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Alkali 방법을 이용한 Block Silicone Softener 합성 및 응용

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Synthesis of a Block Silicone Softener by Alkali Method and Its Application on Cotton Fabric

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Abstract: A block silicone softener (ATSO-PDE) was synthesized by alkali method with amino-terminated polysiloxane (ATSO) and polypropylene glycol diglycidyl ether (PDE) as raw materials. The chemical structure of amino-terminated siloxane (ATS) was characterized by ^{1}H NMR, ^{13}C NMR, and FTIR. The main factors affecting ATSO conversion rate and properties of product were investigated. The optimal ring opening reaction condition of ATSO was 110 °C for 2 h. The application of ATSO-PDE on cotton fabrics indicated that fabrics treated by softener with high ammonia value (0.70 mmol/g) expressed good softness while softener with low ammonia value (0.40 mmol/g) expressed good smoothness. The adsorption mechanism and orientation distribution of silicone softener on the fibers were analyzed by the establishment of the orientation distribution model. It was indicated that the different properties and surface morphology of ATSO-PDE were related to the molecular structure and the orientation on the surface of the fiber.

Keywords: alkali method, softener, block silicone, film morphology, orientation.

Introduction

The method for synthesizing block silicone oil was generally divided into acid method and alkali method. The acid method process was prepared by octamethylcyclotetrasiloxane (D4) and 1,1,3,3-tetramethyldisiloxane which were ring-opened under acidic conditions, and then reacted with allyl epoxy polyether and polyether amine.[1-3] The block silicone softener prepared by acid method had a lower cost, stable performance and strong controllability. But the process had many reaction steps which affected the productivity and the utilization rate. In order to improve productivity, many factories purchased epoxy-terminated polysiloxane directly from suppliers. But this led to an increase in raw materials cost.

Alkali method was one of the simplest and most efficient ways to synthesize polysiloxane. It had also become a common method of industrial production. Many researchers used D4 to react with amino-coupling agents under alkaline conditions to prepare amino-polysiloxanes.[4-9] The side chain amino groups were effectively adsorbed onto the fibers, so that the silicone molecules could combine with the fibers and penetrate into the fibers. On the one hand, the friction coefficient between the fibers and the internal stress of the fibers reduced. The fibers and yarns were easy to move and reduced the rigidity of the fabric. The softness and bulkiness of the fabric were improved. On the other hand, the silicone molecules were adsorbed on the surface of the fiber to form a film, which could fill the pores on the surface of the fiber. Thus the flatness of the fiber surface was improved and the smoothness was increased. But due to the ordered arrangement of the methyl groups and the small proportion of hydrophilic groups, the treated fabric was hydrophobic. In order to solve the problem,

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polyether segments were commonly used for graft modification of amino polysiloxanes.[10]

Some factories also used 1,3-bis(3-glycidoxypropyl)-1,1,3,3-tetramethyldisiloxane to react with D4 under alkaline conditions, then reacted with polyether amine. This method was simple and high efficiency, but the epoxy group was easy to open under alkaline and water conditions, which directly led to unstable epoxy value of the end epoxy polysiloxanes. In particular, when the molecular weight of the epoxy silicone oil was large, the ring opening of the epoxy group may cause insufficient reaction with the polyether amine and result in stratification of the final product. Therefore, it was urgent to find a low-cost and high efficiency method to synthesize block silicone softener. In this study, a block silicone softener was synthesized by alkali method with amino-terminated polysiloxane (ATSO) and polypropylene glycol diglycidyl ether (PDE) as raw materials, and its application and distribution model on cotton fabrics were studied.

