

New Polymer Materials Based on Silicone-Acrylic Copolymer to Improve Fastness Properties of Reactive Dyes on Cotton Fabrics

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ABSTRACT: New polymer materials, based on silicone-acrylic copolymer containing cationic groups, were synthesized through radical mechanism and ring-opening polymerization of cyclosiloxane. The polymers of polyacrylate/polysiloxane improved the fastness properties of reactive dyes on cotton. In comparison with those of polyacrylate-containing cationic groups, the wash fastness and wet rub-

bing fastness of the dyed cotton fabric treated with the new polymer materials were better. The handle of the fabric with aftertreatment was also good. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 720–725, 2006

Key words: silicones; radical polymerization; ring-opening polymerization; dyes

INTRODUCTION

Reactive and direct dyes are widely used for dyeing of cotton and its blends. They offer advantages such as wide color ranges, excellent dye penetration, low cost, short dyeing time, dyeing stability at boiling point, etc. Although the reactive dyes form covalent bonding with the fiber, the fastness property of cotton fabrics dyed with these dyes is not satisfied, especially wash fastness and wet rubbing fastness.^{1,2} Some studies on improving wash fastness and wet rubbing fastness properties of reactive dyes on cotton have already been carried out. The cationic compounds, crosslinking agent, and sol-gel process are used in dyeing and aftertreatment of cotton to improve the fastness.^{3–5} The fixing agents are usually polymers containing cationic group. Because the reactive dyes have anionic chromospheres, polymers containing cationic group increase electrostatic effect through aftertreatment. Most polymers, however, decrease the handle of the dyed fabrics.

It is common knowledge that polyacrylate and polysiloxane are an extremely important class of materials used for coating, adhesives, impact-resistance plastics, etc.⁶ Most studies have focused on the composite latex particles prepared from methyl methacrylate (MMA), butyl acrylate (BA), styrene (St), and vinyl acetate (VAc), but only a few reports are available that

investigate the system of siloxane and acrylic monomers.^{7–9} With regard to polyacrylate and polysiloxane their difference in polarity is very large; in addition, the polyacrylate is usually synthesized through radical mechanism. Polysiloxane is often prepared through ring-opening polymerization of cyclosiloxane. In application, polysiloxane has many specific properties by virtue of its good water repellency, lubricity, high flexibility, and excellent thermal stability. In comparison with polysiloxane, polyacrylate exhibits quite different properties, such as good cohesiveness and excellent film-forming properties. Therefore, the various kinds of polyacrylate and polysiloxane lattices, concerning interpenetrating polymer networks (IPN) and graft copolymers have been synthesized by some researchers.¹⁰

In this paper, new polymer materials, based on silicone-acrylic (methacryloyloxyethyl trimethylammonium chloride) copolymer containing cationic groups, are synthesized through radical mechanism and ring-opening polymerization of cyclosiloxane. The effect of the new polymer on fastness of dyed cotton fabrics with reactive dyes is investigated. The handle of the fabric with aftertreatment is also discussed.

EXPERIMENTAL

Materials

Methacryloyloxyethyl trimethylammonium chloride (MATMC) was provided by Xinyu Chemical Industry Company (Wuxi, China). Octamethyl cyclotetrasilox-

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TABLE I
Ingredients of Copolymer Emulsions

Sample	MATMC (g)	OP-10 (g)	SDBS (g)	DBSA (g)	D4 (g)	MATS (g)	602 (g)	APS (g)	Water (g)
A1	20							0.1	80
A2	25	8	5	1	5	1	0.5	0.1	110
A3	25	8	5	1	10	2	1	0.1	120

ane(D₄) was obtained from Xinghuo Petrochemical Plant of Jiangxi (Jiangxi, China) and fractionated under reduced pressure before being used. 3-Methacryloyloxypropyl trimethoxysilane (MATS) and N-(β-aminoethyl)-γ-aminopropyl dimethoxysilane (602) were from Shanghai Handa Chemical Company. Dodecylbenzene sulfonic acid (DBSA, D4 polymerization catalyst and surfactant), sodium dodecylbenzene sulfonate (SDBS), nonionic surfactant OP-10, TX-10, and ammonium persulfate (APS) were from Shanghai Chemical Reagent Plant.

