

Modification and Application of the Polysiloxane with Amino Groups

Kong-Liang Xie*, Lei Xu, Ya-Qi Shi

Modern Textile Institute, Donghua University, 1882 West Yan-an Road, Shanghai 200051, China

Abstract: A series of the polysiloxanes modified with amino groups are synthesized. FTIR, ¹HNMR are used to characterize the polysiloxane structure. Surface properties of the polysiloxane materials with amino groups are discussed. The results show that the polysiloxanes modified with tertiary amino groups had good flexibility and repellency to water. With increasing the amino value of the polysiloxanes, the flexibilities of the fabrics treated with the emulsion were improved. After the samples were treated with the polysiloxanes, the thermal yellowing had emerged. The whiteness of the fabrics treated with the polysiloxane decreased. The reflectance spectra of the fabrics treated without and with the modified polysiloxanes had not significant change.

Keywords: synthesis, modification, surface properties, fabrics, reflection

1. Introduction

Many silicone compounds are able to reduce the surface energy of materials, which is responsible for many applications. The origins of these unusual and useful properties are closely related to silicones' unique chemistry [1-3]. The hydrophobic character of Si-O segments is well known and commonly used in water repellency. They have received much attention for its attractive properties of good water repellency, lubricity, high flexibility, excellent thermal stability, oxidation resistance and climate resistance, etc. Linear polydimethylsiloxane fluid is one of important industrial silicones. Properties, such as low surface tension, water repellence, and high thermal and chemical stability, make silicone fluid-in-water emulsions useful for impregnating surfaces, as antifoaming agents, fabric softeners, and in many personal, automotive and household care products. The polysiloxane modification using functional polymers or compounds has become increasingly important for a wide range of application [4-6]. The aminofunctional polydimethylsiloxanes open a new dimension for textile softening. They confer high lubricity to the fiber owing to their low surface energy. Aminofunctional groups which are bound to a polydimethylsiloxane backbone improve the orientation and substantivity of the silicon on the fiber. The improved orientation of aminofunctional silicone leads to an extremely soft handle [7-10].

When polyorganosiloxane is modified with amino and hydroxy groups, the modified polyorganosiloxane could form thin film of low reflectance index to change material surface properties. The low reflectance materials have wide application in the color fields [11, 12].

Some of the polysiloxane materials modified with primary or secondary amino group are synthesized. They are frequently named as "supersoft". However, the polysiloxane materials modified with primary or secondary amino group cause the thermal yellowing. The thermal yellowing is of oxidation decomposition of the amino group forming chromophoric group. By comparing the effects of primary, secondary, or tertiary amino, it is clear that whiteness and water absorbency is improved with increasing the degree of substitution, from primary to tertiary. To improve the whiteness and decrease the thermal yellowing have been studied [13,14]. It arises partly from the chemical structure of the amino functional groups.

The polysiloxane modified with functional groups may also be prepared through ring-opening polymerization. All the polysiloxane molecules are insoluble in water. The water-based textile finishing process necessitates the development of adequate polysiloxane emulsions or microemulsions.

* Corresponding author's email: klXie@dhu.edu.cn

Emulsification technology of polysiloxane is very important for its application. The ideal emulsifying agent is the one which is destroyed or rendered inter during the processing of the fabrics. One of the key factors in emulsion stability is proper choice of emulsifier. The selected non-ionic surfactants were used to prepare microemulsions containing more than 30% silicone softener. They can be diluted to the application and provide a soft handle.

In this paper, a series of the polysiloxane materials modified with tertiary amino groups are synthesized through ring-opening polymerization. The emulsions of the modified polysiloxanes are prepared. Some surface properties of the polysiloxane materials are investigated.

2. Experimental

2.1 Materials

Octamethyl cyclotetrasiloxane (D_4) was obtained from Xinghuo Petrochemical Plant of Jiangxi and fractionated under the reduced pressure before used. N, N - (γ -dimethylamino-propyl)- γ -aminopropyl dimethoxysilane (121) was obtained from Zhejiang Dadi Chemicals Co., Zhejiang. KOH (the catalyst of D_4 polymerization) and other chemicals used were obtained from Shanghai Chemical Reagent Plant, Shanghai. Scoured polyester fabrics were obtained from Zhejiang Jinqiu Textile Company, Shaoxing, China.