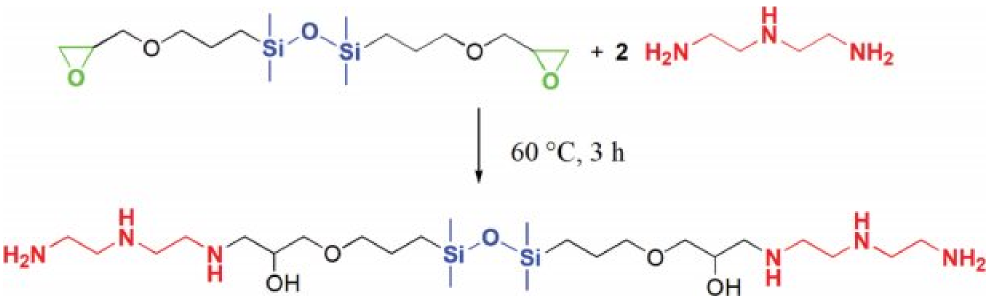
Experimental

Materials. The knitted 100% cotton fabric with a weight of 122 g/m^2 was supplied by Zhejiang Hangmin Co., Ltd.. Octamethyl cyclotetrasiloxane (D4) was provided by Dow Corning Co., Ltd. Polypropylene glycol diglycidyl ether was purchased from Dongguan Dofriends Biological Technology Co., Ltd.. Diethylenetriamine was purchased from Dow Chemical Co., Ltd.. Emulsifier AEO9 was purchased from BASF-YPC Co., Ltd.. 1,3-Bis(3-glycidoxypropyl)-1,1,3,3-tetramethyldisiloxane was purchased from Jiaxing United Chemical Co., Ltd.. Tetramethylammonium hydroxide, isopropanol and acetic acid were purchased from Zhejiang Transfar Co., Ltd..

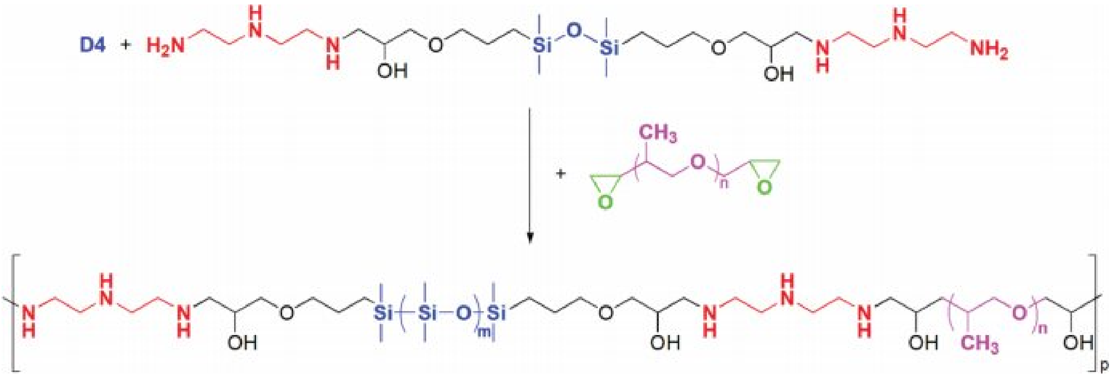
Synthesis. Synthesis of Amino-Terminated Siloxane (ATS): The synthesis equation of ATS is shown in Scheme 1. Firstly, diethylenetriamine was added into a round-bottom flask equipped with a nitrogen inlet and outlet, temperature controller, reflux condenser and a stirrer. Then the flask was fastened into an oil bath at 60 °C.

Then 1,3-bis(3-glycidoxypropyl)-1,1,3,3-tetramethyldisiloxane was dropped slowly into the reaction system, then stirring at 200 rpm for about 3 h. After reaction, the low boiler impurities in ATS were removed by evaporation under reduced pressure (1000 Pa) at 120 ºC for 30 min and ATS was obtained.

Synthesis of ATSO-PDE: The synthesis equation of ATSO-PDE is shown in Scheme 2. Firstly, a certain amount of ATS, D4 and tetramethylammonium hydroxide with 0.05%



Scheme 1. Reaction equation of ATS.



Scheme 2. Reaction equation of ATSO-PDE.

total mass of the reactant were added into a reactor equipped with a stirrer, a thermometer and a reflux condenser. Then the flask was fastened into an oil bath at 90~120 °C, stirring at 200 rpm for about 2~4 h, the ATSO was obtained. After the temperature was reduced to 80 °C, a certain amount of PDE and isopropanol were added, and the reaction was kept at this temperature for 3 h. Finally, the final products were purified by vacuum distillation to remove unreacted material and solvent.

Emulsions Preparation. Block silicone softeners were usually used as emulsions in textile industry. The ATSO-PDE emulsion (ATSO-PDE 10 g, AEO9 1.5 g, acetic acid 0.3 g, H_2O 50 g as raw materials) was prepared.

