducing the surface energy of the coating [29-32]. There are some differences in the effect of silane coupling agents for different modification systems, However, all have improved the water-resistance of the waterborne acrylic resin.

3.2 The effect of fluorine and silicones on the water-resistance of aqueous acrylates

Inorganic materials mixed with polymers to form composites will to some extent, improve the performance of polymer-based composites, e.g., fluorine and silicones in aqueous acrylates can have a positive effect on the water-resistance of resin coatings. Yang, Du, Li et al. [33-35] all used silane-based substances to pretreat SiO₂ particles, and then the modified SiO₂ particles were then mixed with WA. the water-resistance properties were characterized. Yang et al. modified SiO₂ particles with 3-(methacrylate)propyltrimethoxysilane and prepared fluorinated acrylic acid/ SiO₂ composite emulsions (F1) by emulsion polymerization, as shown in Fig. 4. The results showed a significant increase in the water contact angle of the resin film, e.g., S2b (modified SiO₂) compared to S2 (unmodified SiO₂), the water contact angle of the resin film increased from 93° to 100°. With increasing fluorine content, as in S4-S7, the water contact angle remained steady at nearly 110°. In addition, the surface roughness (Rq) of the resin film was explored by characterizing its AFM/nm. Du et al. modified the nano-TiO₂/ SiO₂ composite particles with a silane coupling agent (KH-570) and a titanate coupling agent (NDZ-101) and then embedded them into the acrylic resin by a co-blending method to obtain a nano-TiO₂/ SiO₂ composite modified acrylic resin (F2), probably due to the addition of nano-TiO₂/ SiO₂ composite particles and the hydrophobic effect of the coupling agent, thus forming a nano-convex structure on the surface of the acrylic resin coating. As a result, the water absorption of the nano-

TiO₂/ SiO₂ acrylic resin was less than 5%, and the water-resistance of the resin material was improved.

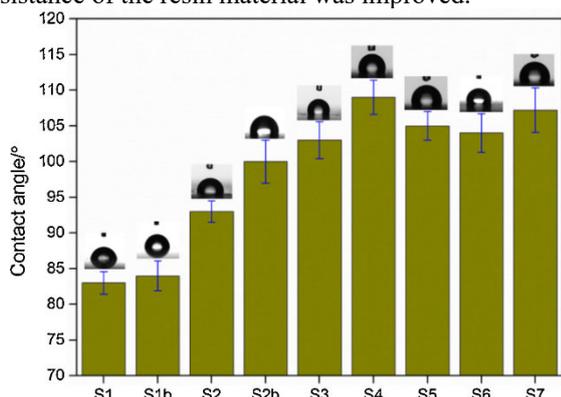


Figure 4. Water contact angle of films.

From the analysis in F2, it can speculate that the reason for the change of the water contact angle in F1 is that the functionalized SiO₂ forms a nano-convex surface in the resin film, and the hydrophobic effect of the fluorine substance itself also has a certain degree of influence on the system. It increases the hydrophobicity of the system. Similarly, Li et al. prepared functionalized SiO₂-modified aqueous fluorinated acrylate emulsions (F3) using KH-570 for surface treatment of SiO₂ nanoparticles, and the water absorption and water contact angle of the resin films in Fig. 5. Overall, the water absorption of the films decreased gradually with increasing SiO₂ content, with the SiO₂ content at 3%. To further investigate the intrinsic reason for the effect of SiO₂ content on water absorption, the surface morphology of the resin film was also characterized by AFM, as shown in Fig. 6. From the 3D image in Fig. 6(a), there is no doubt that the unmodified SiO₂ corresponds to the surface morphology of the resin film is relatively flat. As the SiO₂ content increases, the raised structure on the film surface gradually increases, with the most significant number of micro-convex facilities appearing at 3% SiO₂ content. When the SiO₂ content continues to grow, as shown in Fig. 6(e), due to aggregation and combined with the above data on water absorption and contact angle, this reduces its water resistance, as shown in Fig. 6(b). The water absorption, water contact angle, and AFM analysis show that the amount of functionalized SiO₂ affects the surface microconvex structure of the resin film and thus the hydrophobic ability of the film.

