

Synthesis of self-crosslinking acrylate emulsion and self-crosslinking reaction in film formation

Jiansheng Wu, Wenjing Wang, Wei Suo

Nanjing Branch of China Coal Technology and Engineering Group Co.Ltd, Nanjing Jiangsu, 210018, China

Keywords: Self-crosslinking; Acrylate emulsion; Resistivity against water

Abstract: Self-crosslinking acrylate emulsion has been widely used because of its excellent performance and convenient use, so the research of various self-crosslinking systems has been a hot spot in this field. In this paper, the self-crosslinking acrylate microemulsion with excellent performance was prepared by semi-continuous seed emulsion polymerization with the combination of reactive emulsifier and anionic-nonionic emulsifier and potassium persulfate as thermal initiator. By analyzing and testing the basic properties of the film, the correlation between the physicochemical properties of the film and the technical parameters such as monomer ratio was explored, in order to provide technical ideas and methods for the preparation of new leather acrylic resin coating film-forming agent. The results show that in different crosslinking systems, with the increase of crosslinking degree, the water absorption at 24 days tends to be the same, and it only swells but does not dissolve. Because of the strong water absorption of protein, the water absorption of the coating film is higher than that of the uncrosslinked acrylic resin coating film. The amount of mixed emulsifier is less than 3% of the total monomer, which has good water resistance.

1. Introduction

At present, the acrylic ester emulsion on the market has large particle size, low gloss, hot viscosity and cold brittleness, which can't meet the requirements of high-grade waterborne wood paint. Therefore, it is necessary to modify the emulsion to improve its performance. In contrast, water-based coatings, with the advantage of using water as solvent, have been paid more and more attention and developed rapidly in the competition of many green coatings [1-2]. Among them, the acrylate emulsion obtained by emulsion polymerization has the advantages of good light resistance, weather resistance, transparency and high strength, and can be used in coating, wood, material protection, building and other fields.

In this paper, reactive emulsifier and anionic-nonionic emulsifier were compounded, and functional monomer containing ketocarbonyl group was introduced for modification, and acrylate microemulsion with high solid content and self-crosslinking at room temperature was prepared. The effects of emulsifier dosage, functional monomer dosage, electrolyte dosage and initiator on emulsion synthesis system were discussed.

2. Research progress of acrylic resin

At present, cationic monomers are divided into two categories, namely tertiary amines and quaternary ammonium salts, mainly dimethylaminoethyl acrylate, dimethylaminoethyl methacrylate, diallyl dimethyl ammonium chloride and methacryloyloxyethyl trimethyl ammonium chloride. However, in the early days, some scholars prepared cationic monomers through chemical reactions.

And acrylic acid and dimethylaminoethanol are two chemical raw materials with abundant sources and easy access, and the esterification reaction between them is very easy. Literature [3] Dimethylaminoethyl acrylate, a tertiary amine cationic monomer, was prepared by esterification of acrylic acid and dimethylaminoethanol. Literature [4] A new reactive surfactant, methacryloyloxyethyl cetyl dimethyl ammonium bromide, was synthesized from dimethylaminoethyl methacrylate and 1- bromohexadecane. Literature [5] Cationic styrene-acrylic

emulsion was prepared by seed emulsion polymerization with styrene, butyl acrylate, methyl methacrylate, dimethyl diallyl ammonium chloride and N-hydroxymethyl acrylamide as comonomers. Compared with ammonium persulfate (APS) and water-soluble azo initiator azodiisobutyramidine hydrochloride (AIBA), the differences of the influences of two initiators on the properties of cationic styrene-acrylic emulsion were obtained: Cationic styrene-acrylic emulsion with higher solid content, smaller average particle size and higher Zeta potential can be synthesized by AIBA. The amount of AIBA has a great influence on the performance of cationic styrene-acrylic emulsion. In this study, when the amount of AIBA is 0.3%, the performance of cationic styrene-acrylic emulsion is the best.

The properties of pure cationic acrylic resin film can hardly meet the requirements of modern industrial technology, such as yellowing resistance, poor mechanical properties and poor optical properties. Therefore, the functional modification of cationic acrylic resin has always been the research focus in this field. At present, the research on the modification of cationic acrylic resin mainly focuses on two aspects: fluorination modification and core-shell structure modification.

