



Asian Journal of Chemistry; Vol. 26, No. 14 (2014), 4435-4438

# ASIAN JOURNAL OF CHEMISTRY

<http://dx.doi.org/10.14233/ajchem.2014.16790>



## Preparation of Silicone-Modified Acrylic Ester Emulsion Adhesive with Core-Shell Structure

ZHIHUI SUI\*, WEIWEI PANG, JIA SONG, LEI ZHANG and XIN ZHAO

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

\*Corresponding author: Tel/Fax: +86 452 2733192; E-mail: szh2736@163.com

Received: 30 November 2013;

Accepted: 9 April 2014;

Published online: 5 July 2014;

AJC-15490

Silicone-modified acrylate emulsion adhesives with core-shell structure was synthesized by semi-continuous seed emulsion polymerization with vinyl silane three oxygen radicals (A-171), methyl methacrylate, butyl acrylate and acrylic acid as raw material and was used for fabric pigment printing. The structure of the adhesive was characterized and analyzed by FT-IR spectrum, XPS and TEM. The results indicated that the organic silicon modified acrylate emulsion adhesive was synthesized in the optimum condition that the dosage of initiator, emulsifier and A-171 was 1.3, 3 and 4 %, respectively and reaction temperature was 80 °C for 1 h. At this point, the monomer conversion rate was as high as 95.01 %, the gel rate was 0.71 % and the water absorption was only 35.60 % of the unmodified latex film. After adhesive was used for pigment printing, the fabric dry and wet friction fastness reached level 4-5 and 3-4, soaping staining and fading grade reached 4-5 and 4, respectively and bending rigidity was 2.13; Compared with the commercial adhesives, good comprehensive performance such as high colour fastness and soft hand feel could be obtained and free of formaldehyde was released.

**Keywords:** Organic silicon, Acrylic ester, Core-shell emulsion, Pigment printing, Adhesive.

### INTRODUCTION

Pigment printing, with simple process, complete colour atlas and unnecessary washing after colour fixing, reducing emissions of printing and dyeing wastewater and saving energy and water, has been widely used in printing and dyeing industry. As coating has no affinity to fiber, the adhesive is used to help it fix mechanically onto fiber surface to form patterns<sup>1</sup>. The current widely used polyacrylate adhesive, with fast film-forming, high transparency, good adhesion, low release of organic compounds<sup>2</sup> and the wide raw material sources, has been widely used in textile printing. But the adhesive has problems of the limitation called "sticky when heated and fragile when cooled", bad wet rubbing fastness, chemical resistance and handle<sup>3</sup>. It is difficult to be used for high-grade printing products. Most of the polyacrylate adhesives contain N-methylol acrylamide (NMA) and formaldehyde will be released in the process of curing and storage. It is imperative to develop environmental friendly adhesives in order that printing products meet environmental requirements.

Polysiloxane has properties such as excellent flexibility and resistance to high and low temperature, hydrophobic, stain and oxidative degradation, but its application was limited by the high cost, low cohesiveness, poor film-forming and low strength. It has been solved by domestic and overseas researchers owing to the forced mutual capacitance effect formed through

grafting using core-shell emulsion polymerization technology. Used in pigment printing, it can significantly improve the printing fabric properties of softness, abrasion resistance, contamination resistance, etc.<sup>4,5</sup>. The organic silicon is as nuclear and the polyacrylate as shell in the present most research of core-shell silicon acrylic emulsion, but the modification effect will be affected by this structure that the organic silicon is wrapped in the polyacrylate. The imported high-priced organic silicon and catalyst is adopted in the most polymerization of silicon acrylic emulsion and the synthesis is too costly, so it is difficult to be promoted in industrial production. Therefore, in this research, the pigment printing binder, with polyacrylate as nucleus and organic silicon as shell, was prepared by seed emulsion polymerization using the readily available initiator and domestic silicon. This made silicon modified acrylate emulsion get the advantages of both silicon and acrylate, at the same time, the cost reduced greatly. In addition, it was carried on the actual printing and the application effect was compared with the sold commodity adhesive.

### EXPERIMENTAL

100 % cotton fabric, methyl methacrylate (MMA), butyl acrylate, acrylic acid, sodium dodecyl sulfate (SDS), sodium bicarbonate, potassium persulfate (KPS), anhydrous sodium sulfate, sodium hydroxide, anhydrous sodium carbonate, all above were analytical reagent. Emulsifier OP-10, chemical

pure. Vinyl silane three oxygen radicals(A-171), pigment printing ink scarlet FFG 8111, thickener BE903, commercial adhesives: SUPERPRINT301, CL-833, CU-651H-45, all of the above were industrial products.

