

Study on Cationic Acrylate Microemulsion Polymerization

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Abstract: Cationic acrylate copolymer emulsion is widely used in metal surface treatment, paper industry, sewage treatment and paint dyeing. However, its film has insufficient water resistance, acid and alkali resistance and mechanical properties, which limit the expansion of its application fields and Further applications. The phase diagram of the microemulsion has important guiding significance for selecting the appropriate polymerization system with high monomer content. This article firstly studies the phase diagram of the acrylic microemulsion. According to the characteristics of the cationic polymer emulsion, the increase The content of monomers in the microemulsion system, the polymerization mechanism and the application of the resulting microlatex were preliminarily discussed.

1. Introduction

Cationic polymer emulsion system refers to a polymer or copolymer emulsion prepared by using cationic surfactants or positively charged polymer materials. In addition to the general emulsion polymer production safety, no pollution to the environment, low system viscosity, In addition to the characteristics of easy heat transfer, high polymerization reaction rate and higher polymer molecular weight emulsion products, it also has the following characteristics: it has strong adhesion to negatively charged surfaces and can be firmly adsorbed; It can be used in acidic media and environments [1]. Therefore, the metal parts treated by the acid solution can be directly constructed or even added to the metal surface treatment solution. The earliest cationic polymer latex was the neoprene cationic latex synthesized by Davies in 1938. In the 1950s, there were patent documents reporting that the monomer containing quaternary ammonium ion groups was used to prepare cationic polymer emulsions by free radical polymerization. The emulsion prepared by this method has low solid content and slow polymerization reaction; literature [2] et al. used dodecyltrimethylammonium chloride as emulsifier to prepare cationic acrylate/styrene/butadiene latex. In this method, a cationic emulsifier is added under the condition of $\text{pH} < 7$ to make monomers without cationic groups form positively charged latex particles [3], but the surface of the latex particles obtained by this post-treatment contains a higher charge Density, so the emulsion is exceptionally stable after this treatment. At present, the conversion rate and solid content of cationic emulsion synthesis are very low, and the performance after synthesis cannot reach the expected result [4].

In this paper, vinyl monomers, cationic emulsifiers or polymer emulsifiers are used to synthesize cationic emulsions under the action of free radical initiators or cationic initiators. The ordered aggregates of surfactants have been widely used in the fields of life, medicine, energy, materials, etc., due to the ordered aggregation of surfactants [5]. Body is formed by intermolecular forces, and the formed structure is easily unstable with changes in external conditions (such as concentration, salt ionic strength, temperature, etc.). Therefore, improving the stability of ordered aggregates of surfactants has become a hot topic. If polymerizable surfactants are used to form ordered aggregates, and then their structure is fixed by polymerization, this will effectively improve the stability of the ordered aggregates [6].

2. Features of cationic polymer emulsion

Cationic polymer emulsion system refers to a polymer or copolymer emulsion prepared by using

cationic surfactants or positively charged polymer materials. It has the following characteristics: it has strong adhesion to negatively charged surfaces. It can be firmly adsorbed; because the cationic polymer emulsion is implemented by the emulsion polymerization method, it has production safety, no pollution to the environment, low viscosity of the system, easy heat transfer, high polymerization reaction rate and higher polymer molecular weight. The emulsion products [7].

The advantages of cationic acrylate polymer emulsion: light color, good transparency, no toxic gas, no pollution to the environment, safe and non-toxic; low price, rich source of raw materials, wide range of uses; acrylic coating film has good toughness, Excellent mechanical stability, film-forming properties, and hardness; it can be cured at room temperature and the curing speed is faster; the film is colorless and transparent, does not pollute stickies, and is easy to process. At present, various manufacturers choose different initiators, emulsifiers, and additives in the production of cationic acrylate emulsion polymerization, their dosages are different, and the synthesis process is different, but they all have some shortcomings, that is, they are more sensitive to temperature. It is easy to show "cold, brittle, hot and sticky", and has poor water resistance, acid and alkali resistance, easy to lose gloss, and poor low-temperature toughness. As a result, the application of cationic acrylate copolymer emulsion has been restricted [8].