Literature [6-7] DFMA-DM copolymer was prepared by free radical solution copolymerization at 75°C with dodecafluoroheptyl methacrylate (DFMA) and dimethylaminoethyl methacrylate (DM) as comonomers, azobisisobutyronitrile as initiator and dioxane as solvent, and the cationic fluoroacrylate copolymer QFD was finally obtained by quaternizing the copolymer with benzyl chloride. The existence of fluorine in QFD was characterized by IR, ¹H NMR, elemental analysis, thermogravimetric analysis, differential scanning calorimetry, gel permeation chromatography and other analytical instruments. The related properties of QFD films were measured, and it was confirmed that QFD had certain surface activity in pure water.

On the basis of the above research, literature [8] prepared cationic core-shell fluoropropene emulsion by seed emulsion polymerization, discussed and optimized many main factors affecting the stability of emulsion polymerization, and obtained cationic fluoropropene emulsion with good stability and small gel amount under the optimal conditions.

3. Experimental part

3.1. Reagents and instruments

Butyl acrylate (BA), methyl methacrylate (MMA), methacrylic acid (MAA) and ammonium persulfate (APS): analytically pure; Tertiary vinyl carbonate (Veova10): industrial grade; Acetyl allyl acetate (AAA) and 1,6-hexamethylenediamine (HDA): analytically pure; Modified isomeric tridecanol ether (H-606): industrial grade; Sodium bicarbonate (NaHCO₃): analytically pure; Sodium dodecyl sulfate (SDS): analytically pure; Distilled water: homemade.

NICOLET IS10 infrared spectrometer, RGI-30A rubber tensile tester, DSC Q200 differential scanning calorimeter, 101-1 constant temperature drying oven, 500 mL Soxhlet extractor, Zeta Plus potential and laser particle size analyzer, TGA Q50 thermogravimetric analyzer, UV-2100 ultraviolet spectrophotometer.

3.2. Synthesis of self-crosslinking acrylate emulsion

3.2.1. Pre-emulsification of monomer shell

Adding a proper amount of deionized water into a three-necked flask with a stirring device, adding a certain amount of emulsifier, stirring evenly, then gradually adding the mixed monomer into the three-necked flask with stirring, and dispersing at a high speed for 15min after adding, thus obtaining the shell monomer pre-emulsion for later use.

3.2.2. Preparation of seed emulsion

Add metered deionized water, compound emulsifier and 40% APS aqueous solution into a four-necked reaction flask equipped with stirrer, thermometer and nitrogen protection device, stir, add 10% monomer pre-emulsion and heat up to 85°C. When the emulsion turns blue slightly, start dripping the remaining monomer pre-emulsion and 60% APS aqueous solution, and finish dripping

within 2 hours.

Heat preservation and stirring at 80°C for 60min, cooling to 35-40°C, adjusting the pH of emulsion system, adding 1/2 molar amount of functional monomer ADH(adipicacid dihydrazide) or HDA(hexamethylene diamine), stirring for 30min, filtering and discharging.

3.2.3. Synthesis of coating film

Uniformly coating the prepared acrylic resin emulsion on the PTFE plate, naturally drying to form a film, drying the film in an oven at 70°C to obtain a film with a thickness of about 1mm, then standing for 24 hours, and sampling the film for testing.

3.3. Testing and characterization

Cross-linking degree test: put the dried latex film into Soxhlet extractor, and heat and reflux it in ethyl acetate solvent for 24 hours. After Soxhlet extraction, the remaining crosslinked polymer was put into an oven and dried at 80°C for 72 hours. According to formula (1), calculate the cross-linking density C of latex film, and take three samples to measure once and take the average value.

$$C = \frac{m_3}{m_2} \times 100\% \quad (1)$$

Where: m_3 is the sample mass after Soxhlet extraction; m_2 is the sample mass before Soxhlet extraction.

Gel rate test: the stability of emulsion polymerization is expressed by gel rate m_c , which is obtained by weighing method. After the end of emulsion polymerization, collect the condensate from the reactor wall, the stirring paddle and the reaction mixture filtered by filter cloth, bake it in an oven to a constant amount, and calculate the coagulation rate according to formula (2):

$$m_c = \frac{W_c}{W_m} \quad (2)$$

Where: W_c is the mass of condensate; W_m is the total mass of monomer.