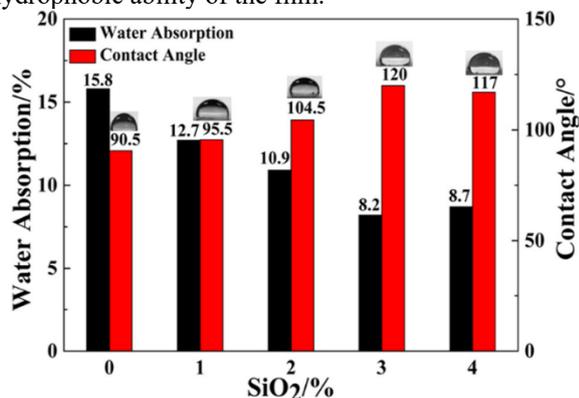


Figure 5. Comparative analysis of water absorption and contact angle.

A common rule was found by analyzing F1, F2, and F3. Through the treatment of SiO₂ functionalization, the internal reason for changing the water-resistance of WA film is the degree of influence on the micro-convex structure on the surface of the film, and the micro-convex network is dense. And the larger the number, the rougher the surface of the film and the better the water resistance. The surface roughness (Ra, Rq) of F1 and F3 in Table 2 goes without saying that F3 has a tremendous advantage in water resistance over the F1 system.

Table 2. F1、F3 Surface roughness

| F1 | Rq(nm) | F3 | Ra(nm) |
|-----|--------|--------------------|--------|
| S1 | 1.45 | 0%SiO ₂ | 1.92 |
| S1b | 1.75 | 1%SiO ₂ | 3.13 |
| S2 | 1.86 | 2%SiO ₂ | 4.0 |
| S2b | 3.33 | 3%SiO ₂ | 6.02 |
| S4 | 0.426 | 4%SiO ₂ | 6.91 |

Organic or inorganic substances containing fluorine, silicon, etc., which are inherently hydrophobic, strengthen the water-resistance of aqueous resins to a certain extent. Li et al. [36] prepared aqueous organic/inorganic hybrids by dispersing superhydrophobic SiO₂ nanoparticles in acrylate copolymers, and the water contact angle of the original hybrid coating reached 164°. As shown in Fig. 6(a), the SiO₂ nanoparticles were more uniformly dispersed in the acrylate copolymer. The nanoparticles showed a specific raised structure, which was closely related to the superhydrophobic nature of the coating, Fig. 6(d-f) shows the surface of the layer after a certain number of cycles of wear. Hao et al. [37] prepared a fluorosilicone propylene emulsion using 2,2,3,4,4-hexafluorobutyl acrylate (HFBA) and vinyltriethoxysilane (VTES) for emulsion polymerization with acrylic acid monomers liquid and the magnitude of water absorption of resin coatings with 10%F, 10%Si, and 10%F/Si additions were measured, respectively, as shown in Fig. Fig. 7. It can see that the water absorption of 10%F films grew more rapidly with time. The water absorption of 10%Si films was significantly lower than that of others. In addition, the water absorption of the 10% F/Si film is 8% due to the cross-linking reaction of silicon in the system, forming a three-dimensional cross-linked network, which is similar to the role of silane coupling agents in the resin modification above, and the synergistic

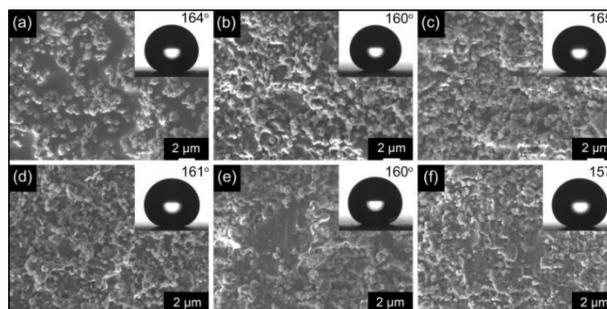


Figure 6. SEM images of an original superhydrophobic hybrid coating surface (a), and the

surfaces of superhydrophobic hybrid coating after 50(b), 100(c), 200(d), 250(e) and 300(f) cycles of abrasion, the insets are the corresponding CAs of the corresponding surfaces.

effect of fluorine. It is identical to the position of silane coupling agents in the resin modification above. The synergistic effect of fluorine contributes to the outstanding advantages of the films in terms of water resistance over single fluorine or silicon modifications. Xiong et al. [38] synthesized an acrylic copolymer emulsion containing fluorine, silicone, and epoxy resin. The surface tension decreased due to the aggregation of fluorine chains on the film's surface, resulting in a more hydrophobic modified film. F. Sbardella et al. [39] synthesized a waterborne acrylic resin coating of silica-coated polymer particles. They coated it on Carrara marble and Lecce stone, where the water penetration rate was slowest at 10% SiO₂ content. Due to differences in the internal pore size of Carrara marble and Lecce stone, the water penetration rate was also inconsistent.