Fabric Treatment Procedure. Prior to finishing, the cotton fabrics were subject to conventional desizing, scouring, and bleaching processes. The bleached fabrics were then dipped in 30 g/L finishing solution, and nipped in a laboratory-scale padding machine at 5 kg/cm^2 and speed of 5 m/min to achieve 80% wet pickup, then cured at 170 °C for 60 s. All samples were preconditioned under standard conditions (temperature 20±1 °C, relative humidity 65±2%) for 24 h before tests were conducted.

Characterization and Measurement. Ammonia value testing was according to HG/T 4260-2011 'Determination of total ammonia value of textile dyeing and finishing auxiliaries'. The calculation formula is as follows:

$$T = (V - V_0) \times c/m \tag{1}$$

Where, c is concentration of perchloric acid-acetic acid standard titration solution (mol/L); V was the volume of perchloric acid-acetic acid standard solution (mL) consumed by the titration sample solution; V_0 is the volume of perchloric acid-acetic acid standard solution consumed by the blank test (mL); m is the mass of the sample (g);

Fourier-transform infrared (FTIR) spectrometer (Thermo Nicolet Corporation, USA) was used to characterize the chemical structure of ATS. The sample was applied to a potassium bromide wafer. ^{1}H NMR and ^{13}C NMR spectra were recorded at 26 °C on a Varian INOVA 400 with $CDCl_3$ as solvent and tetramethylsilane (TMS, $\delta = 0$ ppm) as internal standard. The mechanical properties of the fabrics, reflecting their handle, including bending, compression, and surface properties, were measured on fabric style instrument by using a Kawabata evaluation system for fabric (KESFBAUTO-A, Japan). The bending rigidity (*B*) indicated the ability of a fabric to resist bending. The surface roughness (*SMD*) indicated the variation in surface geometry of the fabric in units of microns. The compressional energy (*WC*) and compressional resilience (*RC*) were referred to the fluffy feeling of the fabric and the ability to render the fullness to the fabric after being compressed, respectively. All these measurements were repeated in both warp and weft directions, and the mean value was the average of both warp and weft directions. Each test was performed for five times. Moreover, we combined the subjective evaluation method with a three-person group to evaluate the properties of the treated fabric out of 5 points on average. The breaking strength of fabrics was measured on a LFY-201D electrical fabric strength tester according to GB/T 3923.1-1997. The whiteness of fabrics was measured according to GB/T 8424.2-2001 on a WSB-2 whiteness meter. The fabric resilience was tested on the YG542A type wrinkle elastic meter according to GB/T3819-1997 'Determination of the recovery of creases of textile fabrics'. The warp and weft were measured 3 times and averaged.

Results and Discussion

FTIR Analysis of ATS. The FTIR spectra of ATS are shown in Figure 1. The characteristic peak at 3291 and 1591 cm^{-1} was the amino group. 1251 cm^{-1} was the symmetrical deformation of -Si-CH_3.[11] 1000~1150 cm^{-1} was the characteristic peak of Si-O-Si. 760~860 cm^{-1} was the plane sway of Si-C, and the characteristic peak of epoxy group disappears at 910 cm^{-1}.

Further characterization of structure by nuclear magnetic spectroscopy is shown in Figure 2. Scheme 3 is the expected

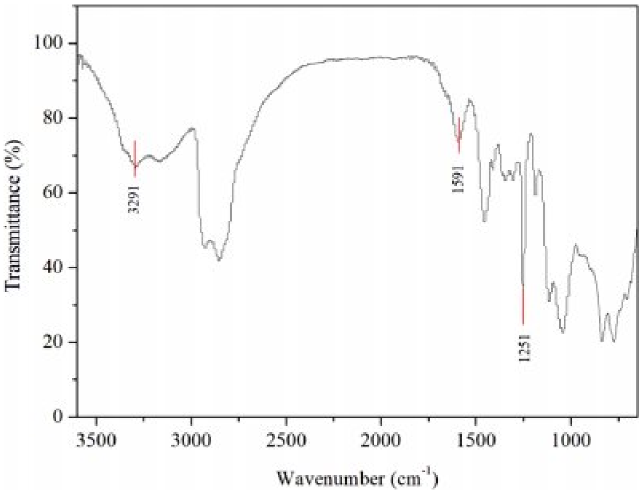


Figure 1. Infrared spectrum of ATS.

