

Synthesis and Application of Cationic Polyacrylate Emulsion with Core—Shell Structure**

*Xin Zhao *, Zhihui Sui, Xumei Song*

School of Light Industry and Textile Engineering, Qiqihar University, Qiqihar 161006, P.R. China

Abstract: A type of cationic polyacrylate emulsion was prepared by means of seeding polymerization. The emulsion copolymerization was carried out with the core monomers of butyl acrylate (BA) and methyl methacrylate (MMA), the shell monomers of BA, MMA and home-made cationic monomer and the initiator of potassium persulphate. The structure of cationic polyacrylate emulsion was characterized. No “C=C” was detected in the structure of cationic polyacrylate emulsion by FT-IR and ¹H-NMR, indicating that the polymerization reaction was complete. DSC spectrum showed that there were two glass transition temperatures in the structure of cationic polymer. The core-shell structure of cationic polymer was confirmed by TEM. Many improvements emerged when it was used as leather finishing agent. The resultant leathers have more uniform grain and better hand feeling. The mechanical action resistance and waterproofing quality of the coating were also increased.

Key words: cationic polyacrylate; core—shell emulsion; leather finishing agent; emulsion polymerization; application properties

1 Introduction

Among various leather finishing materials, acrylic resin finishing agents are popular in leather industry thanks to its good film-forming performance, good adherence, simple production process and low production cost, it takes a large market share in both product kinds and yields, and has a bright market prospect and application prospect. However its disadvantage of becoming sticky at high temperatures and brittle at low temperatures and bad solvent resistance hinder the further popularization of traditional acrylate emulsion film. In order to help acrylic resin finishing agents get over these disadvantages, researchers have tried to modify it by various methods. At present, there are mainly two kinds of modification methods: first, to modify acrylic resin finishing agents with high-molecular materials, for example organic silicon, organic fluoride, polyurethane, nano materials, casein, and cellulose derivatives etc.; second, to improve acrylic resin's performances through new polymerization methods, for example core-shell emulsion polymerization, simultaneous interpenetrating polymerization, micro emulsion copolymerization, and soap-free emulsion polymerization technologies etc..

In recent years, thanks to their special molecular structure, cationic acrylic polymers have played a unique role in leather and some other industries [1-2]. Cationic acrylic polymers are polymers or copolymers made from cationic surfactants or acrylic monomers with positive charge, their basic characteristic is having positive charge on their surface or on themselves. With positive charge, cationic polymers can not only neutralize negative charge, adsorb and collect objects with negative charge on surfaces, but also can control bacteria, resist dust and static, so they have been widely used as surface conditioning agents for super absorbent resins, silk fabrics and paper, antistatic agents for polymer materials, coagulants for sewage treatment, a kind of necessary and effective additive in a solid free solid oil drilling fluid system, and a kind of electrodeposition coating etc[3]. In leather industry, besides a kind of special retanning agent and a kind of new finishing agent, cationic acrylic resin has also been widely

** Supported by the Major Scientific Research Fund of Heilongjiang Provincial Education Department, China (Grant No.1151gzd22)

* Corresponding author. Phone: +86-(0)452-2738152. E-mail: zhaox2738@sina.com

used as a sewage treatment agent. Therefore, the preparation and application of cationic acrylic resins are also hot topics in the research of acrylic resin polymers^[4-10].

This paper describes the preparation of cationic polyacrylate emulsion and its use as a leather finishing agent, and discusses its structure and application properties.

2 Experimental

2.1 Materials

Butyl acrylate (BA): C.P., produced by Suzhou No. 2 Chemical Factory; methyl methacrylate (MMA): A.R., produced by Kepu Chemical Reagent Co. Ltd., Tianjin High-Tech Developmental Zone; quaternary ammonium salt based on acrylic ester (cationic monomer): self-prepared; cetyl trimethyl ammonium bromide: C.P., produced by Tianjin Tiantai Fine Chemical Co., Ltd; nonyl phenol polyethenoxy ether (as the emulsifier): technical grade, produced by Reagents Factory of Qiqihar University; potassium persulphate: A.R., produced by Beijing Chemical Reagent Factory.