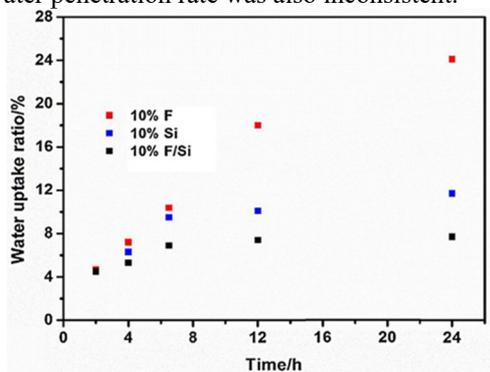


Figure 7. Water absorption of the films.

By analyzing the effect of substances such as fluorine and silicon on the water-resistance of waterborne acrylic resin, it is pretty clear that the principle of its modification of waterborne acrylic resin is forcing the roughness of the film surface. When such substances are mixed with the resin by physical or chemical, the fluorine substances will act on the resin surface, making the raised structure of the coating surface more evident than before the modification. In addition, the cross-linking effect of silicon will physically build upon the coating surface, which will also affect the roughness of the coating surface, making the water absorption of waterborne acrylic resin decrease and water resistance increase.

3.3 Resin copolymer modified aqueous acrylate.

The resin copolymerization method can give full play to the advantages of each polymer in specific properties to achieve the purpose of modification. Ji et al. [40] synthesized acrylic acid-alkyd copolymer by free radical polymerization and studied its water resistance and alkyd acid. Resin content. As shown in Fig. 8(a), when the alkyd content is 10%, the water contact angle of the copolymer reaches more than 90°, and when the content is 25%, the water contact angle keeps at about 95°. From the point of view of contact angle alone, the range of alkyd will have a specific influence on the hydrophilicity of acrylic acid-alkyd copolymer. When the content of alkyd is 10%, the acrylic acid-alkyd copolymer has a specific hydrophobic

type. It is due to hydrophobic alkyd species [41, 42]. The change of the contact angle with time was also qualitatively studied. It can see from Fig. 8(b) that with the increase of the alkyd content, the decreasing trend of the water contact angle is more and more gentle. When the alkyd content

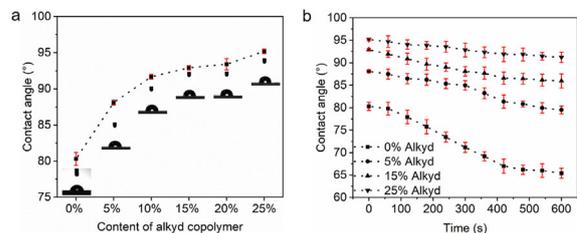


Figure 8. (a) Water contact angles of the acrylic-alkyd copolymer films at 0 s, and (b) the change of water contact angles of the acrylic-alkyd copolymer films.

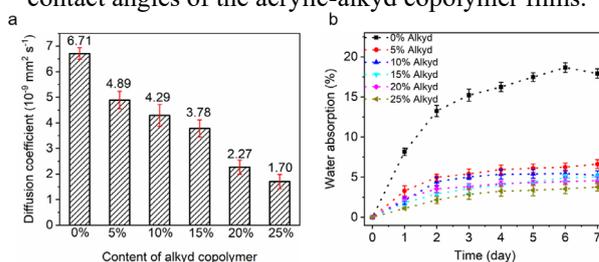


Figure 9. (a) Water diffusion coefficients of the acrylic-alkyd copolymer films, and (b) water uptake of the copolymer films at room temperature.

is 25 %, the decreasing trend tends to the level, indicating that the hydrophobicity of the copolymer film at this time has a higher level.

In addition, the pattern of variation of the water diffusion coefficient and water absorption of the acrylic-alcoholic acid copolymer is also consistent with the results of the above analysis, as shown in Fig. 9(a), where the water diffusion coefficient changes from $6.71 \times 10^{-9} \text{ mm}^2 \cdot \text{s}^{-1}$ to $1.70 \times 10^{-9} \text{ mm}^2 \cdot \text{s}^{-1}$ as the alkyd content increases. And the water absorption is also significantly lower, as shown by the results in Fig. 9(b). This lower water diffusion coefficient and water absorption rate will help improve the copolymer film's corrosion resistance [43].