The reactive dyes, Yellow B-3RD, Red B-2BF, and Blue B-2GN, were obtained from Shanghai Matex Chemical Company. Scoured and bleached cotton fabrics were obtained from Beijing Textile Company.

Preparation of silicone-acrylic (methacryloyloxyethyl trimethylammonium chloride) copolymer

The emulsion agents, dodecylbenzene sulfonic acid (DBSA, D4 polymerization catalyst and surfactant), SDBS, nonionic surfactant OP-10 were first dissolved in water. The MATMC, D4, MATS, and 602 were added into the reactor according to the recipes and were sufficiently mixed by stirring at room temperature. The recipes are given in Table I. The polymerization mixture was heated at 85°C for 30 min in a nitrogen atmosphere. Then ammonium persulfate (APS) solution was added three times in the following sequence: during heating at 85°C for 30 min, after 60 min, and after 120 min. The polymerization was conducted at 85°C for 7 h.

Dyeing and aftertreatment

The dyeing solution was prepared by using 5% (o.w.f.) of dye based on weight of the fabric. The fabrics were dyed in an IR dyeing machine (PYROTEC-2000), the liquor ratio being 1:15, sodium chloride (60 g/L), and

sodium carbonate (10 g/L). Fabrics were immersed in the dye bath at room temperature and the temperature was increased to 65°C at a rate of 1°C/min. Dyeing was carried out at this temperature for 60 min. The dyed fabrics were rinsed thoroughly in hot water and soaped in a solution of a nonionic surfactant (TX-10) at 85°C for 20 min at liquor ratio 1:30 in a laboratory dyeing machine. The fabrics were removed, rinsed thoroughly in hot tap water, and air dried.

The dyed cotton samples were padded with the solutions of different concentrations of silicone-acrylic copolymer to give 75% wet pick-up. The dry temperature and time were 95°C and 3 min, respectively. The cure temperature was 165°C, and the cure time was 1.5 min.

Color yield analysis

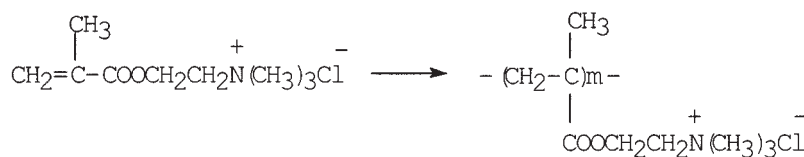
The color yield (*K/S*) of the dyed fabric was determined by Datacolor SP600⁺ spectrophotometer. The dye absorbance was measured in the visible region of the spectrum from 400 to 700 nm, and the reflectance at the wavelength of maximum absorption (λ_{\max}) was used to calculate the color yield of dyed fabrics by the Kubelka-Munk Equation (eq.(1))¹¹:

$$K/S = \frac{(1 - R)^2}{2R} \quad (1)$$

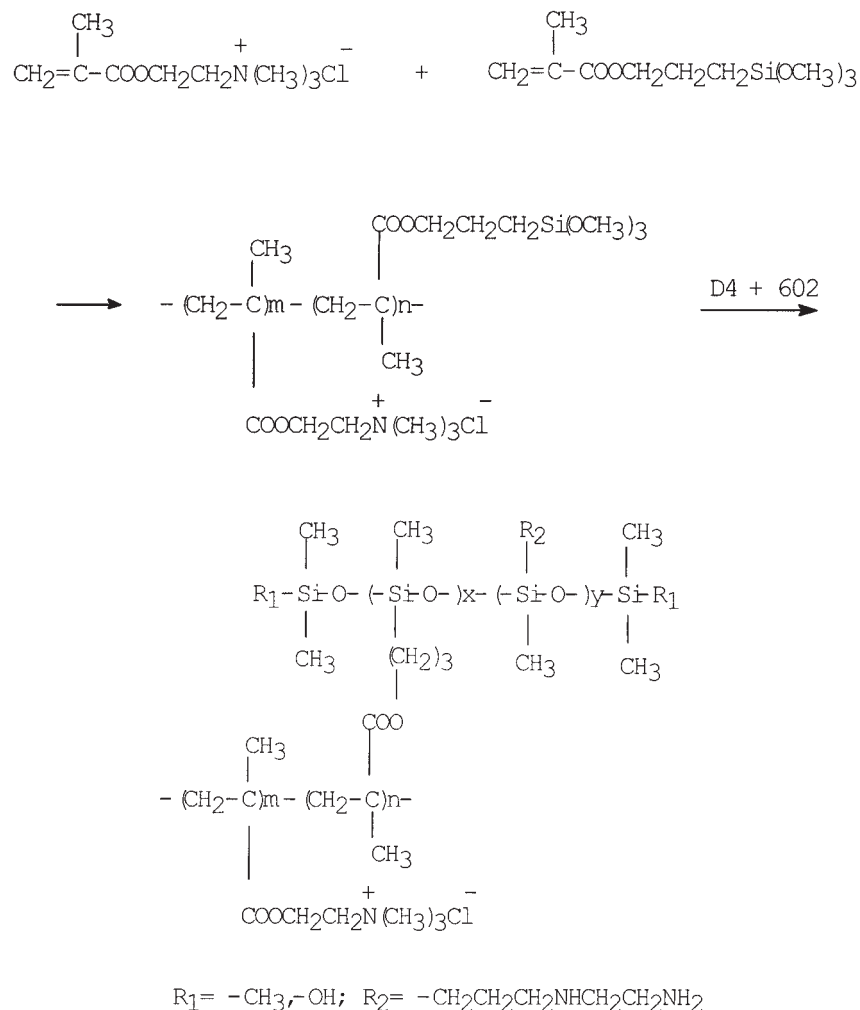
where *K* is the absorption coefficient of the substrate, *S* is the scattering coefficient of the substrate and *R* is the reflectance of the dyed fabric at λ_{\max} .

Measurements

Color fastness of the untreated and treated dyed cotton samples was determined according to the respective international standards: fastness to washing, ISO



Scheme 1



Scheme 2

105-C04 (1989); fastness to perspiration, ISO 105-E04(1994); fastness to rubbing, ISO 105-X12(1993).

The handle of the samples was tested according to ASTM D1388 test method.¹²

RESULTS AND DISCUSSION

Polymerization of silicone-acrylic

MATMC is a cationic monomer, which can form cationic polymer through the radical reaction (Scheme 1) It is a water soluble polymer (A1 prepared from only MATMC).

When MATMC, MATS, Octamethyl cyclotetrasiloxane(D₄), and 602 polymerized using initiator and catalyst (Dodecylbenzene sulfonic acid) through emulsion polymerization, surfactant admicelles structure was formed: hydrophobic core containing —NH— through ring-opening polymerization of cyclosiloxane and hydrophilic shell containing cationic groups with silicone-acrylic (methacryloyloxyethyl trimethylammonium choribe) copolymer. As a coupling agent containing one C=C and three SiOCH₃ groups, MATS can undergo not only radical polymerization with residual acrylic monomer but also condensation with

TABLE II
Some Properties of Copolymers

Polymer	Appearance	Polymer content (%)	Viscosity (cp)	Si content (%)
A1	Colorless solution	20	450	0
A2	Translucent emulsion	21	1690	4.8
A3	Translucent emulsion	22	2100	8.1

TABLE III
Fastness Properties of Reactive Yellow B-3RD for Cotton

Samples	Fastness to rubbing		Fastness to washing		Fastness to perspiration	
	Dry	Wet	SC	SW	SC	SW
Without polymer	4	3	3	3	3	3
A1	4	3-4	3-4	3-4	4	4
A2	4-5	4	4	4	4	4
A3	4-5	4	4	4	4	4

SC, staining on cotton; SW, staining on wool.

Si—OH terminal groups of polysiloxanes. MATS is an ideal coupling agent, which may form an intermediate layer and chemical bonds between hydrophobic compound and hydrophilic monomer. The polymerization reaction is shown in Scheme 2.