2.2 Instruments

JB-90 electric mixer: Shanghai Specimen Model Factory; 101-3 cabinet dryer: Shanghai Experimental Instrument Factory; HH.S precision thermostat water bath: Jintan City Medical Instrument Plant in Jiangsu Province; Spectrum-one infra-red spectrometer: made in America; Avance 400 nuclear magnetic resonance spectrometer: made in America; JEM-100 CXII transmission electron microscope: made in Japan; Dia-mond DSC differential scanning calorimeter: made by PerkinElmer corporation; PBQ81-100 leather break-up strength tester: Yuyao County testing machine plant in Zhejiang Province; GJ9E1 colour rubbing fastness tester: Yuyao Light Industry Machinery Factory in Zhejiang Province; flexing endurance tester for leather: made by BALLY corporation.

2.3 Methods of Preparation

Preparation of cationic polyacrylate emulsion is exerted in two steps.

Step 1: preparation of aqueous solutions of core monomer, shell monomer, and initiator, respectively

Aqueous solutions of core monomer A (20g BA/5g MMA), shell monomer B (6.5g BA/13.5g MMA), and initiator C (0.25g potassium persulphate/40mL distilled water) were respectively filled in 3 tap funnels.

Step 2: preparation of cationic polyacrylate emulsion

Mixed 3g A, a small amount of emulsifier and 90mL distilled water in a 500mL 3-neck flask with stirring device, heated the solution up to 50°C following by addition of 20mL C, and when the solution was warmed to 80°C, added the rest A dropwisely in 1hr, while added 4mL C every 0.5h also, and then kept the mixture at this temperature for 1h; added 4mL C and drops of B within 1hr, while added 4mL C every 0.5h also, and then kept the mixture at this temperature for 1h before cooling down to 50°C, finally, adjusted to pH 6-7 and filtered to discharge the product.

2.4 Infrared Characterization of the Product

Put the compound synthesized into reduced pressure distillation, wash it with anhydrous ether, after distilling off the ether put the compound into vacuum distillation, you will get a white crystal. After drying the crystal in vacuum, make it into KBr discs, and measure the synthesis product's infrared spectrum using the Spectrum-one infrared spectrometer.

2.5 Nuclear Magnetic Resonance Spectroscopy of the Product

Measure the product's nuclear magnetic resonance spectroscopy on a Avance 400 nuclear magnetic resonance spectrometer.

2.6 TEM Observation

Put 2-3 drops of emulsion of the product into 10 mL distilled water, mix them well, put 1 drop of the mixture on a copper gauze covered with a formvar membrane, put the copper gauze into a petri dish after it is dried and drop 1-2 drops of 1% phosphotungstic acid solution on it, after being colored by phosphotungstic acid whose mass fraction is 2%, store it for 12 hours, and finally measure the product using a JEM-100 CXII transmission electron microscope after it is dried.

2.7 DSC Method

After drying it under a reduced pressure at room temperature, measure the product's T_g on a Diamond DSC differential scanning calorimeter. The measurement temperature range is -50 — 300 °C, and the heating-up speed is 20 °C/min.

2.8 Finishing Application Experiment

Held an experiment on application of the product as a finishing agent for sheep skin garment leather according to literature [11].

3 Results and discussion

3.1 Analysis on IR of the Product

The infra-red spectrogram of the product is shown in Figure 1.

Peak at 3400cm^{-1} is attributed to the stretching vibration of $-\text{CONH}_2$. Peaks at 2958cm^{-1} and 2874cm^{-1} are attributed to the stretching vibration of $-\text{CH}_3$ and $-\text{CH}_2$, respectively; the stretching vibration of carbonyl $\text{C}=\text{O}$ appears as the peak at 1734cm^{-1} ; peaks at 1448cm^{-1} and 1380cm^{-1} are interpreted as the bending vibration of $-\text{CH}_3$ and $-\text{CH}_2$, respectively; peaks at 1164cm^{-1} and 1240cm^{-1} come from the stretching vibration of $\text{C}-\text{O}$ in the ester group; the peak at 955cm^{-1} is characterized as quaternary ammonium salt. The characteristic absorption peaks from all 3 monomer units in the structure of the product are therefore identified. No absorption at 1650cm^{-1} indicates the absence of $\text{C}=\text{C}$ in the product, i.e., the absence of unreacted monomers, which confirms the polymerization of monomers.