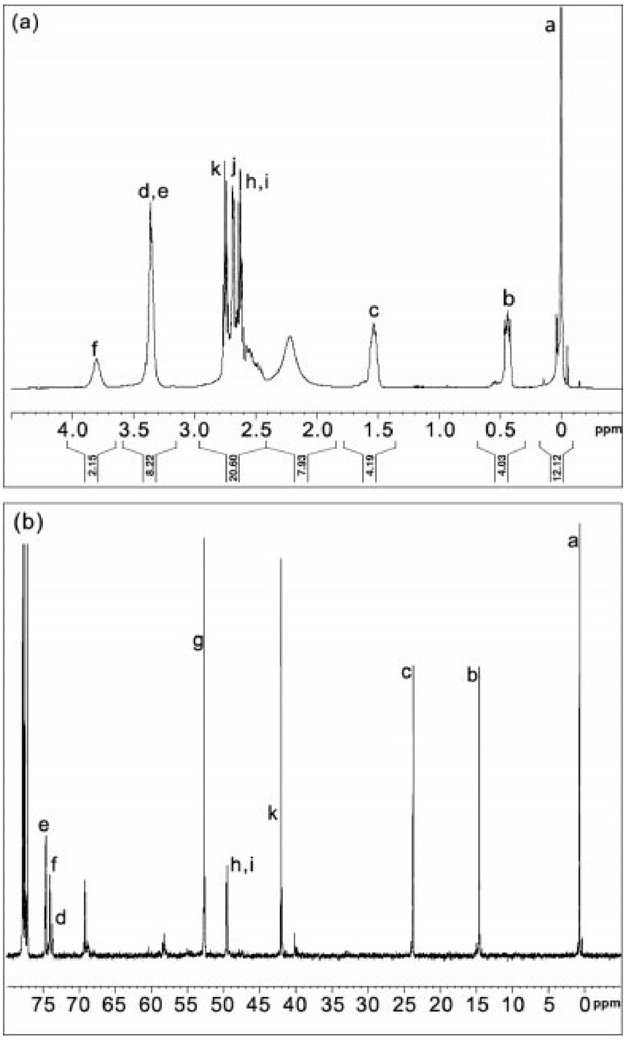


Figure 2. NMR spectroscopy of ATS (a) ^{1}H NMR; (b) ^{13}C NMR.

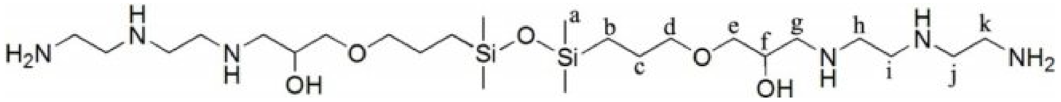
Table 1. Synthetic Recipe of ATSO-PDE

No.	D4 (g)	ATS (g)	PDE (g)	Ammonia value of ATSO-PDE (mmol/g)
1	100	10.46	8.84	0.96
2	100	7.64	6.46	0.70
3	100	6.04	5.10	0.57
4	100	4.97	4.20	0.48
5	100	4.24	3.58	0.40