Water absorption rate of coating film: evenly coat the emulsion on the PTFE plate, form a film at room temperature for 24 hours, and form a film with a thickness of about 1 mm. Take about 59%, take a clean glass slide baked to a constant weight, weigh it, attach the film to the glass slide, bake it to a constant weight in a 70°C oven, cool it to room temperature, weigh it again, soak it in water for 24 hours, take it out, and then suck the water on the surface with filter paper and weigh it. The result calculation formula is as follows:

$$S = \frac{m_2 - m_1}{m_2 - m_0} \times 100\% \quad (3)$$

Where: S is the water absorption rate (%) of the coating film; m_0 is the mass of the slide (g); m_1 is the total mass (g) of the dried coating film and glass slide; m_2 is the total mass (g) of coating film and glass slide after water absorption.

4. Results and discussion

4.1. Effect of ratio on emulsion

Fixed m (BA): m (MMA) = 45: 35, the dosage of AAA is 2% of the total monomer mass, and the feeding time of AAA is 20% of monomer dropping. The influence of the mass ratio of AAA to HDA on the performance of emulsion and latex film was measured, and the results are shown in Figure 1.

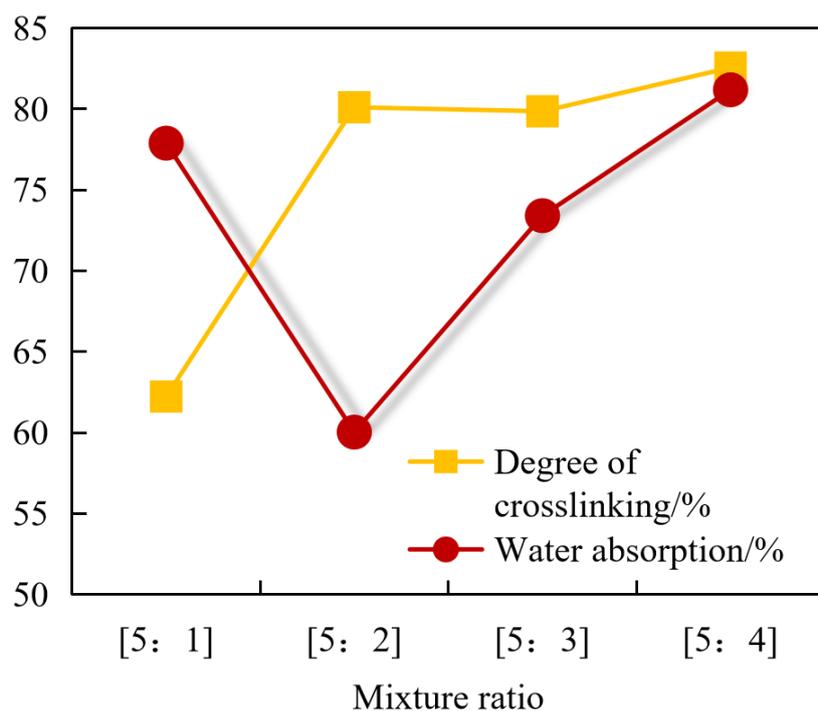


Figure 1 The influence of the ratio of latex film properties

Referring to Figure 1, when the ratio of M (AAA): M (HDA) reaches 5: 2, with the increase of HDA dosage, the crosslinking degree of latex film has no obvious change, but the water absorption rate gradually increases, which indicates that HDA has gradually exceeded. Therefore, the ratio of m (AAA): m (hda) in this system is 5: 2.

4.2. Effect of emulsifier

On the one hand, reactive emulsifier can emulsify monomer, and at the same time, it can copolymerize with monomer and graft onto copolymer molecular chain. Compared with traditional emulsifiers, reactive emulsifiers have obvious advantages in improving the stability of polymer emulsion, water resistance and adhesion of coatings.