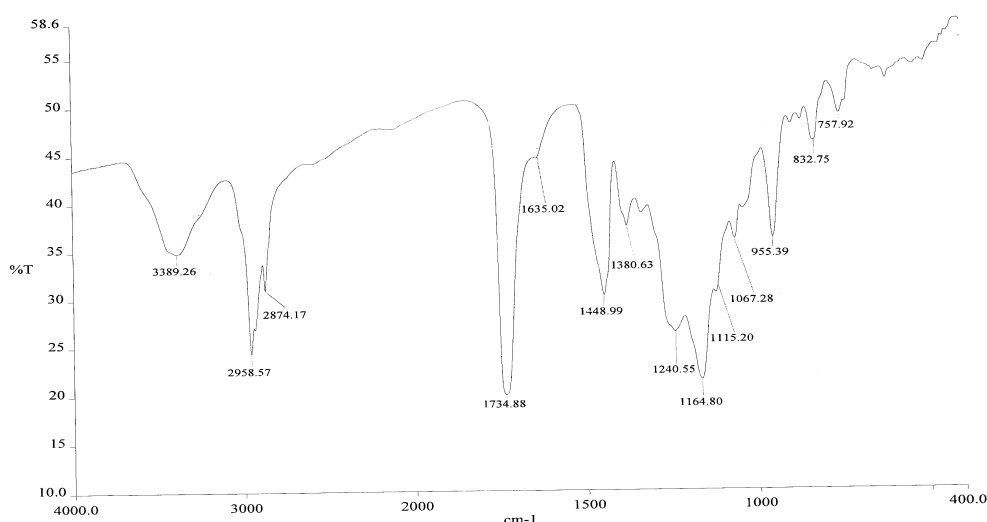


Fig. 1 IR spectrum of the cationic emulsion polymer

3.2 Analysis on Nuclear Magnetic Resonance Spectroscopy of the Product

Figure 2 shows the nuclear magnetic resonance spectroscopy of the product.

In Figure 2, absorption peaks around 0.9ppm—1.0ppm is of methyl on $\text{C}_7\text{H}_{12}\text{O}_2$, methyl on methylester end groups of $\text{C}_5\text{H}_8\text{O}_2$, and substituent methyl; absorption peak around 1.3ppm is of

methylene adjacent to methyl on $C_7H_{12}O_2$; absorption peak around 1.6ppm is of methylene which is one-methylene parting from methyl on $C_7H_{12}O_2$; absorption peak around 3.6ppm is of methylene connected to O on $C_5H_8O_2$, methyl on $C_7H_{12}O_2$ and 3 methyl connected to N on cationic monomers; absorption peak around 4.0ppm is of methylene connected to O on $C_7H_{12}O_2$ and methylene on cationic monomers.

