Research progress in polymerization methods of emulsion acrylic acid pressure sensitive adhesive

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Abstract. In this paper, the characteristics of pressure-sensitive adhesive, the properties of pressure-sensitive adhesive and the preparation of pressure-sensitive adhesive are introduced. The research progress of emulsion acrylic pressure-sensitive adhesive is the focus of this paper. The methods of producing this kind of pressure-sensitive adhesive and their advantages and disadvantages in recent years are summarized.

1. Introduction
Pressure-sensitive adhesives, as adhesives, do not need solvents or heat energy. They only need a little pressure to stick the things they want to stick well, and the initial and subsequent persistent stickiness are good [1-2]. Another thing is very good: it can be used repeatedly when it is not contaminated by other objects, and it usually does not destroy the surface of the adhesive after use. Over time, people have developed new products - internal cross-linking without external cross-linking. For example, pressure-sensitive adhesives formed by copolymerization of N-hydroxymethylacrylamide and glycidyl acrylate can be internally cross-linked [3]. The pressure sensitive adhesive is mainly emulsion type and solvent type.

2. Polymerization of emulsion acrylic pressure sensitive adhesive at present
At present, emulsion type polyacrylate pressure-sensitive adhesive mainly consists of traditional emulsion polymerization, seed emulsion polymerization, emulsion polymerization using reactive emulsifiers, miniemulsion polymerization, in situ emulsion polymerization and other methods [4].

2.1. Traditional emulsion polymerization
The development of traditional emulsion polymerization process has been very mature now, and its operation process is very simple, there is no special requirement or high requirement for the production equipment, and it is very beneficial to industrial production. So we can see the industrial production of the emulsion type pressure sensitive adhesive factory in the society at present, many of which are traditional emulsion polymerization [5]. In the traditional emulsion polymerization, we need to take into account the following factors: feeding mode, reaction time, temperature change, speed of agitation, initiator, buffer, dosage of emulsifier, type and proportion, monomer type and proportion, which are the key factors affecting production. In addition, traditional emulsion polymerization is the basis of other emulsion polymerization methods.
Aymonier et al. [6-7] studied the traditional emulsion polymerization method, and obtained the different ways of adding materials that affected the adhesive properties and latex particle morphology. The synthetic monomer they chose to use is MMA and its complementary monomer EHA, and there is a very important point. The molar mass ratio of the two monomers should be set at 1:1, and then several comparisons are made on the choice of the feeding mode of the emulsion. After comparison, the results show that the semi continuous constant concentration feeding method has the disadvantage of insufficient viscosity of the adhesive film. The one-time feeding method will produce serious heterogeneity, which will make the film viscous not meet the standards, and the specific performance is too viscous. The semi continuous gradient monomer feeding method has excellent both in terms of the length of the chain, the winding of the synthetic emulsion, or the heterogeneity of the latex particles.

In the study of traditional emulsion polymerization, Tang Zhonghua [8] et al only used the semi continuous one time feeding method. They examined how the amount of emulsifier, initiator and polymerization process affected the size and bonding strength of latex particles. The results show that if the dosage of emulsifier and initiator is reduced or the time of dropping is shortened, the particle size of latex particles will be enlarged in a wide range; if the speed of stirring is increased, the particle size will decrease in the early stage and then increase; if we want to improve the bonding performance of pressure sensitive adhesives, it can be achieved by reducing the amount of emulsifier and dropping time. When the amount of initiator is reduced, the shear strength will increase, but at the same time the peeling strength will decrease. In addition, the bonding performance is relatively stable. As a result, the traditional emulsion polymerization method is affected by the above conditions, so it can only produce low pressure sensitive adhesive products. And the properties of pressure-sensitive adhesives produced are very unsatisfactory in peeling strength, initial adhesion and holding force.