2.2 Synthesis of The Polysiloxanes Modified with Tertiary Amino Groups

D_4 and KOH were added into the reactor and sufficiently mixed with stirring at room temperature. The polymerization mixture was heated to 85°C for 60 min in nitrogen atmosphere. Then N, N - (γ -dimethylamino-propyl)- γ -aminopropyl dimethoxysilane was added into the reactor according to the ingredients (shown in Table 1). The mixture was heated to 120°C. The polymerization was conducted at 120°C for 7 h. The copolymer was fractionated for 30 min under the reduced pressure. The polysiloxane material modified with tertiary amino side chains was achieved.

Table 1 Ingredients and yields of the polysiloxanes modified with tertiary amino groups [gram]

Samples	D4	121	KOH	Yields [%]
1	98	2	0.5	89.80
2	95	5	0.5	90.76
3	90	10	0.5	88.04
4	80	20	0.5	92.53

2.3 Preparation of The Emulsions of The Polysiloxane with Tertiary Amino Groups

The emulsion agent (nonionic surfactant NP-9), 15 g, was dissolved in 105 ml water. The modified polysiloxane, 30 g, was added and sufficiently mixed with stirring at room temperature for 2 h. The translucent emulsions containing modified polysiloxane, 20%, were achieved. The translucent emulsions according to the ingredient were called S-1, S-2, S-3 and S-4, respectively.

2.4 Aftertreatment

The scoured polyester fabrics were padded with the solutions of 30 g/l polysiloxane emulsions 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 cure time was 1.5 min. In order to compare, the sample without the aminofunctional polysilixane was cured under the same condition.

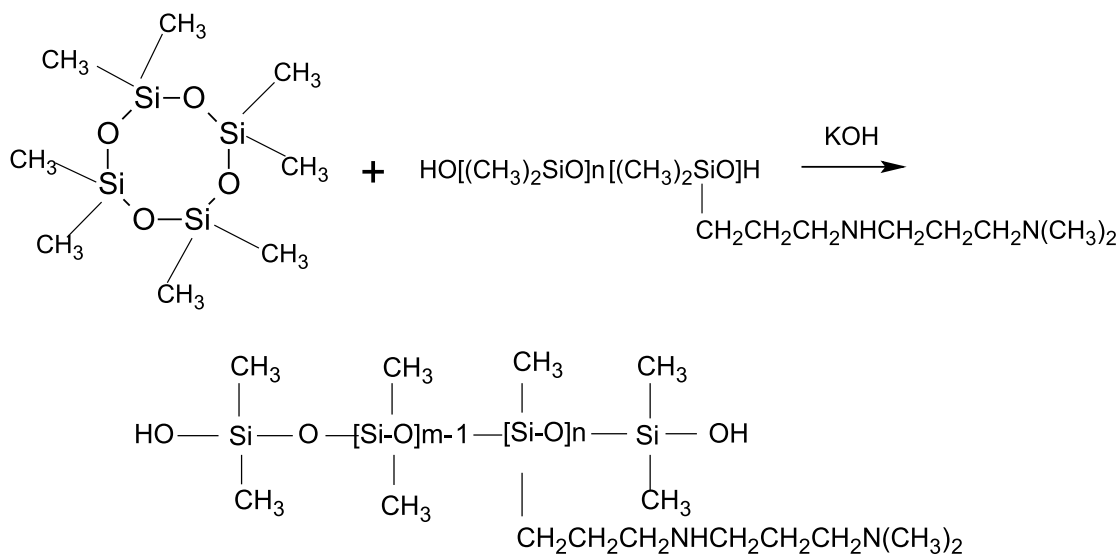
2.5 Measurements

FTIR spectrum of the copolymer was measured by NICOLET 20 DXB FTIR. ^1H NMR spectrum was recorded on a Bruker AV 400 (Bruker Co., Faellanden, Switzerland). The contact angle was measured using an automatic video contact angle testing apparatus OCA 40 (Dataphysics Co., Germany). The whiteness of the fabrics were determined by Datacolor SP600⁺ spEctrophotometer (datacol/r, USA). The handle of the samples was tested according to ASTM D1388 test method [15].