3. Preparation method of cationic polymer emulsion

In order to overcome the temperature sensitivity and poor water resistance of the cationic acrylate copolymer emulsion, improve the performance of the emulsion, adapt to actual application requirements, and broaden the application range, people have carried out modification studies on the cationic acrylate copolymer emulsion, such as using physical blending, Chemical copolymerization (such as copolymerization modification with epoxy resin, copolymerization modification with styrene, modification with silicone copolymerization, modification with acrylonitrile or multiple copolymerization, etc.), and the application of new emulsion polymerization methods and polymerization processes, currently Some progress has been made. In this study, epoxy resin and organic silicon were selected as modified substances, and two polymerization processes of microemulsion polymerization and miniemulsion polymerization were used to explore the effects of the addition of modified substances, monomer ratio, and different solid content on the performance of the emulsion. Influence [9].

The epoxy and hydroxyl groups in the epoxy resin react with the active end groups in the acrylate such as amino groups and alkoxy groups to form grafted or block copolymers to solve the compatibility problem and in the cured structure Introduce a stable flexible chain to improve the mechanical properties of the emulsion. The epoxy resin chosen in this article is E-51, and its chemical structure is shown in Figure 1 [10]:

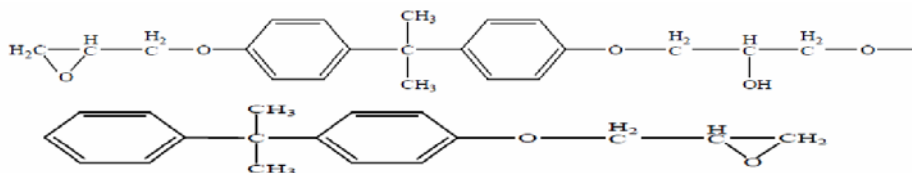


Figure 1 The chemical structure of epoxy resin E-51

After curing, the modified resin not only has the advantages of chemical stability and adhesion, but also good heat resistance, high elongation, simple curing, etc.; at the same time, the copolymerized segment methacrylate is added to reduce the degree of crosslinking during curing of the system, The introduction of side groups increases the free volume of the main chain molecule movement, thus improving the impact performance of the modified system.

4. Experimental analysis of cationic acrylate microemulsion polymerization

This article chooses butyl acrylate as the soft monomer, methyl methacrylate as the hard monomer, NMAM as the functional monomer, and epoxy resin as the modified monomer. The

mini-emulsion polymerization method is used to synthesize and stabilize the epoxy resin modified cation. Type polymer mini-emulsion, and test its corresponding performance. The effects of the addition of oil-soluble initiator (BPO), polymerization temperature, polymerization time, and curing agent addition on the performance of the emulsion were investigated; the stability, viscosity, monomer conversion, and monomer conversion of the cationic polymer mini-emulsion were discussed. The water absorption rate of the coating film, the minimum film forming temperature and the mechanical properties of the coating film.

Because there is no additional co-emulsifier in the system, and the presence of co-emulsifier often leads to phase separation during the polymerization process or acts as a chain transfer agent to affect the reaction rate, so this ternary microemulsion system is very suitable for the study of microemulsion polymerization mechanism. We use 3 different types of initiators: water-soluble anionic initiator potassium persulfate (KPs), oil-soluble initiator azobisisobutyronitrile (IABN) and cationic initiator, azobisisobutyl fat Hydrochloride (ABIA), found that the type of initiator has a great influence on the reaction. The reaction rate initiated by ABIA is the fastest and the final conversion rate is the highest (>70%), followed by BN (>50%), and the reaction rate with KPs as the initiator is the slowest and the final conversion rate is very low (<20%),

Based on the characteristics of the cationic compound emulsion, it is analyzed that the polymerization temperature has a great influence on the polymerization reaction speed of the mini-emulsion and the stability of the emulsion. The choice is not only restricted by the decomposition temperature and half-life of the initiator, but also restricted by the reactivity of the components in the system. The other experimental conditions remain unchanged, and only the effect of the polymerization temperature on the stability and performance of the emulsion polymerization is changed. The results are shown in Table 1 and Figure 2.