3.3 TEM Analysis

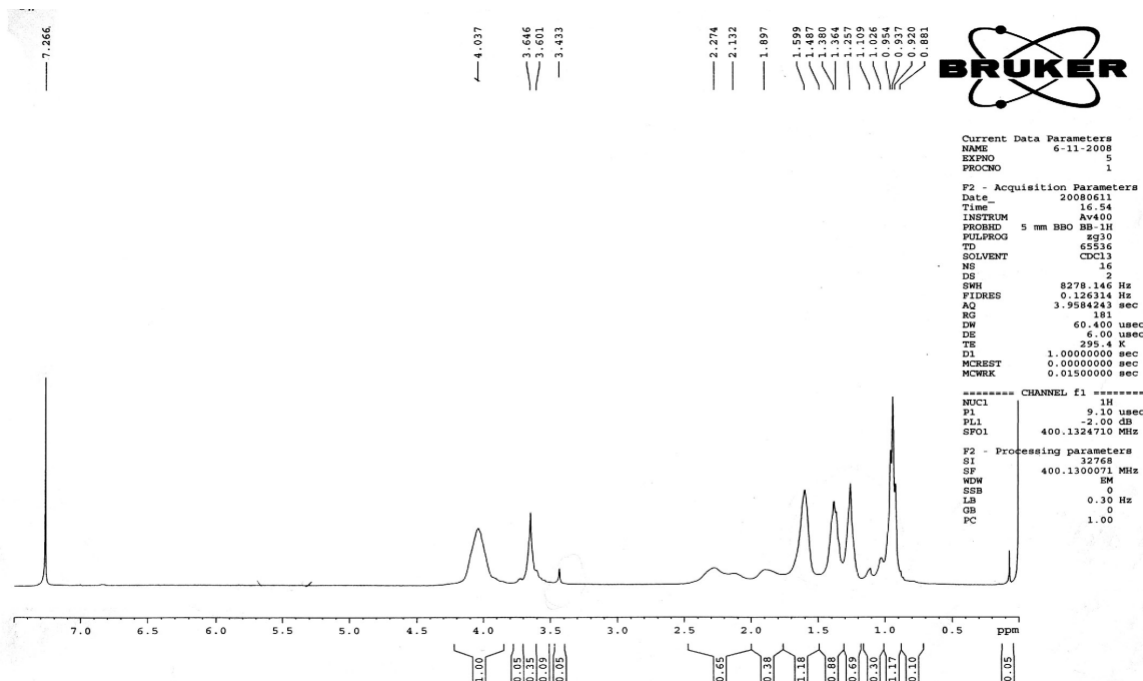


Fig. 2 NMR spectrum of the cationic emulsion polymer

The product's TEM picture is given in Figure 3.

From Figure 3, we can clearly see the core-shell structure of cationic polyacrylate emulsion, this strongly supports the differential thermal analysis' conclusion that the product is a substance of core-shell structure.

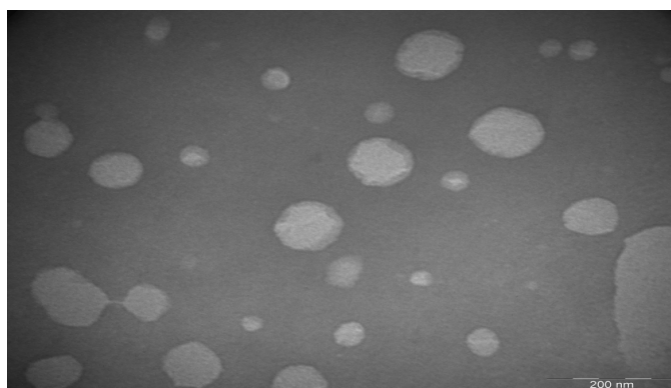


Fig. 3 TEM of the cationic emulsion polymer (×30000)

3.4 DSC Analysis

Figure 4 is the diagram of DSC analysis of the product.

After analyzing peaks in Figure 4, we can clearly see that rather than one T_g which is not limited in a special scope, the product has two T_g , and T_g spans are large. So it can be concluded that the product is a

substance of core-shell structure. No matter in lower or higher temperature condition, the product shows good stability, that is to say modified acrylic resin can overcome the disadvantage of becoming sticky at high temperatures and brittle at low temperatures.