Ultrasonic cleaner SY-3200-T (Shanghai Ultrasonic Instruments Limited Company), Y571B friction fastness tester (Wenzhou Textile Factory), SW-12 A II washing fastness tester (Wenzhou Darong Textile Standard Instrument Factory), WSD-III whiteness meter (Beijing Kangguang Instrument Limited Company), YG821L fabric style instrument (Laizhou Electronic Instrument Limited Company), Spectrum one infrared spectrometer (Perkin Elmer Corporation of USA), H-7650 transmission electron microscopy (Japan Hitachi), K-Alpha X-ray photoelectron spectrometer (Thermofisher Scientific Company of USA).

**Synthesis of silicon modified acrylate emulsion:** The part of emulsifier compound with SDS and OP-10, NaHCO<sub>3</sub> and deionized water were mixed into the four-mouthed bottle and ultrasound dissolved. Then inhibitor-removed acrylic monomers were added and ultrasonic scattered evenly for 5 min. The four-mouthed bottle was moved into water bath pot at 50 °C. Up to 80 °C with high-speed stirring, half of the initiator was added stirring slower. The remaining initiator and shell emulsion were added after blue phase appeared for 20 min and the shell emulsion was prepared with emulsifier, acrylic monomers and A-171 after ultrasonic for 40 min. After thermal reaction for a given time, cooled rapidly. The finished product was made through sieving with 200 mesh.

**Pigment printing:** Printing paste was made up with 5 % of pigment printing ink scarlet, 20 % of binder, 2 % of thickener and 73 % of water. Printed by hand, then prebaked at 80 °C for 3 min and cured at 150 °C for 3 min.

#### Emulsion and coating performance testing

**Gel rate:** The reaction gel was filtered, washed and dried to constant weight in drying oven at 105 °C. The gel rate was calculated according to the type (1):

$$\text{Gel rate (\%)} = \frac{M}{G} \times 100 \% \quad (1)$$

where M is gel quality and G is quality of all monomer.

**Monomer conversion:** The emulsion of 1.5 g was dried to constant weight in drying oven at 105 °C. The conversion was calculated according to the type (2):

$$\text{Conversion (\%)} = \frac{(G \times \frac{W}{W_0} - X)}{G_0} \times 100 \% \quad (2)$$

where G is feeding quantity, W is dried sample quality, W<sub>0</sub> is sample quality, X is non-volatile matter quality in the emulsion and G<sub>0</sub> is the total monomer quality.

**Appearance:** Visual test under natural light.

**Storage stability:** The emulsion was sealed for 3 months to observe the demulsification phenomenon such as latex coagulation and precipitation.

**Film bibulous rate:** Take a certain quality of emulsion in a petri dish, drying naturally for 2 days and forming film in drying oven at 60 °C. After drying and cooling, a film with both length and width for 2 cm was sheared and weighed; It was soaked in deionized water for 24 h; The moisture was blotted out with filter paper, then weighed the film; The bibulous rate was calculated according to the type (3):

$$\text{Bibulousrate (\%)} = \frac{m_0 - m}{m} \times 100 \% \quad (3)$$

where m<sub>0</sub> is the quality before absorbing water and M is the quality after absorbing water.

The emulsion was dried naturally to form film and its infrared spectrum was measured by infrared spectrometer. The latex film was made according to the above and tested by X ray photoelectron spectrometer. The dilute emulsion was dropped in the copper online coating with carbon membrane; The damp-dry samples was dyed with 2 % phosphotungstic acid and the drying was observed and photographed by transmission electron microscope.

#### Application performance testing:

(1) **Dry and wet rubbing fastness:** Test according to GB/T 3920-3920.

(2) **Soaping fastness:** Test according to GB/T 3921-3921.

(3) **Hand feeling:** Fabric style tester is used to test the fabric bending rigidity values and characterize the fabric handle. The smaller the bending stiffness, the softer the fabric.

(4) **Viscous resistance:** Test according to FZ/T 01063-01063.

(5) **Chromaticity:** Measure by WSD-III whiteness meter.