molecular structure of ATS. Figure 2(a) and 2(b) were ^{1}H NMR and ^{13}C NMR spectra of ATS, respectively. Several important characteristic peak positions in hydrogen spectrum were: Si-C$\boldsymbol{H}_3$ (δ=0.04 ppm); -Si-C$\boldsymbol{H}_2$- (δ=0.45 ppm); Si-CH$_3$-C$\boldsymbol{H}_2$- (δ=1.52 ppm); -CH$_2$-C$\boldsymbol{H}_2$-O-C$\boldsymbol{H}_2$- (δ=3.30~3.40 ppm); -CH$_2$-C$\boldsymbol{H}$(OH)-CH$_2$- (δ=3.80 ppm) and several characteristic peaks in the range of δ=2.50~2.80 ppm. According to the peak area, using Si-C$\boldsymbol{H}_3$ at δ=0.04 ppm as internal standard, the peak area was 12.12 corresponding to 12 hydrogen atoms in Scheme 3 structure, and the peak area at δ=3.80 ppm was 2.15, corresponding to two hydrogen atoms at f place in the structure. It indicated the reaction of diethylenetriamine with 1,3-bis(3-glycidylpropyl)-1,1,3,3-tetramethyldisiloxane was happened. Combined with ^{13}C NMR spectroscopy, the important characteristic peak positions were: Si-$\boldsymbol{C}$H$_3$ (δ=0.70 ppm); -Si-$\boldsymbol{C}$H$_2$- (δ=14.58 ppm); Si-CH$_3$-$\boldsymbol{C}$H$_2$- (δ=23.77 ppm); -CH$_2$-$\boldsymbol{C}$H$_2$-O-$\boldsymbol{C}$H$_2$- (δ=73.00~74.00 ppm); -$\boldsymbol{C}$H$_2$-NH$_2$ (δ=42.00 ppm).

Analysis of Main Factors Affecting Properties of ATSO-PDE. Ammonia Value: The effects of different ammonia values of ATSO-PDE on the properties of the treated fabrics were investigated. The synthetic recipe of ATSO-PDE was shown in Table 1. The results are shown in Table 2 and Figure 3.

It can be seen from Table 1 that the ammonia value was from 0.40 to 0.96 mmol/g with the increase of ATS. Different ammonia values showed different properties on cotton fabric in Table 2 and Figure 3. When the ammonia value was 0.96 mmol/g, the ring opening reaction was carried out with more reaction center, which resulted in a high proportion of polyether segment in the structure and led to a higher adsorption and permeability to the fiber during finishing. The *WC* value of treated fabric was 0.242 N·cm/cm^2 which expressed an excellent fluffiness. When ammonia value was 0.70 mmol/g, vertical bending rigidity was 0.0812 gf·cm^2/cm which expressed a best softness of the fabric. When ammonia value was 0.40 mmol/g, the active center involved in capping reduced. The adsorption and permeability of the emulsion were also reduced during finishing. The most obvious change was slip property. The value of *SMD* changed from 0.276 to 0.190, and the style of the fabric changed as Figure 3 showed. The performance of ATSO-PDE on cotton fabric was closely related to the molecular weight of the silicone segment, the polyether



Scheme 3. Expected molecular structure of ATS.

Table 2. Effect of Ammonia Values of ATSO-PDE on Properties of the Treated Fabric

No.	*SMD*	*B* ($gf\cdot cm^2/cm$)		*WC* ($N\cdot cm/cm^2$)	*RC* (%)
		Vertical	Latitude		
Untreated fabric	0.276	0.1426	0.0544	0.188	56.51
1	0.217	0.1006	0.0331	0.242	79.62
2	0.195	0.0812	0.0254	0.235	73.08
3	0.205	0.0907	0.0285	0.233	71.80
4	0.208	0.0859	0.0249	0.216	73.71
5	0.190	0.0912	0.0266	0.228	73.84

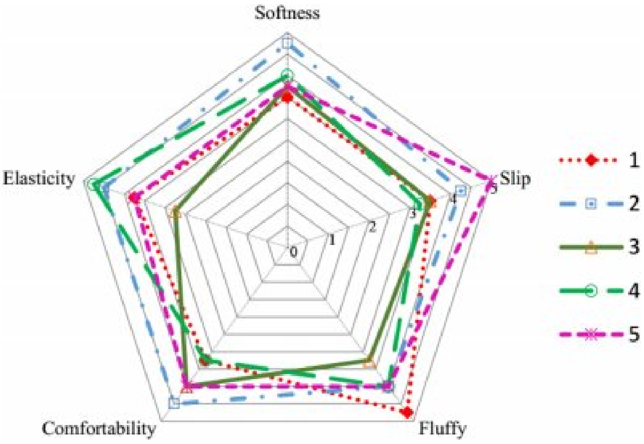


Figure 3. Subjective evaluation method on treated fabric properties.