3. Results and Discussion

3.1 Synthesis of The Modified Polysiloxanes and Preparation of The Emulsions

The polysiloxane modified with functional groups may be prepared through ring-opening polymerization. Octamethyl cyclotetrasiloxane (D4) and N, N - (γ -dimethylamino-propyl)- γ -aminopropyl dimethoxysilane (121) can copolymerize using KOH as catalyst. The polymerizing reaction is shown in Scheme 1. The ingredients and the yields of the polysiloxanes modified with tertiary amine groups are shown in Table 1.



Scheme 1

FTIR and HNMR spectra of the polysiloxane 4 are measured. The IR spectrum of the polysiloxane is shown in Figure 1. It can be seen that the sharp bands at 1020 cm^{-1} and 1093 cm^{-1} are the typical signals of Si-O-Si group, the bands at 1020 cm^{-1} and 1261 cm^{-1} are the typical signals of C-N group. HNMR spectrum of the polysiloxane 4 is shown in Figure 2. HNMR spectrum of the polysiloxane shows that the signal for $-\text{CH}_3$ appears at 0.1 ppm, the signal for $-\text{CH}_2$ at 0.5-1.6 ppm and the signal for $-\text{NH}-$ at 1.76 ppm.

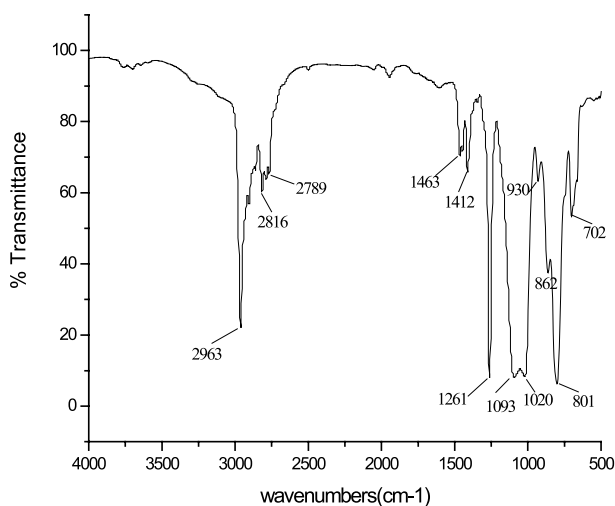


Figure 1 FT-IR of the polysiloxane 4

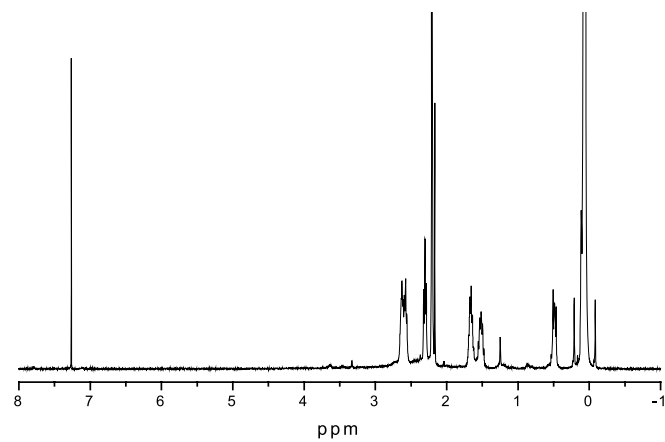


Figure 2 ¹H NMR spectrum of the polysiloxane 4

The polysiloxanes modified with tertiary amino groups were emulsified with nonionic surfactant NP-9. The translucent emulsions containing 20% polysiloxane were achieved, respectively. Some properties of the modified polysiloxanes are shown in Table 2.

Table 2 Some properties of the polysiloxanes modified with tertiary amino groups				
Samples	Amines content [mmol/g]	Polysiloxanes content [%]	Emulsifying agent content [%]	Appearance
S-1	0.2	20	10	Translucent emulsion
S-2	0.5	20	10	Translucent emulsion
S-3	1.0	20	10	Translucent emulsion
S-4	2.0	20	10	Translucent emulsion

3.2 Surface Properties of The Treated Fabric with The Polysiloxanes

Scoured polyester fabrics were treated with the polysiloxane emulsions, 30 g/l and 50 g/l, respectively. The contact angles of the treated polyester fabrics with and without the polysiloxane were measured. The contact angle of the polyester fabric without the polysiloxane is 0°. The results are listed in Table 3. It indicates that the samples treated with the polysiloxane emulsions had good repellency to water. With increasing the amino value of the polysiloxane, the repellency to water of the fabric treated with the emulsion increased. The thick layer of the aminofunctional polysilixane was formed on the fabric.