The cationic section of the polymer molecular forms complexes with reactive dyes to improve the fastness of the dyed fabrics. Terminal group of polysiloxanes imparts good water repellency and high flexibility to improve fabric handle. The polymer and copolymer were called A1, A2, and A3. Some properties of them see Table II.

Application properties of silicone-acrylic copolymer containing cationic groups

To investigate the application properties of silicone-acrylic copolymer reactive dyes Yellow B-3RD, Red B-2BF, and Blue B-2GN were used for cotton fabric. The dyed cotton samples were padded without polymer but with 20 g/L of solutions A1, A2, and A3, respectively. The fastnesses of dyed cotton fabrics are summarized in Tables III–V. The tables show that wet rubbing fastness, wash fastness, and fastness to perspiration of dyed sample with three reactive dyes

without polymer are not very good. The wet rubbing fastness of treated sample with A1 was better than that without the polymer. The higher fastness obtained for the fabric treated with A1 may be due to the formation of ionic bonds between the quaternary ammonium groups on the polymer and the anionic sites on the reactive dyes. The wet fastnesses of the fabrics treated with A2 and A3 were better than those with A1. The wet rubbing fastnesses of treated sample with A3 were the best among the three polymers. The results show that higher the Si content of copolymer, better is the wet fastness of the fabric. This can be explained by the fact that hydrophilic chains containing cationic groups of copolymer on the surface of cotton fabric remove into the fabric and hydrophobic chains of polysiloxane remove into air to improve water repellency and lubricity.

Effect of copolymer concentration

To investigate the effect of the concentration of silicone-acrylic copolymer, the dyed cotton samples with reactive dye Blue B-2GN were padded with the solutions of different concentrations (0 g/L, 10 g/L, 20 g/L,

TABLE IV
Fastness Properties of Reactive Red B-2BF for Cotton

Samples	Fastness to rubbing		Fastness to washing		Fastness to perspiration	
	Dry	Wet	SC	SW	SC	SW
Without polymer	4	2-3	3	3	3	3-4
A1	4-5	3	3-4	3-4	4	4
A2	4-5	3-4	3-4	4	4	4
A3	4-5	4	3-4	4	4	4

TABLE V
Fastness Properties of Reactive Blue B-2GN for Cotton

Samples	Fastness to rubbing		Fastness to washing		Fastness to perspiration	
	Dry	Wet	SC	SW	SC	SW
Without polymer	4	2-3	3	2-3	3	3
A1	4-5	3-4	4	3	3-4	3-4
A2	4-5	4	4	3-4	3-4	4
A3	4-5	4	4	4	3-4	4

TABLE VI
Effect of the Concentration of Copolymer A2

Copolymer A2 (g/L)	Fastness to rubbing		Fastness to washing		Fastness to perspiration	
	Dry	Wet	SC	SW	SC	SW
0	4	2-3	3	2-3	3	3
10	4-5	3	3-4	3	3	3-4
20	4-5	4	4	3-4	3-4	4
30	4-5	4	4	4	3-4	4
40	4-5	4	4	4	3-4	4

30 g/L, and 40 g/L) of silicone-acrylic copolymer of A2 and A3. The fastnesses of dyed cotton treated with A2 and A3 are summarized in Table VI and VII, respectively. The tables show that when the concentration of silicone-acrylic copolymer was 10 g/L, silicone-acrylic copolymer could obviously improve wet rubbing fastness and wash fastness. When the concentration of silicone-acrylic copolymer increased, copolymer could also more obviously improve wet fastness. However, when concentration of silicone-acrylic copolymer exceeded 20 g/L, wet rubbing fastness and wash fastness had no further improvement. Therefore, the optimum concentration of silicone-acrylic copolymer was 20 g/L.

Color yield (K/S) values of dyed fabric with copolymer

The dyed fabric, treated with silicone-acrylic copolymer, may lead to color change. The K/S of the dyed fabric with copolymer and without copolymer was measured and is shown in Table VIII. Table VIII shows K/S of the dyed fabric with copolymer and without copolymer having no significant change.