The crosslinking density of the acrylic copolymer can be changed by the esterification synthesis method that can enhance the water resistance of the coating. Esterified the epoxy resin with methacrylate in the first step by Duan et al. [44]. Then added acrylamide to the esterification reaction product, obtaining the bisphenol A epoxy resin modified acrylic resin in

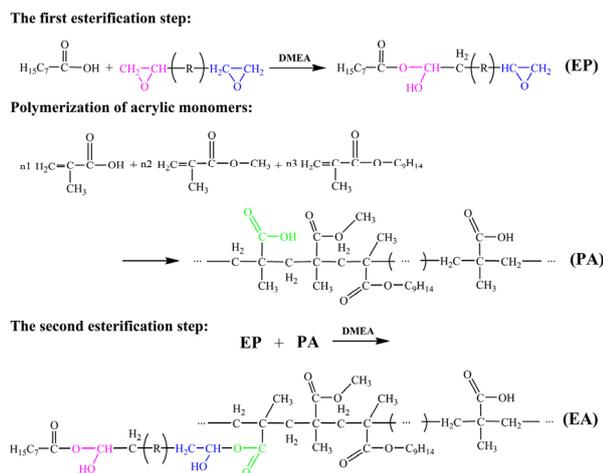


Figure 10. The schematic diagram for the two-step esterification process.

the end. Liu et al. [45] synthesized the waterborne epoxy-acrylic graft copolymer resin by a two-step esterification method. The synthesis method in Fig. 10.

Both of the above synthesis methods are used to change the internal structure of aqueous acrylic resins, forming a cross-linked network with a specific strength that can hinder the attack of water molecules. As in the case of acrylic resins modified with bisphenol epoxy resins, a cross-linked structure is formed between the O-H and amide groups in acrylamide and polar groups such as epoxy and carboxyl groups; Concerning waterborne epoxy-acrylic graft copolymer resins, the molecular weight of the resin and the carboxyl group content affect the degree of cross-linking of the coating, thus affecting the water-resistance of the layer.

Similarly, crosslinking agents can also chemically modify water-based acrylic resins. Shen et al. [46] added aziridine crosslinking agents to crosslink with carboxyl groups in acrylic resins, thereby reducing the content of carboxyl groups and making them hydrophilic. The groups are facilitated, and the water-resistance of the water-based polish is improved. Pi et al. [47] used adipic acid dihydrazide (ADH) as the crosslinking agent to synthesize a room temperature self-crosslinking acrylic resin by solution polymerization. The content of the diacetone acrylamide (DAAM) monomer affects the crosslinking density. The water absorption of the film was reduced from 37.14% to 9.2%. Sumit Parvate et al. [48] used butyl acrylate (BA), styrene, acrylic acid (AA), acrylamide,

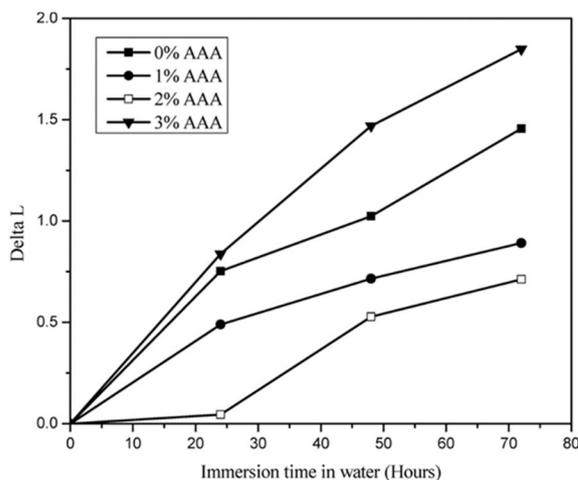


Figure 11. ΔL versus immersion time in water (hours).

and allyl acetoacetate (AAA) as monomers and hexamethylenediamine (HDA) as the crosslinking agent. A stable one-component room temperature-curing copolymer was synthesized by seed emulsion polymerization. The degree of crosslinking between AAA and HAD affects the water absorption of the film. By testing the degree of whiteness of binder film as a function of the time of the resin, it is clear that when the content of AAA is 2%, the ΔL value is relatively low, and the film has the best water resistance at this time, as shown in Fig. 11. It is because too much AAA will introduce more amide-based hydrophilic groups. It can see from the comparison with 0% AAA that this effect is more dominant than the promotion effect of cross-linking on the water resistance. The above modification of the resin utilizing cross-linking is similar to the modification principle of the silane coupling agent above, both of which form a specific cross-linked network structure, thereby improving the hydrophobicity of the resin film.

