Paper B30

The Effect of Ambient Temperature Crosslinking Systems on Performance of Acrylic Emulsion Film for Leather

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Abstract

The ambient temperature self-crosslinked acrylic emulsion was synthesized by semi-continuous seed emulsion polymerization method through the introduction of functional monomers (DAAM, AAEM, and GMA) into the acrylic resin molecular chain and the addition of crosslinking agents(ADH or HAD). Then the influence of the three self-crosslinked systems (DAAM-ADH, AAEM-HDA, GMA-HAD) on the basic performance of the acrylic resin emulsion films was examined by Tg, tensile strength, elongation at break and anti-swelling rate as indicators. The result showed that: the performance of emulsion film was significantly enhanced in the preparation of acrylic resin emulsion by adding the cross-linking functional monomers to produce an appropriate crosslinking among the acrylic resins. It was also a good reference on the preparation of acrylic resin leather coating agents.

1. Introduction

With the gradual awareness of environmental protection and energy conservation ,countries around the world have begun to formulate related laws and regulations to restrict the emission of volatile organic compounds (VOC)[1~2]of finishing products Since 1990s. As a low VOC finishing paint, the water-based finishing agent is an important direction of the development of environmentally friendly coatings, among which the water-based acrylic resin coating agent is very popular for its excellent gloss, fullness and weatherability. But at this stage, the large-scale application of water-based acrylic resin coating agent is limited for its film's defect of cold crisp and hot sticky property.

In this experiment which was based on the principle of molecular design method, the ambient temperature self-crosslinked acrylic resin emulsio was prepared through the introduction of a certain amount of special functional monomers into the acrylic resin molecular chain and the addition of an appropriate amount of crosslinking agent by seed emulsion polymerization. The product was able to obviously improve the acrylic resin emulsion film's performance defects of cold crisp and hot sticky, and this technology idea was a good reference on the preparation of acrylic resin leather coating agent[3~4].

2. Materials and method

Emulsion Polymerization

The measured amount of deionized water and compound emulsifier of AES, OS-15 were added into the three-mouth pre-emulsification mixing bottle equipped with stirrer to be stirred till the mixture were dissolved, Then the measured methacrylate, butyl acrylate, methacrylic

acid and functional monomer (DAAM, AAEM or GMA) were gradually dropped in at room temperature, and the monomer pre-emulsion could be obtained after pre-emulsification for 30 min.

The measurement of deionized water compound emulsifier and APS (30%) solution were added into a four-mouth pre-emulsification mixing bottle equipped with stirrer, thermometer, nitrogen protection, stirred till the mixture were dissolved, heated to 80□, gradually dropped with some monomer pre-emulsion (10%) till the emulsion began to grow blue, then dropped with the left monomer pre-emulsion and APS(70%)solution in 2 hours. Finally, the mixture was stirred at 80□ for 1 hour, Cooled to 35 □~40 □, dropped with half of the functional monomers (DAAM, AAEM or GMA) after adjusting pH emulsion system, stirred for 30 minutes, then the product could be obtained after filtering.

Preparation of film[5]

The product of acrylic resin emulsion was coated in a Teflon plate, so that the film could be dried naturally at 80□ and peeled off for test.

Film Performance Test[6]

Water absorption

The prepared film was cut, weighed and soaked in water for 24h, then be taken out and dried the surface water with filter paper and weighed. The formula is as follows:

$$X = \frac{m - m_0}{m}$$

X ——the water absorption of film (%)

m_0—— the quality of film (g)

m ——the quality of wicked film (g)

Anti-swelling

Determined by QB / T 2223-96.

Hardness

Tested by GB / T 6739-1996.

DSC analysis

The glass transition temperature of dried latex film was determined by DSC, nitrogen protection, nitrogen flow (20mL/min), temperature range (-30~150□), heating rate (30 □/min).

Mechanical Properties

In accordance with the QB/T 2223—1996, the elongation at break and the tensile strength of the film were determined by AI3000 universal testing machine.