The handle of fabric through aftertreatment

When a certain amount of polymer was used to treat the dyed fabrics, a thick layer was formed on the fabric and thus resulted in the treated fabric feeling stiff. This was one of disadvantages of most fixing agents. The handle of the samples treated with A1, A2, and A3 was tested and the results are displayed in Table IX. It is clear that the handle of dyed fabrics treated with copolymers A2 and A3 containing Si were obviously better than that with polymer A1 without hydrophobic chains of polysiloxane. The handle of dyed fabrics treated by copolymer A1 was worse than that of the dyed fabrics treated without polymer. As can be seen, chains of polysiloxane containing $-\text{NH}_2$ impart high flexibility to the fabric. Compared with the fabric treated without polymer, the handle of the fabric treated with A2 or A3 does not deteriorate.

CONCLUSIONS

1. New polymer materials, based on silicone-acrylic copolymer containing cationic groups, were synthesized through radical mechanism and ring-

TABLE VII
Effect of the Concentration of Copolymer A3

Copolymer A2 (g/L)	Fastness to rubbing		Fastness to washing		Fastness to perspiration	
	Dry	Wet	SC	SW	SC	SW
0	4	2-3	3	2-3	3	3
10	4-5	3	3-4	3	3	3-4
20	4-5	4	4	4	3-4	4
30	4-5	4	4	4	3-4	4
40	4-5	4	4	4	3-4	4

TABLE VIII
K/S of Dyed Fabric Treated with Copolymer^a

Samples	K/S (Yellow B-3RD)	K/S (Red B-2BF)	K/S (Blue B-2GN)
Without copolymer	12.235	11.460	14.542
A1	13.258	12.137	15.275
A2	12.132	11.126	14.229
A3	12.278	11.297	14.397

^a 20 g/L of copolymer was used.

TABLE IX
Measure of the Handle of Fabrics Treated with Copolymer^a

Samples (yellow)	Bending length	
	Warp (cm)	Weft (cm)
Without polymer	1.8	1.3
A1-treated	2.0	1.5
A2-treated	1.7	1.3
A3-treated	1.6	1.2

^a 20 g/L of copolymer was used.

opening polymerization of cyclosiloxane. The copolymer of polyacrylate/polysiloxane improved the fastness properties of the dyed cotton fabric with reactive dyes.

- In comparison with polyacrylate containing cationic groups, the wash fastness and wet rubbing fastness of dyed cotton fabric treated with the copolymer of polyacrylate/polysiloxane were better.
- The treatment with copolymer had no significant effect on *K/S* of the dyed fabric. The handle of

dyed fabrics treated with copolymers containing Si was obviously better than that with the polymer without hydrophobic chains of polysiloxane. Compared with the fabric treated without polymer, it does not deteriorate.

References

- Fu, J.; Yang, L. *Dyeing Finish* 2004, 30, 13.
- Lei, X. P.; Lewis, D. M.; Wang, Y. N. *J Soc Dyers Colour* 1992, 108, 383.
- Zheng, Q.; Zhu, P. *Textile Auxiliaries* 2001, 4, 5.
- Lim, S. H.; Hudson, S. M. *Coloration Technol* 2004, 120, 108.
- Min, L.; Xiaoli, Z.; Shuilin, C. *Coloration Technol* 2003, 119, 297.
- Park, H.; Yang, I.; Wu, J.; Kim, M.; Hahm, H.; Kim, S.; Rhee, H. *J Appl Polym Sci* 2001, 81, 1614.
- Yahaya, G. O.; Brisdon, B. J.; Maxwell, M.; England, R. *J Appl Polym Sci* 2001, 82, 808.
- He, W.; Tong, J.; Mang, W.; Pan, C.; Zhu, Q. *J Appl Polym Sci* 1995, 55, 667.
- Kong, X. Z.; Kan, C. Y.; Yuan, Q. *Polym Adv Technol* 1996, 7, 888.
- Kan, C. Y.; Kong, X. Z.; Yuan, Q.; Liu, D. S. *J Appl Polym Sci* 2001, 80, 2251.
- Kubelka, P.; Munk, F. Z. *Techn Physik* 1931, 12, 593.
- ASTM. *Standard Test Method for Stiffness of Fabrics*; ASTM: Pennsylvania, 2002; ASTM D1388-96 (2002).