In this study, a reactive emulsifier and an anionic-nonionic emulsifier were used in combination, and the effects of emulsifier dosage and adding methods were studied. The ratio of fixed emulsifier to non-reactive emulsifier is 2: L. The influence of the amount of mixed emulsifier on the water absorption of the film is investigated, and the results are shown in Figure 2.

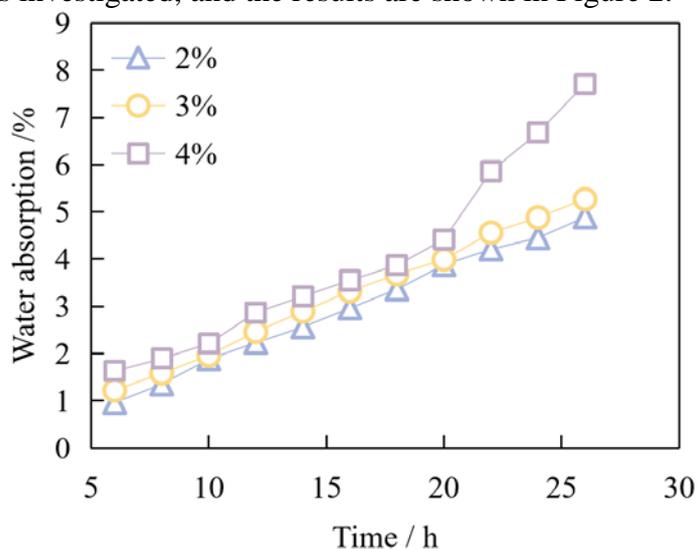


Figure 2 Effect of different dosage of emulsifying agent on water absorption of film

As can be seen from Figure 2, with the increase of emulsifier dosage, the water absorption rate of the paint film increases, which indicates that the water resistance of the paint film begins to deteriorate. It is found that the mixed emulsifier dosage is less than 3% of the total monomer and has good water resistance.

For the emulsion with a certain amount of total emulsifier. The smaller the particle size is, the greater the capillary force that causes the particles to deform, the faster the latex particles coalesce into a film, and the higher the transparency of the film. When all emulsifiers are added into the nucleus stage, a large number of fine latex particles will be produced simultaneously at the initial stage of the reaction, which will make the viscosity of emulsion increase rapidly and the probability of collision between latex particles increase. At the same time, if there is no emulsifier in the system to be added in time, the emulsifier needed for the increased surface of latex particles in the later stage of the reaction will not be supplemented, resulting in more gels.

4.3. Solvent resistance of coating film

By introducing crosslinking system into acrylic resin chain, the acrylic resin can form a crosslinked network structure, the amount of functional monomer and crosslinking agent increases, and the crosslinking degree of acrylic resin molecular chain also increases correspondingly, which will eventually lead to the enhancement of solvent resistance of its coating film. Through the solvent resistance test of the coating film, it is known that the solvent resistance of the crosslinked acrylic emulsion coating film is obviously improved, while that of the uncrosslinked coating film is extremely poor, and the coating film is almost completely dissolved after 24 hours.

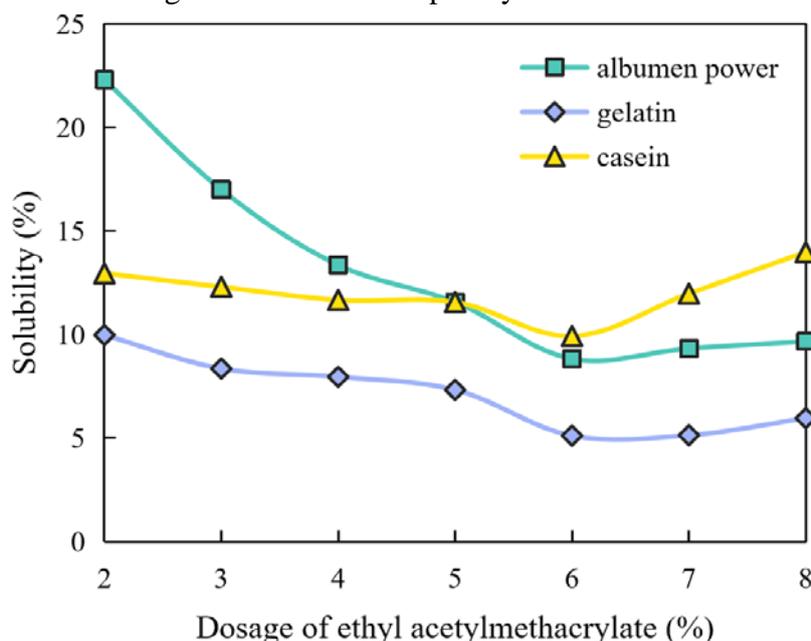


Figure 3 Effect of different crosslinking systems on solvent resistance of coating film