Table 1 The influence of reaction temperature on the performance of emulsion

Polymerization temperature/°C	Water absorption rate/%	Viscosity/s	stability/%	Minimum film forming temperature/°C
79	3.68	11.89	Stablize	18
86	2.88	12.76	Stablize	18
94	2.57	13	Stablize	18
96	3.64	13.53	Stablize	18

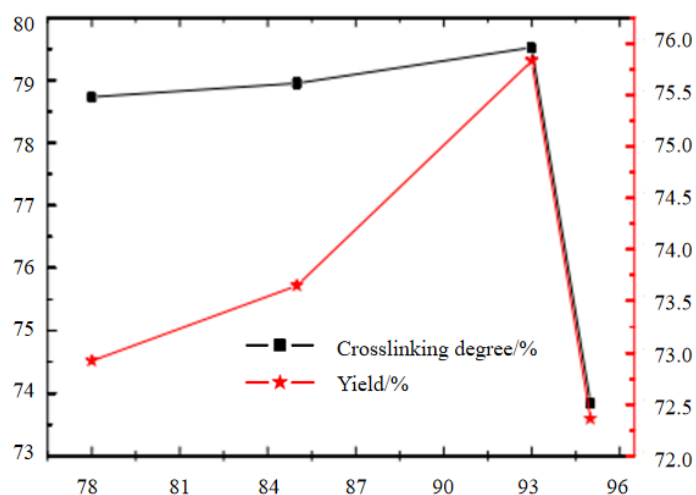


Figure 2 The effect of reaction temperature on emulsion crosslinking degree and yield

The final monomer conversion rate increases with the increase of the reaction temperature, and the water absorption rate first decreases and then increases. When the polymerization temperature is 93°C, the emulsion performance is the best. It can be seen that when the temperature is too low, the initiation time of the initiator is prolonged, and the polymerization rate of the system is reduced, so that the monomers in the system cannot be polymerized quickly, which is easy to cause the local

monomer concentration to be too large and cause explosion; when the temperature is too high, the initiator The decomposition rate is accelerated, which accelerates the collision and aggregation of the latex particles. This article found that temperature has a greater impact on the formation of microemulsion. For MA (methyl acrylate) C/TAB (hexadecyl trimethyl Australian dollar) old 20 microemulsion system, as the temperature increases, the microemulsion The area of the emulsion phase area increases significantly, and it does not change much after reaching a certain temperature (60°C). Therefore, when the microemulsion polymerization is carried out, the appropriate reaction temperature should be selected according to different systems. Add other acrylic monomers to the system such as methacrylophthaleoxyethyl trimethyl chloride (DM) C, dimethylaminohexyl methacrylate (DM) and dimethyl methacrylate The hexaalkyl Australian money (C, 6B) can also significantly increase the area of the microemulsion phase area.

Obviously, the reaction rate of the polymerization reaction is directly proportional to the monomer concentration and initiator concentration, and inversely proportional to the emulsifier concentration. This is because in the microemulsion system, the size of the monomer droplets and micelles are not much different, so the initiator can initiate the polymerization of the monomers in the droplets. When the amount of emulsifier is reduced, the number of micelles formed decreases. At the same time, the number of monomer droplets increases, the droplets increase, and the monomer content in the droplets increases, which speeds up the reaction rate. In addition, with the increase of the emulsifier concentration, the polymer growth chain has more opportunities to transfer to the emulsifier and terminate, which also reduces the overall reaction rate. In the reaction, DMC is both a comonomer and an emulsifier. Therefore, in the reaction where DMC participates, the reaction speed decreases faster with the increase of the emulsifier content. In addition, as the reaction temperature increases, the polymerization rate also increases. This is obviously because the thermal decomposition of ABIA is affected by temperature. The higher the temperature, the faster the decomposition rate of the initiator ABIA. In terms of application, we mainly studied the flocculation of the obtained microlatex, in order to explore new organic polymer flocculants.

5. Conclusions

The two polymerization processes of microemulsion polymerization and miniemulsion polymerization have achieved results in improving the properties of the emulsion, making the emulsion have excellent water resistance, stability and mechanical properties. Comparing the two processes, it is found that each process does not achieve the expected results in some properties of the emulsion. The emulsion synthesized by the microemulsion process has a lower crosslinking degree, a higher water absorption rate and a higher minimum film-forming temperature [11]; The yield and hardness of the emulsion synthesized by the emulsion process are relatively low. The research of epoxy resin and silicone modified cationic acrylate copolymer emulsion has promoted the development of epoxy resin, silicone and acrylate industries, and expanded the application scope of the three. In future development research, efforts should be made to conduct research on high yield, high hardness, low toxicity or non-toxic solvent selection, search for new formulas, improve process flow, use new technologies, and accelerate the pace of industrialization to implement green environmental protection. Production.

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