4. Conclusion

Waterborne acrylic resins are widely used in architectural coatings, road adhesives, and other applications as environmentally friendly materials. To prolong the life of the material, different modifiers play a role in waterborne acrylic resins for the water-resistance aspect of the wax, and waterborne materials with excellent water resistance are obtained.

Silane coupling agents can crosslink with resin to form a stable three-dimensional network structure, thereby increasing the crosslinking density, reducing the surface energy of the coating, and achieving the purpose of hydrophobic modification of the resin. The resin copolymerization modification method also has a similar effect. The principle of improvement of water-based acrylic resin with fluorine, silicon, and other substances is mainly focused on the impact of surface roughness. When such substances are physically or chemically mixed with the resin, the fluorine substances will make the surface of the resin convex. The degree of modification is changed. In addition, the chemical crosslinking reaction of silicon substances or the physical accumulation on the surface of the coating also affects the surface roughness of the layer, which reduces the water absorption rate of water-based

acrylic resin and increases water resistance. These modification methods have played a positive role in the water-resistance modification of water-based acrylic resins. However, in specific industrial applications, such as when used as road adhesives, the cost will directly affect the possibility of the resin application. Therefore, based on the above-mentioned various research methods, it is necessary to consider the dosage ratio of a specific modifier or use a variety of modifiers to modify the resin to achieve low cost while maintaining performance: development and application. Additionally, there are still some problems and challenges in the water-resistant modification of water-based acrylic resins, such as the influence of the crosslinked structure of the modified resin on the resin film-forming temperature, the relationship between the solid content of the water-based polish and its water resistance, etc. are questions that need to be researched. It is hoped that the water-based acrylic resin will continue to develop in a green and sustainable direction while maintaining excellent application performance.

Acknowledgments

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References

1. Padget J C. Polymers for water-based coatings-a systematic overview[J]. *Journal of coatings technology*, 1994, 66(839): 89-105.
2. Annable T, Brown R A, Padget J C, et al. Improvements in the application properties of water-based low VOC coatings[J]. *Surface coatings international*, 1998, 81(7): 321-329.
3. Jackson K. Recent advances in water-borne protective coatings[J]. *Surface coatings international*, 1999, 82(7): 340-343.
4. Ifijen I H, Maliki M, Odiachi I J, et al. Review on Solvents Based Alkyd Resins and Water Borne Alkyd Resins: Impacts of Modification on Their Coating Properties[J]. *Chemistry Africa*, 2022: 1-15.
5. MENG X, GAO Y. Development of Studies on Water-based Epoxy Resin[J]. *Materials Review*, 2006, 11(20): 384-386.
6. Si P, Zhao B. Water-based polyurethanes for sustainable advanced manufacture[J]. *The Canadian Journal of Chemical Engineering*, 2021, 99(9): 1851-1869.
7. Guo K Y, Wu Q, Mao M, et al. Water-based hybrid coatings toward mechanically flexible, superhydrophobic and flame-retardant polyurethane foam nanocomposites with high-efficiency and reliable fire alarm response[J]. *Composites Part B: Engineering*, 2020, 193: 108017.
8. Jiao C, Sun L, Shao Q, et al. Advances in waterborne acrylic resins: Synthesis principle, modification strategies, and their applications[J]. *ACS omega*, 2021, 6(4): 2443-2449.
9. Sainz M F, Souto J A, Regentova D, et al. A facile and green route to terpene derived acrylate and methacrylate monomers and simple free radical polymerisation to yield new renewable polymers and coatings[J]. *Polymer Chemistry*, 2016, 7(16): 2882-2887.
10. Karami S, Motahari S, Pishvaei M, et al. Improvement of thermal properties of pigmented acrylic resin using silica aerogel[J]. *Journal of Applied Polymer Science*, 2018, 135(1): 45640.
11. Li M, Li Y, Xue F, et al. Water-based acrylate copolymer/silica hybrids for facile preparation of robust and durable superhydrophobic coatings[J]. *Applied Surface Science*, 2018, 447: 489-499.
12. Zhong S, Li J, Cai Y, et al. Novel surfactant-free waterborne acrylic-silicone modified alkyd hybrid resin coatings containing nano-silica for the corrosion protection of carbon steel[J]. *Polymer-Plastics Technology and Materials*, 2019, 58(8): 866-878.
13. Ou J, Zhang M, Liu H, et al. Matting films prepared from waterborne acrylic/micro-SiO₂ blends[J]. *Journal of Applied Polymer Science*, 2015, 132(13).
14. Peruzzo P J, Anbinder P S, Pardini O R, et al. Waterborne polyurethane/acrylate: Comparison of hybrid and blend systems[J]. *Progress in Organic Coatings*, 2011, 72(3): 429-437.
15. Jiao C, Shao Q, Wu M, et al. 2-(3, 4-Epoxy) ethyltriethoxysilane-modified waterborne acrylic resin: preparation and property analysis[J]. *Polymer*, 2020, 190: 122196.
16. Wang Y, Wu J, Zhang D, et al. Design of salt-responsive and regenerative antibacterial polymer brushes with integrated bacterial resistance, killing, and release properties[J]. *Journal of Materials Chemistry B*, 2019, 7(38): 5762-5774.
17. Zheng B, Ge S, Wang S, et al. Effect of γ -aminopropyltriethoxysilane on the properties of cellulose acetate butyrate modified acrylic waterborne coatings[J]. *Reactive and Functional Polymers*, 2020, 154: 104657.
18. Shukla S, Rai J S P. Synthesis and characterizations of waterborne poly (acrylate) latexes[J]. *High Performance Polymers*, 2014, 26(6): 653-659.
19. Guo X, Ge S, Wang J, et al. Waterborne acrylic resin modified with glycidyl methacrylate (GMA): Formula optimization and property analysis[J]. *Polymer*, 2018, 143: 155-163.
20. Paul S. Water-borne acrylic emulsion paints[J]. *Progress in Organic Coatings*, 1977, 5(1): 79-96.
21. Zhai L, Berg M C, Cebeci F C, et al. Patterned superhydrophobic surfaces: toward a synthetic mimic of the Namib Desert beetle[J]. *Nano Letters*, 2006, 6(6): 1213-1217.