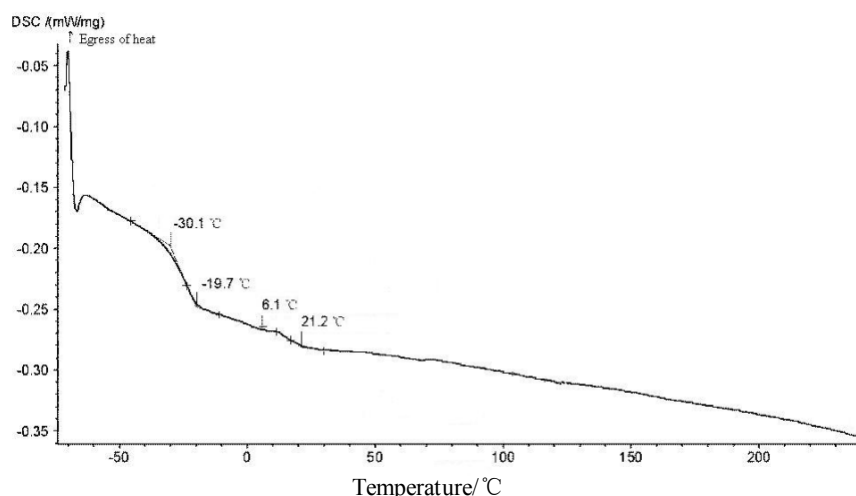


Fig. 4 DSC of the cationic emulsion polymer

3.5 Application Results of Finishing Agent

In application experiment, the product is used as a kind of cationic finishing agent, to treat sheep skin garment leather. The technique process is shown as follows:

bottom coating → middle-layer coating → top coating

Bottom coat recipe: pigment paste: cationic finish: water = 100:150:100 and some other substances.

Middle-layer coat recipe: pigment paste: cationic finish: water = 100:200:200 and some other substances.

Lustre-coating recipe: cationic finish: water = 100:100 and some other substances.

Operation: Coat the bottom layer twice and dry it at 50~60°C; coat the middle layer twice and dry it at 50~60°C; and spray lustre-coating on top layer twice and dry it at 50~60°C.

After being treated by the cationic finishing agent, the leather became soft, its grain side became very clear, luster became bright, hand feeling became comfort, and flexure resistance was improved, its coats are tenaciously clinging, water repellent and mildew resistant for long term, and these coats' fastness to wet/dry rubbing can reach a 4.5 or higher grade.

4 Conclusions

(1) The product's infrared spectrum and nuclear magnetic resonance performance have proved that the preparation of quaternary ammonium salt based cationic polyacrylate through polymerization of core-shell emulsion was successful.

(2) The DSC analysis shows that rather than having one T_g the product has two T_g , and they are not limited in a special scope, and the T_g spans are large; the TEM analysis proves that the cationic polymer is a substance of core-shell structure.

(3) Results of above application experiment on the cationic polyacrylate emulsion are ideal: with good stability, excellent dry/wet rubbing resistance and water repellence, the emulsion has improved the leather's luster, hand feeling, softness and mechanical strength.

References

- [1] C. Y. Liu; Z. J. Li; T. Y. Zhang. West Leather, 2008, (12): 8-10.
- [2] J. Wei; L. N. Wang; G. Q. Li. Fine and Specialty Chemicals, 2006, 14(19): 8-9.
- [3] X. H. Qiang; L. L. Liu; F. C. Zhou. China Leather, 2005, 34(9): 21-23.
- [4] D. F. Wu; T. H. Wu; C. L. Sun. Leather Chemicals, 2006, 23(4): 26-28.
- [5] S. Q. Li; J. X. Guo; X. Zuo. China Leather, 2006, 35(21): 17-20.
- [6] J. J. Guan; X. H. Qiang; Y. P. Qian. China Leather, 2007, 36(11): 56-60.
- [7] J. Hu; J. Z. Ma. Fine Chemicals, 2007, 24(7): 688-692.
- [8] Z. J. Zang; J. Z. Ma; J. Hu. Fine Chemicals, 2006, 23(11): 1112-1117.
- [9] X. M. Song. Leather Science and Engineering, 2005, 15(2): 56-58.
- [10] H. J. Fan; B. Shi. Chemistry, 2001, (11): 722-726.
- [11] X. J. Pan; X. R. Li; H. H. Wang. Leather Science and Engineering, 2006, 16(5): 53-57.