2.2. Seeded emulsion polymerization

Compared with the traditional emulsion polymerization, the polymerization process of seed emulsion polymerization has an advantage in the controllable and tunable properties of the prepared latex particles. Before the preparation of the emulsion, a single seed emulsion system is put into the kettle to obtain the seed emulsion, and the emulsion continues to product after [9] surface polymerization. This polymerization method has obvious advantages. This polymerization method can adjust the amount of emulsion and monomer added and how to add steps to control the number, size, diameter and diffusion range of polymer latex particles. Not only that, it can also generate the required core shell structure by controlling the different proportion of monomer.

Chen Yuanwu et al. [10] synthesized a kind of pressure sensitive adhesive in the experiment by using seed emulsion. The pressure sensitive adhesive has core shell structure. The effects of seed emulsion amount were also studied. The results show that if we increase the dosage of seed emulsion, then the reaction rate will accelerate and the particle size will also decrease. The change of viscosity will increase, the proportion of polymer mass will increase, and the initial adhesive force of pressure sensitive adhesive will also be reduced. The optimum ratio of seed emulsion to nuclear emulsion is 1: 7 [11].

After the preparation of pre emulsion by Wang Rong [12], the acrylic emulsion was obtained through a series of experiments through seed emulsion polymerization. The effects of crosslinking and chain transfer agents on the properties of pressure sensitive adhesives were also discussed. It is found that increasing the amount of chain transfer agent will reduce the surface tension of the latex while reducing the particle size. However, it is not expected that the viscosity and stability of the emulsion will not be affected by this process. In addition, the initial adhesion force and the strength of 180 degree peel will increase and the adhesion force will decrease. If the amount of crosslinking agent is increased, then the heat resistance of pressure sensitive adhesive will increase, and the holding force will also rise. The initial adhesion force and the 180 degree peel strength are different from those mentioned above. They appear to rise first and then decrease. Similarly, the viscosity of the emulsion is not affected by these changes. The effect of change on surface tension depends on the amount of use. It can be seen that when the mass fraction of chain transfer agent and cross-linking agent is selected to be 0.06% and 2%, the balance and performance of the prepared pressure sensitive adhesives reach the best.
Wang Fengying [13] also used the above seed emulsion polymerization method to produce emulsion acrylic pressure sensitive adhesive. He repeatedly studied the influence of feeding time, temperature, ratio of soft to hard monomers, amount of emulsifier and initiator, and ratio of initiator. Finally, the initial viscosity, stickiness and 180 degree peeling strength of PSA were satisfactory.

2.3. Emulsion polymerization using reactive emulsifiers.
It can be seen that the traditional emulsion polymerization and seed emulsion polymerization and the use of emulsifiers are very important, and even affect the performance of pressure sensitive adhesives. Through research, we know that this is because a lot of small molecular substances will migrate when pressure sensitive adhesives form films. This migration will directly affect the performance of pressure sensitive adhesives. The reactive emulsifier is very different from the traditional emulsifier structure, such as anion and cation, and non-ionic. It has carbon carbon double bond, and also contains hydrophilic and lipophilic groups. This structure reduces the migration of small molecules after emulsion formation. Because in the process of emulsion polymerization, this structure can copolymerized with acrylates at the same time as emulsifying monomers, so that the final polymers will not contain small molecules.

Liu Jicheng and other [14] prepared acrylic emulsion with active emulsifier, and used the emulsion as protective film. The relationship between the acrylic emulsion and the pressure sensitive adhesive was obtained through research. In the infrared spectrum, the world research shows that the surface activity of the polymer is very good. No residual carbon carbon double bond emulsion, and other tests show that proper addition of active emulsifier can help reduce the size and distribution of acrylic emulsion particle size.