Table 3 Contact angles of the polyester fabrics (distilled water) (°)		
Concentration [g/l]	30 [g/l]	50 [g/l]
S-1	95	105
S-2	107	113
S-3	110	116
S-4	111	117

3.3 Handle of The Fabrics Treated with The Polysilixanes Containing Tertiary Amino Groups

Siloxane-containing polymers made the treated materials lubricity and high flexibility. When a certain

amount of silicones were used to treat the fabrics, the surface properties of the fabric had been changed. The handle of the treated samples was tested. The results are displayed in Table 4. It is clear that the handle of the fabrics treated with the aminofunctional polysiloxane was obvious better than that of the fabric without it. As can be seen, chains of the polysiloxane imparted high flexibility for fabric. With increasing the amino value of the polysiloxane, the flexibility of the fabric treated with the emulsion improved.

Table 4 Handle of the fabrics treated without and with the modified polysiloxanes

Samples	Bending length	
	Warp [cm]	Weft [cm]
Without	18.10	22.67
S-1	17.85	21.83
S-2	17.60	21.14
S-3	17.55	20.95
S-4	17.00	20.44

3.4 Effect of The Polysiloxane with Tertiary Amino Groups on The Thermal Yellowing of The Fabrics

Reflectance spectra and K/S of the samples treated without and with the polysiloxane containing tertiary amino groups were measured. The reflectance spectra and K/S curves of the treated fabrics are shown in Figure 3, 4. Figure 3 indicates that the shapes of the reflectance spectra curves of the fabrics treated without and with the modified polysiloxanes had not noticeable change. However, Figure 4 indicates that the K/S values of the samples treated with the modified polysiloxanes decreased at 360-460 nm. As can be seen, the thermal yellowing of the polysiloxane had emerged. The whiteness of the fabrics treated with the modified polysiloxane was measured and results shown in Figure 5. It shows that the whiteness of the control sample without the polysiloxanes was the best among all the samples. With increasing the amino value of the polysiloxane, the whiteness of treated fabrics decreased.