## RESULTS AND DISCUSSION

**Determination of silicon monomer dosage:** The experimental results of the A-171 dosage were shown in Table-1. Table-1 indicates that emulsion conversion rate of pure polyacrylate without A-171 is high, the gel rate is low, but water resistance is poor. Gradually with the increase of the A-171 dosage, conversion rate decreases and gel ratio increases. This is because the large volume of organic silicon monomer and low surface energy, it is difficult to enter the micelle and polymerize with acrylic monomers and easy to produce gel. A-171 monomer itself and its space steric hindrance are big, double bond is difficult to open in the reaction, so it is difficult to copolymerize with acrylic monomers. At the same time, A-171 and acrylic ester structure polarity differ considerably;

TABLE-1  
DOSAGE OF A-171 EFFECT ON THE PROPERTIES OF EMULSION AND FILM

A-171 Dosage (%)	Conversion (%)	Gel rate (%)	Bibulous rate (%)	Appearance	Storage stability
0	97.96	0.28	37.64	Strong blue light	Stable
1	96.74	0.43	27.47	Strong blue light	Stable
3	95.48	0.62	17.08	Strong blue light	Stable
4	95.01	0.71	13.40	Strong blue light	Stable
5	94.13	0.82	12.64	Strong blue light	Stable
7	92.19	1.17	11.44	Weak blue light	Condensed state

organic silicon monomer surface energy is far lower than the acrylic ester; chain segment containing silicon migrate to the polymer surface, forming hydrophobic layer, so the increase of A-171 can improve the water resistance of latex film. But excessive dosage of A-171, will not only increase the cost, can also cause unstable emulsion polymerization, high condensation rate, low conversion rate and stability decrease, therefore, the appropriate dosage of A-171 is 4 % in this experiment.

**Infrared spectrum detection:** To identify the target product structure, the target product was made the infrared characterization in this experiment, as shown in Fig. 1. The frequency doubling stretching vibration absorption peak of C-O at  $3444\text{ cm}^{-1}$ , the stretching vibration peak of C-H in methyl and methylene at  $2875$  and  $2959\text{ cm}^{-1}$ . The stretching vibration peak of C=O in the acrylic base at  $1736\text{ cm}^{-1}$ , the symmetric and asymmetric deformation vibration absorption peak of methyl at  $1452$  and  $1387\text{ cm}^{-1}$ . The stretching vibration absorption peak of C-C-O-C in methyl methacrylate at  $1240\text{ cm}^{-1}$ . The stretching vibration absorption peak of C-O in butyl acrylate at  $1168\text{ cm}^{-1}$ . The stretching vibration absorption peak of Si-O-C and Si-C at  $1067$  and  $843\text{ cm}^{-1}$ , the plane swing vibration absorption peak of  $-\text{CH}_3$  on the chain of  $\text{Si}(\text{OCH}_3)_3$  at  $757\text{ cm}^{-1}$  can be seen from Fig. 1. In addition, the stretching vibration peak of C=C at  $1680\text{--}1600\text{ cm}^{-1}$  and the stretching vibration absorption peak of  $=\text{C-H}$  at  $3100\text{--}3000\text{ cm}^{-1}$  is not appeared in Fig. 1. It indicates that there is no double bonds in the polymer. That no absorption peak in the range of  $3390\text{--}3200\text{ cm}^{-1}$  indicates that organic silicon didn't hydrolyze into Si-OH. In conclusion, organic silicon took part in the polymerization reaction with acrylic monomers instead of hydrolysis or self condensation.

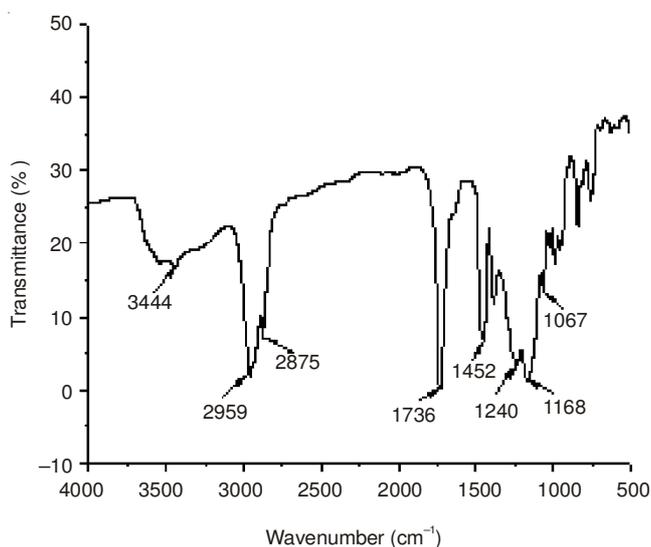


Fig. 1. Infrared spectrum of silicone acrylic-acid latex film

**XPS analysis:** The surface elements of silicone acrylic-acid film were analysed by X-ray photoelectron spectroscopy, the results are shown in Fig. 2a, 2b and Table-2. In Fig. 2a, whether it is the film-air or film-glass interface, the Si2p signal peak is strong and film-air interface Si2p signal is stronger than film-glass. It is illustrated that organic silicon have joined in copolymerization reaction. The film surface atomic number of each element can be concluded in Fig. 2b and the results are shown