3. Results and discussion

Mechanism of cross-linking system

In the experiment, the three cross-linked systems (DAAM-ADH, AAEM-HDA, GMA-HAD) were selected as compared trials. For the DAAM-ADH cross-linking system, the emulsion pH was adjusted to a weak alkaline condition, which could stably save the emulsion because the crosslinked reaction was strongly suppressed in a weak alkaline condition [7], the crosslinked reaction would be gradually completed with the decrease of system pH in the formation process of emulsion film. For the AAEM-HDA and GMA-HDA cross-linking systems, the activity of the crosslinked reaction between HDA and functional monomer was inhibited by adding volatile amino acid in the emulsion to protect the Amino of HAD[8], and the acids evaporated gradually, the reactive of amino was recovered, then the crosslinking reaction occurred with the functional monomer in the filming process[9]. Figure 1 shows the reaction ways of the three crosslinking systems.

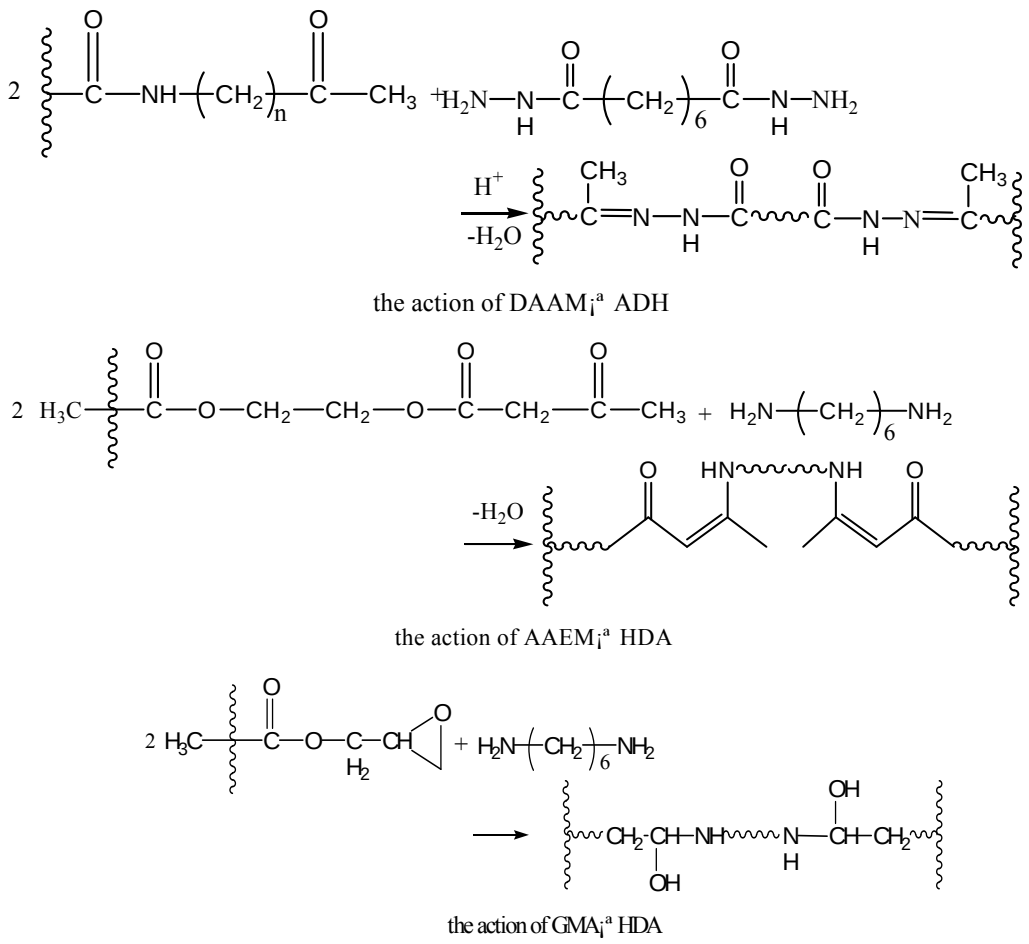


Fig 1 3 kinds of crosslinking system actions

Influence of the cross-linked degree of different systems on the water absorption and anti-swelling of the film