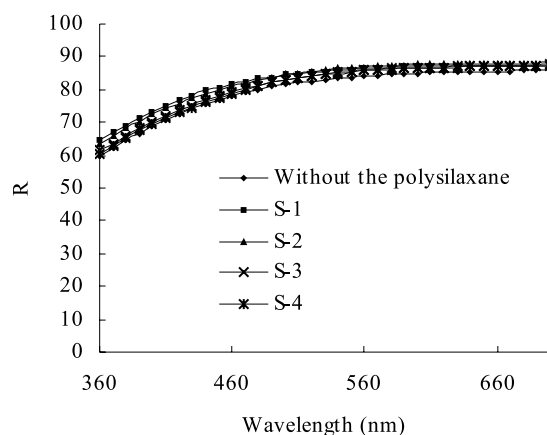


Figure 3 Reflectance spectra of the fabrics

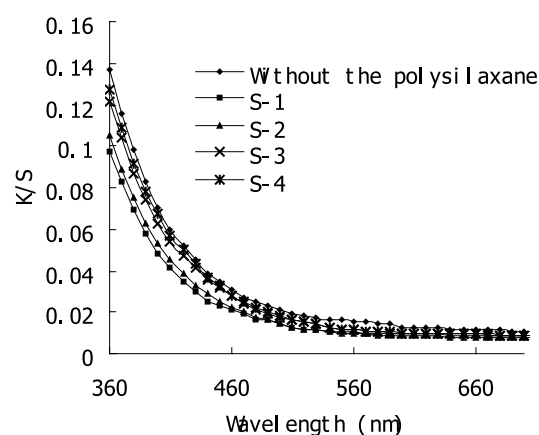


Figure 4 K/S of the samples treated without and with the polysiloxanes

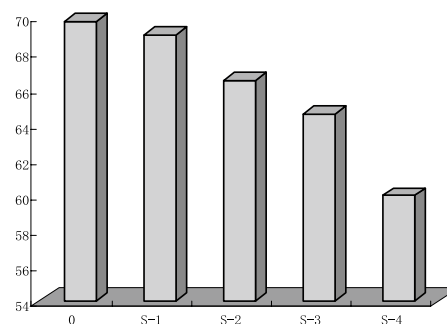


Figure 5 Whiteness of the fabrics treated with the modified polysiloxanes

4. Conclusions

A series of the polysiloxane materials modified with tertiary amine groups were synthesized. They imparted the good flexibility and repellency to water. With increasing the amino values of polysiloxanes, the repellency to water of the fabric treated with the emulsion increased and the flexibility of the fabric treated with the emulsion improved. After treated with the modified polysiloxanes, the K/S values of the samples decreased at 360-460 nm. The thermal yellowing of the polysiloxane had emerged. With increasing the amino value of the polysiloxane, the whiteness of the treated fabrics decreased. The reflectance spectra curves of the treated fabrics without and with the modified polysiloxane had not noticeable change.

References:

- [1] Teixeira ACSC, Guardania R, Braun AM, Oliverosb E, Nascimento CAO. Degradation of an aminosilicone polymer in a water emulsion by the fenton and the photochemically enhanced fenton reactions. *Chem Eng Process* 2005;44:923-931.
- [2] Mazurek M, Kinning DJ, Kinoshita T. Novel materials based on silicone-acrylate copolymer networks. *J Appl Polym Sci* 2001;80:159-180.
- [3] Xie K, Hou A, Zhang Y. New polymer materials based on silicone-acrylic polymer to improve fastness properties of reactive dyes on cotton fabric. *J Appl Polym Sci* 2006;100:720-725.
- [4] Park H, Yang I, Wu J, Kim M, Hahm H, Kim S, Rhee H. Synthesis of silicone-acrylic resins and their applications to superweatherable coatings. *J Appl Polym Sci* 2001;81:1614-1623.
- [5] Yahaya GO, Brisdon BJ, Maxwell M, England R. Preparation and properties of functionalized Polyorganosiloxanes. *J Appl Polym Sci* 2001;82:808-817.
- [6] Xie K, Hou A, Shi Y. Synthesis of fluorine-containing acrylate copolymer and application as resins on dyed polyester microfiber fabric. *J Appl Polym Sci* 2008;108:1778-1782.
- [7] Park K, Koncar V. Diffusion of disperse dyes into super-microfibres. *Color Technol* 2003;119:275-279.
- [8] Xie K, Sun Y. Syntheses and applications of siliconeacrylic polymer novel materials containing cationic groups. *Int J Nonlin Sci Num* 2006;7:477-480.
- [9] Raslan WM, Bendak A. Changes induced in silk like polyester properties by alkoxides treatment. *J Appl Polym Sci* 2005;98:1829-1837.
- [10] Xie K, Yu J, Jiang D. Shade darkening effect of polyorganosiloxane modified with amino and hydroxyl groups on dyed microfiber polyester fabric. *J Appl Polym Sci* 2007;106:1256-1262.
- [11] Xie K, Hou A, Shi Y, Yu J. Surface polymerising of fluoromonomer and shade darkening effect on dyed polyester microfibre fabric. *Color Technol* 2007;123: 293-297.
- [12] Darras V, Fichet O, Perrot F, Boileau S, Teyssie. polysiloxane-poly(fluorinated acrylate) interpenetrating polymer networks: synthesis and characterization. *Polymer* 2007;48:687-695.
- [13] Li K, Wu P, Han Z. Preparation and Surface properties of fluorine containing diblock copolymers. *Polymer* 2002;43:4079-4086.
- [14] Jung A, Wolters B, Berlin P. (Bio)functional surface structural design of substrate materials based on self-assembled monolayers from aminocellulose derivatives and amino(organo)polys iloxanes. *Thin Solid Films* 2007;515:6867-6877.
- [15] Standard test method for stiffness of fabrics. ASTM, Pennsylvania, 2002.p.1388-96.