Items	C1s (%)	O1s (%)	Si2p (%)
Film-air interface	73.11	24.79	2.10
Film-glass interface	75.33	24.03	0.64
Theoretical value	73.90	25.73	0.37

in Table-2. The Si2p element content of film-air interface is much higher than film-glass and both are higher than theory average. This is because the volume of Si is larger than C, the polarity of Si chain segments and other segment also vary widely, Si atoms with low surface energy migrate to the membrane surface in the process of film formation and the migration to air is more, forming the self-stratifying coatings on the film surface, reducing the film surface tension and improving the water resistance<sup>6,7</sup>; But the content of C and O atoms is different from Si.

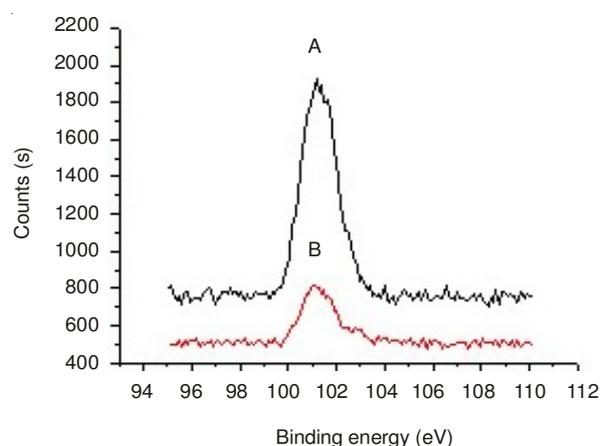


Fig. 2a. XPS spectra of silicon acrylic-acid film surface Si2p: (A) film-air interface Si2p signal peak; (B) film-glass interface Si2p signal peak

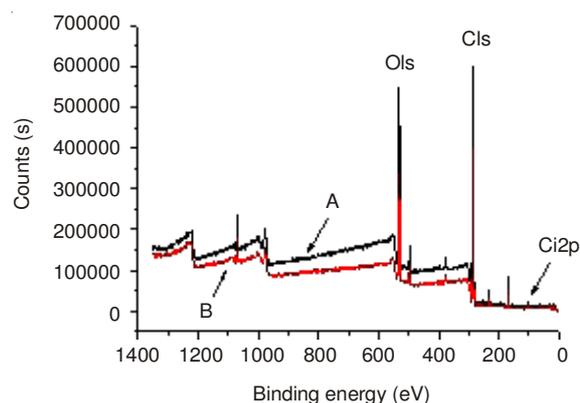


Fig. 2b. XPS full spectra of silicon acrylic-acid film: (A) film-air interface full spectrum; (B) film-glass interface full spectrum

**TEM observation:** The particle morphology and size of silicone acrylic emulsion is observed by transmission electron microscope with scale of 500 nm and 100 nm and the observations are shown in Fig. 3a and 3b.

It can be seen from Fig. 3a that the emulsion colloidal particles with uniform size can be dispersed well in water; Fig. 3b indicates that the size of latex particles with obvious core-shell structure is about 110 nm. Particle internal brighter

TABLE-3  
APPLICATION PERFORMANCE CONTRAST OF SILICON ACRYLIC EMULSION AND THE SOLD COMMODITIES ADHESIVES

Adhesives	Rubbing fastness		Soaping fastness		Adhesion	Chromaticity	Bending stiffness (cN mm <sup>-1</sup> )
	Dry	Wet	Staining	Fading			
Silicone acrylic emulsion	4-5	3-4	4-5	4	-	59.27	2.13
301	4-5	4	4-5	4	-	57.97	2.63
CL-833	4	3-4	4	4	Mild	59.68	1.67
CU-651H-45	4-5	4	4-5	4	-	60.23	6.20