Ye Yang et al. [15] studied the effect of different ratio of composite emulsifier to sodium dodecyl sulfate on the properties of pressure sensitive adhesives. Emulsion polymerization process. The results show that the adhesive strength of PSA increases and then decreases with the increase of the amount of active emulsifier. The initial adhesive force decreases gradually and the water absorption decreases. The peeling strength, adhesion and adhesion decreased at the early stage with the increasing amount of reactive emulsifier free radicals after aging at 60 C for 7 days. It can be seen that the aging resistance of the emulsion pressure sensitive adhesive can be improved. The specific method is to use the polymerizable emulsifier of sodium isoxy propyl sulfonate.

Huang Hongzhi et al. [16] also investigated the reactive emulsifier, and obtained that the highest conversion of monomer was the reactive emulsifier system (98) . The solid content was the highest (49.3%) and the viscosity of the system was moderate (27%). 6 MPa/ seconds), with the best freeze-thaw and storage stability. Gelation is not produced in polymerization process, but gel is produced in other systems. At the same time, the pressure-sensitive adhesives prepared by active emulsifiers also have very good properties. In addition, it is also found that the particle size of the polymer obtained from the experiment of reactive emulsifier is the largest (333 nm). Later studies also found that this is the main reason for the highest solid content and the most appropriate viscosity of the system.

2.4. Miniemulsion polymerization
The development of ultrasonic equipment has made emulsion polymerization a new method - miniemulsion polymerization. There are two stages of, which are fine emulsification and polymerization. In this way, the monomer droplet is treated into sub micron structure. In the process of polymerization, the free radicals will not be transferred to the micelle through the water phase. This process makes the collision between the radicals and the monomer become very easy, and the termination rate of the chain decreases, and the polymer emulsion obtained has very good performance.

Compared with traditional emulsion polymerization, miniemulsion polymerization is more excellent in reaction speed, molecular weight and heat release and viscosity. At the same time, the advantage of microemulsion polymerization is obvious in the preparation of composite emulsion. Microemulsion polymerization can avoid system separation and improve the properties of composites. Therefore, in recent years, this method has also been used in the preparation of polyacrylate pressure sensitive
adhesives. The polyacrylate pressure sensitive adhesives prepared by this method can not only mix other materials very well, but also change the transparency and adhesion of the system very greatly.

Amaia et al. [17] prepared the crystal part of the semi crystal pressure sensitive adhesive by in situ emulsion polymerization. The monomer used was linear eighteen alkyl acrylate. By this method, the water-based pressure sensitive adhesives have high temperature sensitivity and high shear strength in the melting temperature range of crystals. Both polyurethane graft polyacrylate emulsion synthesized by microemulsion polymerization or polyurethane modified polyacrylate emulsion can be used as pressure sensitive adhesive.

2.5. In situ emulsion polymerization

In order to improve the adhesion of emulsion polyacrylate pressure sensitive adhesive, it can be modified by adding inorganic nanoparticles. This is because when inorganic nanoparticles are added, the film of the binder can be realized well in terms of toughness, strength and cohesion. Even the adhesion between the material used and the body of the binder, as well as between the colloid itself and the desired binder, can be strengthened. After that, the fluidity and variability of the original liquid will also be obtained. Improvement. After the application of inorganic nanoparticles in situ emulsion polymerization, the emulsion polyacrylate pressure sensitive adhesive has excellent performance and can still achieve uniform distribution.

Liu Guojun et al. [18] used this method. They first pre-emulsified it. The specific operation was to add monomer water emulsifier and so on to the reaction. When the emulsifier is added to the reactor, the emulsifier is added in the process, and then the heat preservation is carried out after the reaction reaches a certain temperature. Then the remaining pre-emulsifier and initiator are added in the reactor. After a period of time, the pressure-sensitive adhesive prepared has higher performance. It was found that SiO$_2$ reacted with polyacrylate after being dispersed to nanometer scale. Then they tried to add nano SiO$_2$ continuously, and the viscosity of the emulsion decreased. The initial viscosity of the pressure-sensitive adhesive also decreased. On the contrary, the peel strength changed first and then decreased. After a long period of preservation, the performance stability of the composite emulsion is still excellent.

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