22. Mingyang Wu, Shengsong Ge, Cuiyan Jiao, Zhangyin Yan, Heyun Jiang, Yunfeng Zhu, Binbin Dong, Mengyao Dong, Zhanhu Guo. Improving electrical, mechanical, thermal and hydrophobic properties of waterborne acrylic resin-glycidyl methacrylate (GMA) by adding multi-walled carbon nanotubes[J]. *Polymer*, 2020, 200 (prepublish).
23. Li S, Li H, Wang X, et al. Super-hydrophobicity of large-area honeycomb-like aligned carbon nanotubes[J]. *The journal of physical chemistry B*, 2002, 106(36): 9274-9276.
24. Mahadik D B, Rao A V, Rao A P, et al. Effect of concentration of trimethylchlorosilane (TMCS) and hexamethyldisilazane (HMDZ) silylating agents on surface free energy of silica aerogels[J]. *Journal of colloid and interface science*, 2011, 356(1): 298-302.
25. Liu J, Huang J, Wujcik E K, et al. Hydrophobic electrospun polyimide nanofibers for self-cleaning materials[J]. *Macromolecular Materials and Engineering*, 2015, 300(3): 358-368.
26. Brostow W, Dutta M, Rusek P. Modified epoxy coatings on mild steel: tribology and surface energy[J]. *European Polymer Journal*, 2010, 46(11): 2181-2189.
27. Jia S, Zhu Y, Wang Z, et al. Influences of PP-g-MA on the surface free energy, morphologies and mechanical properties of thermoplastic polyurethane/polypropylene blends[J]. *Journal of Polymer Research*, 2015, 22(8): 1-10.
28. Chen J S, Sun Z, Guo P S, et al. Effect of ion implantation on surface energy of ultrahigh molecular weight polyethylene[J]. *Journal of applied physics*, 2003, 93(9): 5103-5108.
29. Xie Q, Xu J, Feng L, et al. Facile creation of a super-amphiphobic coating surface with bionic microstructure[J]. *Advanced materials*, 2004, 16(4): 302-305.
30. Yang X, Zhu L, Zhang Y, et al. Surface properties and self-cleaning ability of the fluorinated acrylate coatings modified with dodecafluoroheptyl methacrylate through two adding ways[J]. *Applied surface science*, 2014, 295: 44-49.
31. Shin M S, Lee Y H, Rahman M M, et al. Synthesis and properties of waterborne fluorinated polyurethane-acrylate using a solvent-/emulsifier-free method[J]. *Polymer*, 2013, 54(18): 4873-4882.
32. Xu H, Qiu F, Wang Y, et al. Preparation, mechanical properties of waterborne polyurethane and crosslinked polyurethane-acrylate composite[J]. *Journal of applied polymer science*, 2012, 124(2): 958-968.
33. Yang W, Zhu L, Chen Y, et al. Surface topography and hydrophobicity of waterborne fluorinated acrylic/silica hybrid coatings[J]. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2015, 484: 62-69.
34. Du B, Chen F, Luo R, et al. Synthesis and characterization of nano-TiO₂/SiO₂-acrylic composite resin[J]. *Advances in Materials Science and Engineering*, 2019, 2019.
35. Li L, Li X, Shen Y, et al. Hydrophobicity and corrosion resistance of waterborne fluorinated acrylate/silica nanocomposite coatings[J]. *e-Polymers*, 2021, 21(1): 779-792.