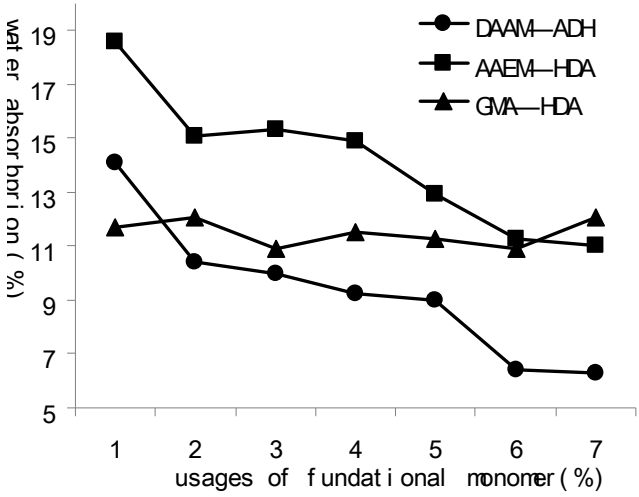


Fig 2 The effect of cross linker content on the the water absorption of acrylate emulsion film

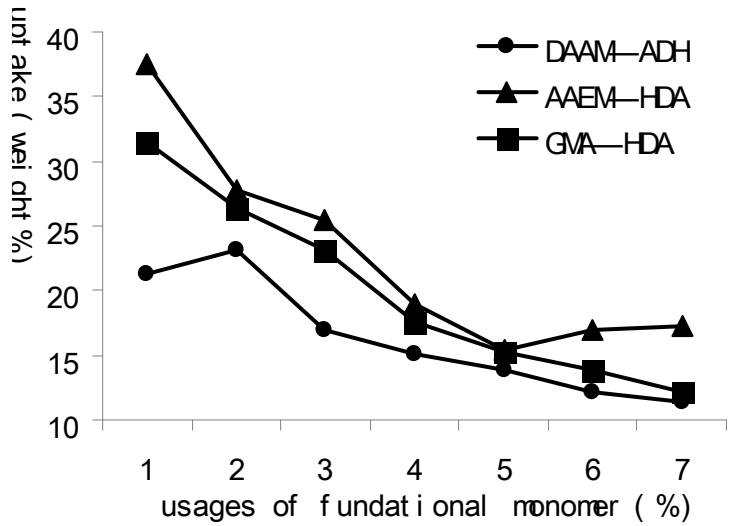


Fig 3 The effect of cross linker content on swelling ratio of acrylate emulsion film

The acrylic resin was able to form a network structure by the introduction of functional monomers and crosslinking agents, and with the increased amount of functional monomers and crosslinking agents, the crosslinking of acrylic resin molecular chains increased, which would eventually lead to changes in film properties. In this experiment, the water absorption of emulsion film without crosslinking agent was Measured by 44%. In Figure 2, the experimental result shows that the water absorptions of acrylic resin emulsion films by introduction of DAAM-ADH, AAEM-HDA and GMA-HDA crosslinked systems were lower than the ones without crosslinked system, the water absorption of film emulsion with the increased amount of functional monomers (monomer mass fraction as a percentage), the water absorption of latex films of the DAAM-ADH and AAEM-HDA crosslinked systems showed an obviously downward trend. This might be because the cohesion of polymer was increased by the establishment and expansion of latex particles' nuclear interior in the network structure, which showed a decline in water absorption; but for the emulsion by introduction of GMA-HDA

crosslinked system, the water absorption was almost immune to the amount of functional monomer.

We can learn from anti-swelling test of the film, the swelling rate of acrylic resin emulsion film without crosslinked systems was 52%. And the film's swelling ratio was significantly reduced by the introduction of the three crosslinked systems into the acrylic resin emulsion, showing that the crosslinked density of the crosslinked copolymer increased with the increase of crosslinking agent's content, and the swelling ratio decreased with the increased crosslinked degree, the swelling ratio of DAAM-ADH system was the lowest one, but the latex film's swelling ratio of the three crosslinked routines would almost in accordance with each other untimately.