segment and the ammonia value. Combined with the assumed distribution model in Figure 4,[12] the amino group in the silicone segment was easily protonated to make it positively charged and directional adsorption on cotton fiber. The polyether segment was a hydrophilic segment which had a certain adsorption effect on cotton fiber. When the ammonia value was 0.96 mmol/g (Figure 4(b)), there were many amino groups and polyether segments in molecular chain. One part was uniformly adsorbed on the surface of the fiber, and another part penetrates into the amorphous region of the fiber, so that the surface of the fiber was smooth and the coefficient of friction between the fibers was reduced. But the silicon segment was short and did not bend and rotate well. So the appearance properties of the fabric were soft and fluffy. When the ammonia value was 0.57 mmol/g (Figure 4(a)), the growth of the silicon segments allowed the molecular chain to rotate freely. When the ammonia value was 0.4 mmol/g (Figure 4(c)), the silicone segment was too long to distribute on the fiber surface evenly, but it was accumulated on the surface. So the smoothness was improved and the softness was decreased.

Ring Opening Reaction Temperature and Time: The ring opening reaction directly affected the properties of the product. So the effect of temperature and time on ATSO conversion rate was analyzed. The effect results of temperature and time are shown in Figure 5 and Table 3. Figure 5(a) is the change in conversion rate of ATSO with reaction temperature and time. The conversion rate of the reaction was calculated approximately by the data of viscosity:

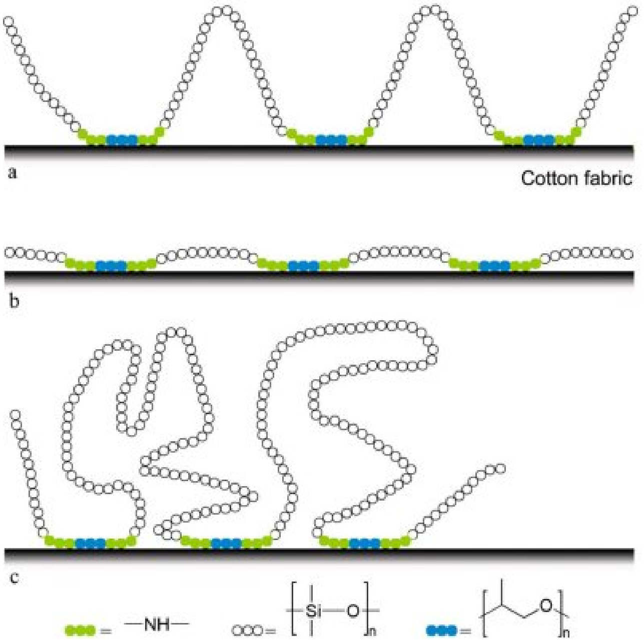


Figure 4. Assumed distribution model of ATSO-PDE with different ammonia value on cotton fiber: (a) ammonia value is 0.57 mmol/g; (b) ammonia value is 0.96 mmol/g; (c) ammonia value is 0.4 mmol/g.

$$y = \frac{\mu_t - \mu_0}{\mu_t} \tag{2}$$

Where, y: conversion rate (%); μ_t: viscosity at the time of t (mPa.s); μ_0: initial viscosity (mPa.s).