36. Meng Li, Yu Li, Fang Xue, Xinli Jing. Water-based acrylate copolymer/silica hybrids for facile preparation of robust and durable superhydrophobic coatings[J]. *Applied Surface Science*, 2018, 447.
37. Hao G, Zhu L, Yang W, et al. Investigation on the film surface and bulk properties of fluorine and silicon contained polyacrylate[J]. *Progress in Organic Coatings*, 2015, 85: 8-14.
38. Xiong P, Guan R, Lu D, et al. Characterization of acrylic copolymer latex modified by fluorine, silicon, and epoxy resin[J]. *e-Polymers*, 2008, 8(1).
39. Sbardella F, Bracciale M P, Santarelli M L, et al. Waterborne modified-silica/acrylates hybrid nanocomposites as surface protective coatings for stone monuments[J]. *Progress in Organic Coatings*, 2020, 149: 105897.
40. Ji S, Gui H, Guan G, et al. Molecular design and copolymerization to enhance the anti-corrosion performance of waterborne acrylic coatings[J]. *Progress in Organic Coatings*, 2021, 153: 106140.
41. Wang S T, Schork F J, Poehlein G W, et al. Emulsion and miniemulsion copolymerization of acrylic monomers in the presence of alkyd resin[J]. *Journal of Applied Polymer Science*, 1996, 60(12): 2069-2076.
42. Wu X Q, Schork F J, Gooch J W. Hybrid miniemulsion polymerization of acrylic/alkyd systems and characterization of the resulting polymers[J]. *Journal of Polymer Science Part A: Polymer Chemistry*, 1999, 37(22): 4159-4168.
43. Zhong S, Li J, Yi L, et al. Cross-linked waterborne alkyd hybrid resin coatings modified by fluorinated acrylate-siloxane with high waterproof and anticorrosive performance[J]. *Polymers for Advanced Technologies*, 2019, 30(2): 292-303.
44. Duan Y, Huo Y, Duan L. Preparation of acrylic resins modified with epoxy resins and their behaviors as binders of waterborne printing ink on plastic film[J]. *Colloids and surfaces a: physicochemical and engineering aspects*, 2017, 535: 225-231.
45. Liu M, Mao X, Zhu H, et al. Water and corrosion resistance of epoxy-acrylic-amine waterborne coatings: Effects of resin molecular weight, polar group and hydrophobic segment[J]. *Corrosion Science*, 2013, 75: 106-113.
46. Shen Y, Zhao C, Zhou J, et al. Application of waterborne acrylic emulsions in coated controlled release fertilizer using reacted layer technology[J]. *Chinese Journal of Chemical Engineering*, 2015, 23(1): 309-314.
47. Pi P, Chen X, Wen X, et al. Preparation and characterization of ambient-temperature self-

crosslinkable water-soluble acrylic resin for PE film ink[J]. *Journal of Coatings Technology and Research*, 2016, 13(1): 73-80.

48. Parvate S, Mahanwar P. Insights into the preparation of water-based acrylic interior decorative paint: tuning binder's properties by self-crosslinking of allyl acetoacetate-hexamethylenediamine[J]. *Progress in Organic Coatings*, 2019, 126: 142-149.