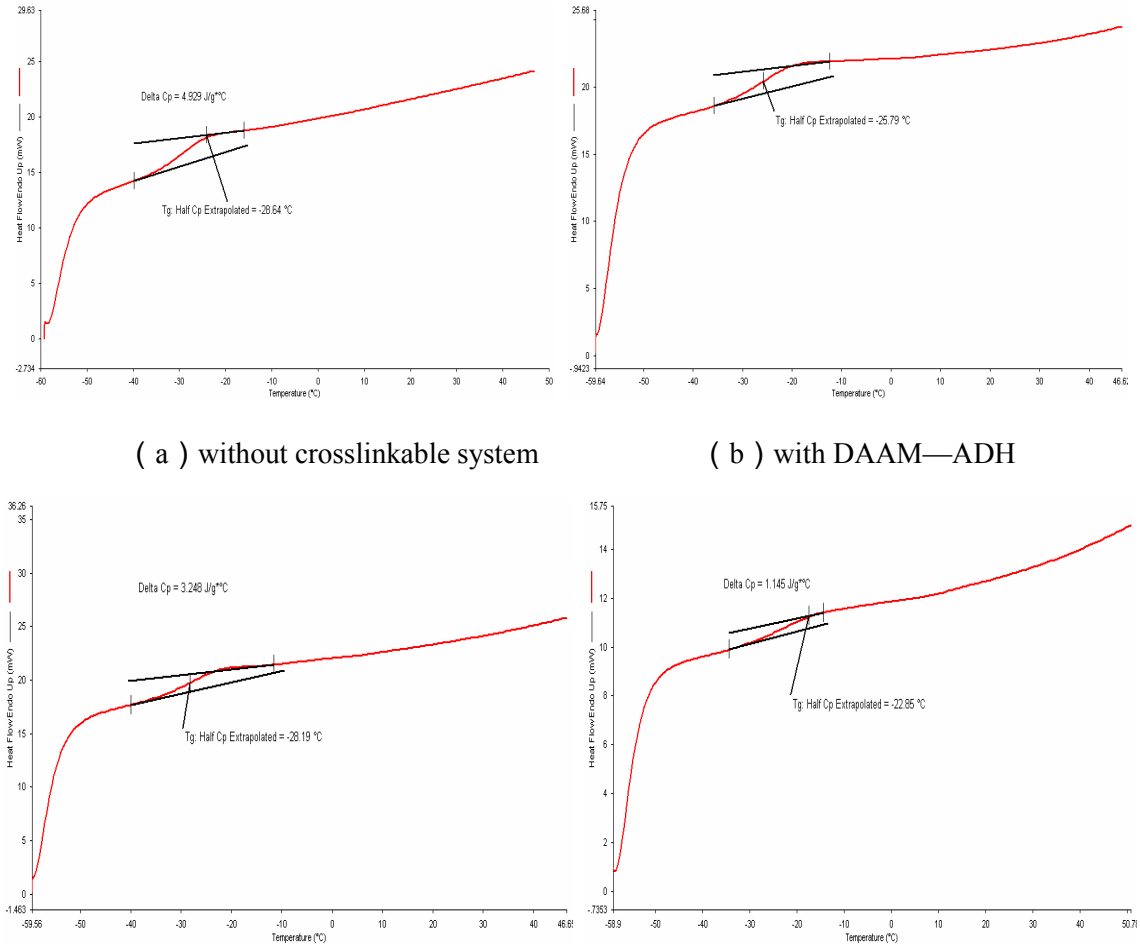
Different crosslinked systems on the film hardness

Table 1 The effect of cross linker on the hardness of acrylate emulsion film

Usage of functional monomer (%)	Without crosslinking	Crosslinking systems		
		DAAM/ADH	AAEM/HDA	GMA/HDA
1	2B	B	HB	B
2	2B	B	HB	B
3	2B	HB	HB	B
4	2B	H	HB	HB
5	2B	H	HB	HB
6	2B	H	HB	HB
7	2B	H	HB	H
8	2B	H	HB	H

Table 1 shows: compared to the one without crosslinked systems, the hardness of acrylic resin emulsion film was improved with the introduction of crosslinked systems. In the three crosslinked systems, the emulsion film had good hardness when the amount of DAAM was above 4%, and wouldn't increase, while the film hardness increased slowly and the film had a sufficient flexibility and hardness with the increase amount of GMA. However, the film hardness was the same and the film was still soft when the amount of AAEM changed.