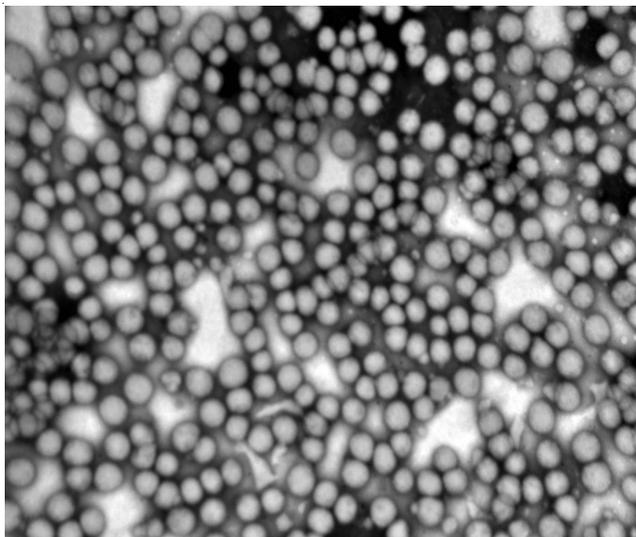


Fig. 3a. TEM photo of the silicon acrylic emulsion (× 50 k)

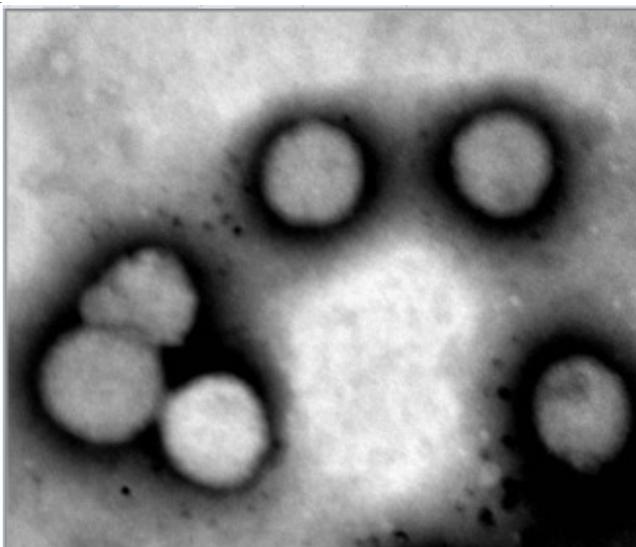


Fig. 3b. TEM photo of the silicon acrylic emulsion (× 200 k)

part is nuclear layer formed by acrylic monomers polymerization, the outer darker package is shell of silicon modified acrylate. When the silicon acrylic emulsion is used in printing process, the hardcore endows the coating strength and the soft shell part can not only improve the fabric hand feel, also give the function of water and stain resistance.

**Application properties:** The printing experiment was carried out with self-made silicon acrylic emulsion and sold commodities adhesives, the results are shown in Table-3.

Table-3 shows that, compared with the fabric printed with the commodity binder, the dry rubbing and soaping fastness of fabric printed with self-made silicon acrylic adhesive are better, the wet rubbing fastness makes little difference, chromaticity is higher, the printed fabric is no adhesion and bending stiffness is small, namely, soft. Thus, the core-shell silicon acrylic emulsion synthesized in this experiment is ideal pigment printing binder.

### Conclusions

- Organic silicon modified acrylate emulsion adhesive was synthesized by emulsion polymerization in the optimum condition that the dosage of initiator, emulsifier and A-171 was 1.3, 3 and 4 %, respectively and reaction temperature was 80 °C for 1 h. It was proved that the organic silicon and acrylic monomers are all involved in the copolymerization reaction by FT-IR and XPS analysis. The core-shell structure of silicon acrylic emulsion was observed by TEM.

- After the synthetic silicon-acrylic emulsion adhesive was used for pigment printing, the fabric dry and wet friction fastness reached level 4-5 and 3-4, soaping staining and fading grade reached 4-5 and 4 and bending rigidity was 2.13. Compared with the commercial adhesives, good comprehensive performance such as high colour fastness and soft hand feel could be obtained, the printing process was no adhesion and the chromaticity value was as high as 59.27. The adhesive synthesis and application process was free of formaldehyde, so it was a kind of environmental friendly pigment printing binder with excellent performance.

### ACKNOWLEDGEMENTS

This research is supported financially by the Key Project of Chinese Ministry of Education (211052), Graduate Innovation Fund Project of Heilongjiang Province (YJSCX2012-393HLJ) and Qiqihar University (YJSCX2013-038X) of China.

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