It was assumed that the ring open reaction was a first-order

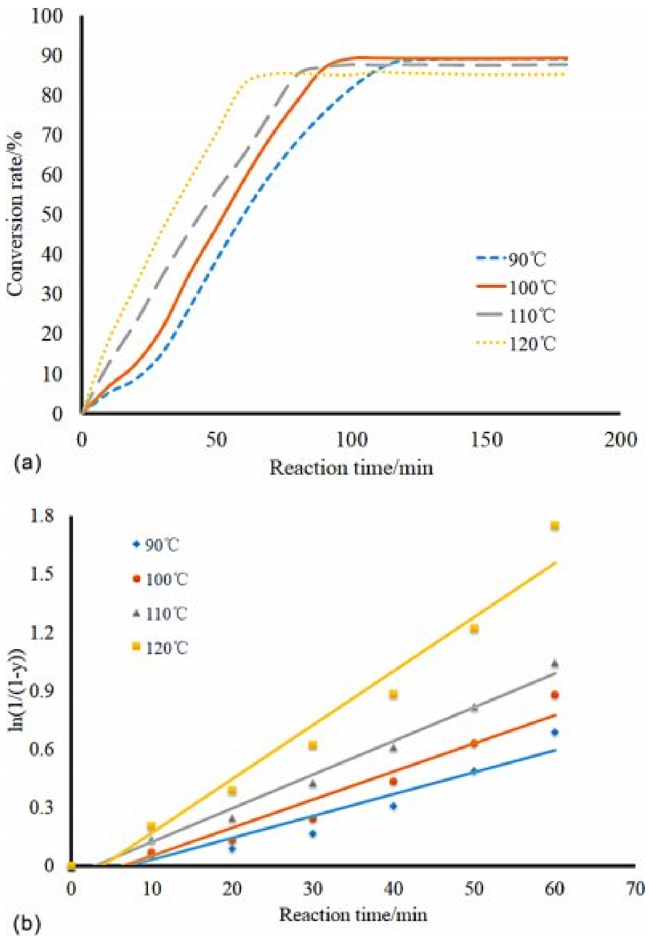


Figure 5. Effect of reaction temperature and time on ATSO conversion rate: (a) the relationship between conversion rate and time; (b) the relationship between 'ln[1/(1 - y)]' and time.

reaction and the experimental data were integrated into the integral formula of the first-order reaction[3];

$$\ln\frac{1}{1-y} = kt \tag{3}$$

Where, y: conversion rate (%); k: rate coefficient (h^{-1}). As Figure 5(b) showed, the reaction temperature has a major influence on the polymerization rate constant of D4. Increase of reaction temperature led to faster reaction rate and decreased the time which the reaction reached equilibrium. In initial stage of ring opening polymerization, the conversion rate was low at 90 °C. With the increase of reaction temperature, the conversion rate increased rapidly. Because of the Si-O bond in D4 was more susceptible to break than the Si-O bond in ATS. So a high final conversion rate could be obtained with the extension of the reaction time at 90 °C. Along with the temperature raised to 120 °C, the end cap reaction rate also increased, which resulted in a decrease of equilibrium conversion rate. Combine with the results in Table 3, the bending rigidity increased and the softness reduced at 120 °C. In summary, the ring opening reaction condition was preferably selected at 110 °C for 2 h.

Physical Properties of Untreated and Treated Cotton Fabrics. The breaking strength and wrinkle recovery angle results of the untreated and treated cotton fabrics are listed in Table 4. The breaking strength of the treated cotton fabrics decreased with the increased concentration. This was attributed to the reduction of fiber surface roughness, the reduction of friction between fibers and the elimination of internal stress.[13] The ordered Si-CH_3 groups in the molecular chain helped to increase the slip of the fiber surface, but the polyether segment in ATSO-PDE destroyed the continuous alignement of Si-CH_3 group, thereby limited the movement of the polysiloxane segment. This is also one of the reasons why the fabric had resilience after treating. It was also found that the whiteness of the cotton fabrics treated by ATSO-PDE (30 g/L) remained similar to the whiteness of the untreated raw samples. Thus, this kind of softener was suitable for color sensitive fabric finishing.

Distribution Pattern, Orientation and Action Model of Silicone Softener on Cotton Fabrics. The adsorption mechanism of ATSO-PDE on cotton fiber could be explained as follows: (1) When cotton fiber was in water, the -OH group in the

Table 3. Effect of Reaction Temperature on ATSO-PDE Treated Fabric Properties

Temperature (°C)	*SMD*	*B* (gf·cm^2/cm)		*WC* (N·cm/cm^2)	*RC* (%)
		Vertical	Latitude		
Untreated fabric	0.276	0.1426	0.0544	0.188	56.51
90	0.205	0.1021	0.0241	0.241	77.46
100	0.193	0.0975	0.0257	0.253	76.55
110	0.190	0.1033	0.0259	0.238	76.32
120	0.192	0.1125	0.0272	0.232	75.86

Table 4. Physical Properties of the Treated Fabrics

	Whiteness (%)	Breaking strength (N)		Wrinkle recovery angle (T+W) (°)	
		Vertical	Latitude	Instant flexibility	Continuous flexibility
Untreated fabric	81.5	625	240	186	208
10 g/L	81.2	608	236	195	212
20 g/L	80.9	593	227	210	220
30 g/L	80.1	567	219	222	237
40 g/L	79.5	516	183	235	241