As can be seen from Figure 3, with the increase of crosslinking degree, the solubility of resin coating film tends to decrease, and there is no chapping phenomenon in solvent, among which gelatin crosslinked coating film has the best solvent resistance.

5. Conclusions

(1) The reactive emulsifier and anionic-nonionic emulsifier were compounded, and acrylate microemulsion with high solid content was prepared by pre-emulsification process and semi-continuous seed emulsion polymerization. It was found that the paint film with mixed emulsifier content less than 3% of the total monomer had good water resistance.

(2) Fixed $m(\text{BA}): m(\text{MMA}) = 45: 35$, the dosage of AAA is 2% of the total monomer mass, and the feeding time of AAA is 20% of monomer dropping. When $m(\text{AAA}): m(\text{HDA})$ reaches 5: 2,

with the increase of HDA dosage, the crosslinking degree of latex film has no obvious change, but the water absorption gradually increases.

(3) In the cross-linking system, with the increase of cross-linking degree, the water absorption of the coating film decreased in different degrees; However, with the increase of crosslinking degree, the water absorption rate of the coating film of crosslinking system emulsion has no obvious change, and the solvent resistance of the coating film of emulsion with different crosslinking methods finally tends to be basically the same.

Acknowledgements

Project fund: China Coal Science and technology group, technology innovation and venture capital special project "fast loading acrylic emulsion preparation"(2020-MS002)

References

- [1] Shao, T, Gong, Y, Chen, X, Chen, L.(2021). Preparation and characterization of modified self-crosslinking fluorocarbon acrylate latex. *Chemical Papers*, vol. 75, no. 3, pp. 853-862.
- [2] Rueda, J. C. , Fátima Santillán, Komber, H, Voit, B.(2020). Synthesis and characterization of stiff, self-crosslinked thermoresponsive dmaa hydrogels. *Polymers*, vol. 12, no. 6, pp. 1401.
- [3] Tung, T. T.(2020). Self-assembly and cross-linking of conducting polymers into 3d hydrogel electrodes for supercapacitor applications. *ACS Applied Energy Materials*, vol. 3, no. 1, pp. 923-932.
- [4] Gao, W, Li, C, Li, J, Zhang, Q, Qu, X.(2019). Effect of the crosslinking agent content on the emulsion polymerization process and adhesive properties of poly(n-butyl acrylate-co-methacrylic acid). *Journal of Adhesion Science and Technology*, vol. 33, no. 18, pp. 1-16.
- [5] Shao, T, Gong, Y, Chen, X, Chen, L.(2021). Preparation and properties of novel self-crosslinking long fluorocarbon acrylate (mma-ba-dfma-hpma) polymer latex with mixed surfactants. *Chemical Papers*, vol. 75, no. 10, pp. 5561-5569.
- [6] Denisa Steinerová, Andréa Kalendová, Jana Machotová, & Marcela Pejchalová. (2020). Environmentally friendly water-based self-crosslinking acrylate dispersion containing magnesium nanoparticles and their films exhibiting antimicrobial properties. *Coatings*, vol. 10, no. 4, pp. 340.
- [7] Liu, X, Zeng, W, Zhao, J, Qiu, X, Chen, D.(2020). Preparation and anti-leakage properties of hydroxyethyl cellulose-g-poly (butyl acrylate-co-vinyl acetate) emulsion. *Carbohydrate Polymers*, vol. 255, no. 3, pp. 117467.
- [8] Huang, T, Yuan, Q. X, Gong, S. L.(2020). Emulsifier-free acrylate-based emulsion prepared by reverse iodine transfer polymerization. *Polymers*, vol. 12, no. 3, pp. 730.