Influence of different crosslinked systems on the film's Tg



(a) without crosslinkable system (b) with DAAM—ADH

(c) with AAEM—HDA (d) with GMA—HAD

Fig 4 The effect of cross linker on the Tg of acrylate emulsion film

Table 2 The effect of usage of DAAM—ADH on the Tg of acrylate emulsion film

Usage of Functional momoner (%)	0	1	2	3	4	5	6	8
Tg (□)	-29.86	-29.20	-28.64	-28.56	-25.79	-24.65	-23.35	-22.85

In figure 4, The effects of the three crosslinked systems on the thermodynamic properties of latex film was examined. The DSC curves in figure 4 showed: among the films of the three crosslinked systems, the DSC curves of emulsion films of AAEM-HDA (c) crosslinked system and non-crosslinked system (a) were almost the same. And it showed a marked change on the thermal analysis curve, Tg was all around -28 □, while the film's Tg of DAAM-ADH and GMA-HDA crosslinked systems were significantly higher than the one without crosslinked

system, the film Tg =- 25.79 □ by the introduction of DAAM-ADH (b), the film Tg =- 22.86 □ by the introduction of GMA-HDA (d). The reason is: the molecular motion is limited with the increase of the crosslinked degree, which result in the increase of glass transition temperature. And the influence degree varies for the different structures of crosslinked systems

Table 2 showed: the influence of the different amount of DAAM-ADH systems on the film Tg increased slowly at the beginning with the increase amount of crosslinked system, Tg changed abruptly when the amount reached at 4%, and rised slowly later.

The influence of different crosslinked systems and usage on the mechanical properties[10]

Figure 5 showed: compared to latex film without cross-linking system, the tensile strength of acrylic resin emulsion film was improved due to the introduction of crosslinked systems the formation of crosslinked structures, the impact of DAAM-ADH system on the film's tensile strength was the greatest one and fastest increased one among the three crosslinked systems.

Figure 6 showed: compared to the film without crosslinked systems, the elongation at break of the film with the three crosslinked systems decreased, and the DAAM-ADH system showed the largest decline, AAEM-HAD system showed the slowest decline.

In a word, for the three films with the crosslinked systems, the elongation at break declined and strength at break increased, The film showed obviously hard and strong features by introduction of DAAM-ADH system, relatively speaking, the AAEM-HAD and GMA-HAD systems showed strong and tough performance.

4. Conclusion

(1) In this experiment, it was based on the principle of molecular design method, the self-crosslinked acrylic resin emulsion at room temperature was prepared through the introduction of DAAM, AAEM, and GMA monomers into the acrylic resin molecular chain and the addition of an appropriate amount of related crosslinking agent by seed emulsion polymerization. Meanwhile, the change of system pH in the filming process controlled the occurrence of self-crosslinked reaction.
(2) The film's water absorption and swelling ratio declined in varied degrees in DAAM-ADH, AAEM-HDA and GMA-HDA crosslinked systems with the increase of crosslinked degree, The water absorption of the cross-linking system GMA-HDA emulsion film changed little with the increased crosslinked degree but the latex film's swelling ratio of the three crosslinked routines would almost in accordance with each other untimately.
(3) The elongation at break of the emulsion film declined, the tensile strength increased and the hardness also increased with the introduction of acrylic resin into the three crosslinked systems, and this trend was even more obvious while the crosslinked degree increased, but the cross-linking degree had little impact on the emulsion film hardness of the AAEM -HDA crosslinked system.
(4) The acrylic resin film processed a proper crosslinked by the introduction of crosslinked systems to improve the film's Tg, to increase the intensity of emulsion film, meanwhile, to guarantee a low temperature while forming emulsion films, which could solve the performance defects of hot sticky and cold crisp occurred in conventional acrylic resin.

5. References

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6. Acknowledgements

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