Figure 6. Adsorption model of ATSO-PDE on cotton fiber.

fiber structure was ionized to make its surface negatively charged, and combined with the positively charged which was formed by amino group; (2) Covalent ether bond between cellulose and amino silicone molecules; (3) Covalent ether bond between amino silicone molecules themselves; (4) Hydrogen bond; (5) Van der Waals forces may exist in the fiber structure and the methyl group on the silicon structure.[9] As Figure 6 showed that the highest orientation distribution of the ATSO-PDE on the surface of the fiber was a single layer covering and the fiber structure played a key role in the orientation distribution of the silicone. Since there were many hydroxyl groups on the surface of the cellulose fiber, the amino group on the silicone chain can be combined. During the rotational movement of the Si-O-Si segment, the molecular chain should be spread as much as possible on the surface, so that the overall surface free energy of the system minimized. It was easy to form a single layer covering where the amino group was combined with the fiber and the methyl group was distributed to the air interface.[14] Due to the strong attraction between the silicone and the surface of the cotton fiber, the atoms in the polymer chain can only move within a small area on the surface of the cotton fiber. The kinetic energy of the molecular chain increased when the chain was subjected to external energy, the orientation of the silicone segment increased and tended to the air interface, and the polyether segment moved toward the fiber surface, so it was macroscopically expressed as a change in the feel of the hand. Moreover, the degree of change will change with the extension of the fabric placement time. As the data shown in Table 5, the softness, slip and elasticity of the fabric increased with the extension of the rest time of the fabric after finishing. As shown in Figure 7, the polysiloxane molecules were distributed in the surface and interior of the finished fibers. After one day, most molecules moved into the cavity, and therefore, the cavity had a higher concentration of polysiloxane molecules. Over time, these molecules migrated again from the lumen to the fibrous body. This also explained why the handle style of the treated fabrics changed with the extension of the placement time.

Table 5. Properties Change of Treated Cotton Fabric Over Time

Time	*SMD*	*B* (gf·cm^2/cm)		*WC* (N·cm/ cm^2)	*RC* (%)
		Vertical	Latitude		
1 day	0.195	0.1021	0.0236	0.248	77.31
1 week	0.208	0.0975	0.0224	0.193	74.62
3 weeks	0.214	0.0925	0.0237	0.202	72.53

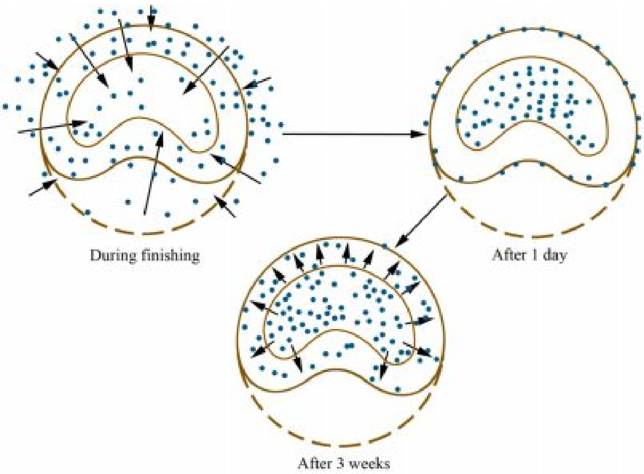


Figure 7. Distribution model of ATSO-PDE on cotton fiber.

Conclusions

A block silicone softener (ATSO-PDE) was synthesized by alkali method with amino terminate polysiloxane (ATSO) and polypropylene glycol diglycidyl ether (PDE) as raw materials. The chemical structure of amino terminated siloxane (ATS) was characterized. The optimal ring opening reaction condition of ATSO was 110 °C for 2 h. The application of ATSO-PDE on cotton fabrics was studied. Results indicated that fabrics treated by high ammonia value (0.70 mmol/g) expressed good softness while the fabrics treated by low ammonia value (0.40 mmol/g) expressed good smoothness.

The adsorption mechanism and orientation distribution of silicone on the fibers were analyzed by the establishment of the orientation distribution model. It was indicated that the different performance and surface morphology of ATSO-PDE were related to the molecular structure and the orientation on the surface, and the constantly moving of the molecular chains as time goes on.

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