

Polyurethane Modified with 3-Aminopropyltriethoxysilane as Wool Antifelting Agent

Hu Yi, Ke-Lu Yan

College of Chemistry and Chemical Engineering, Donghua University, Songjiang, Shanghai 201620, People's Republic of China

Received 13 March 2007; accepted 15 January 2008

DOI 10.1002/app.28012

Published online 2 May 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A wool antifelting agent containing polyurethane modified with 3-aminopropyltriethoxysilane (APTES) was synthesized. Firstly an isocyanate ($-NCO$) group ended prepolymer was gained by a hydrogen shift reaction between isophorone diisocyanate (IPDI) and poly(propylene oxide triol) (PPT), and then NCO -group of the prepolymer was blocked by 3-aminopropyltriethoxysilane to form a precursor PPT-[Si(OEt)₃]₃. After that a sol of the precursor was prepared for an antifelting agent. During heating the sol gelled and formed inorganic-organic hybrid film that was characterized by using FTIR and

TGA. And then the wool fabric samples were treated with sol by pad-dry-cure process at different curing temperature (120, 140, and 160°C). The antifelting effects of different curing temperatures were compared. The results indicated that the new agent could endow a better antifelting effect with the low curing temperature at 120°C and 3 min. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2169–2175, 2008

Key words: 3-aminopropyltriethoxysilane; polyurethane; antifelting finish; thin films; FTIR

INTRODUCTION

Wool is an important raw material in textile process, which can be used to make all kinds of superior fabrics. Because of its shrinking and felting drawback during home laundering, its application was limited. In addition, owing to the high AOX levels produced by using conventional antifelting method such as chlorine/resin process, the researches and techniques focused mainly on the development of non-chlorine shrink-resist treatment.^{1–6}

The polymer-only system based polyurethane product as wool shrink-resist treatment was first developed more than 30 years ago,⁷ probably, the first large scale commercial textile used for bisulfite-blocked isocyanate-terminated polyether polyols for the treatment of woollen fabrics to give antifelting properties. It has been reported that the fabric was treated and fabricated into clothing, and then at relatively higher temperature, pressing resulted in the final crosslinking so that the wool fabrics can be cleaned by laundering rather than dry cleaning.^{8–10}

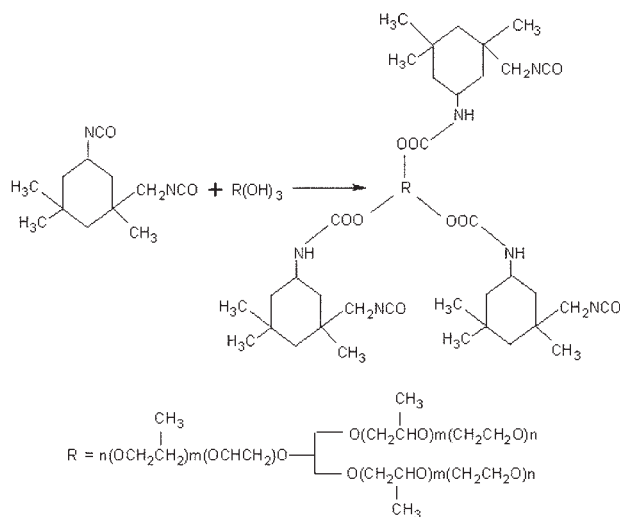
Sol-gel processes, based on the hydrolysis and condensation of metal alkoxide compounds, have various technical applications such as the preparation of special glass, ceramics, and coatings.^{5,6,11–13} Treatment of textile materials with sol-gel process has been studied for application of hydrophilic and hydrophobic coatings on fabrics, for enhancing the wash fastness of direct dyes, for UV blocking of cotton with titanium alcosol, and for application of an antibacterial photocatalyst.^{1,14,15}

Among the various methods of the antifelting finishing on the wool explored up to now, the sol-gel process is a new direction in textile field, especially on wool finishing. The work of Textor et al.^{16,17} proved that sol mixed with nano-alumina could give wool water-resist and antifelting effects. An industrial antifelting process by using GPTMS (3-glycidylpropyltrimethoxysilane) sol was investigated by Ye and Yan¹⁸ and the results showed wool fabric treated with sol-gel technique can obtain a machine-washable property with the curing condition as 180°C and 3 min. It would be convenient if the curing temperature is lower or curing time is shorter.

In this article, a new PPT-[Si(OEt)₃]₃ precursor was synthesized and a sol was prepared with the precursor to decrease curing temperature of wool antifelting treatment. The synthesis of the polyurethane modified with 3-aminopropyltriethoxysilane would be fully explored by FTIR spectra and thermal analysis; Wool fabrics were treated with the sol by different curing temperatures and the antifelting

Correspondence to: K.-L. Yan (klyan@dhu.edu.cn).

Contract grant sponsors: China Australia Wool Innovation Network (CAWIN) project; Australian Wool Producers; the Australian Government (through Australian Wool Innovation Limited).



Scheme 1 NCO group ended prepolymer.

effects were compared, and the effect of antifelting on the wool fabric and other mechanical character was analyzed by the corresponding test methods.

EXPERIMENTAL

Materials

3-aminopropyltriethoxysilane (APTES), polyols (propylene oxide triol) (PPT) (molecular weight: 3500), and isophorone diisocyanate (IPDI) were commercial and industrial grade.

PROTOLAN 367 as a common antifelting agent was supplied by German Rotta Co. PPT was dehydrated by distillation for 1 h at 120°C at 600 mmHg before use. Scoured and undyed 100% wool fabric samples (211 g/m²) were supplied by Chinese Shandong Ruyi Wool Co (JiNing, Shandong Province, China).

Chemical synthesis of precursor PPT-[Si(OEt)₃]₃

Since PPT as a raw material prepared of polyurethane in common use in our laboratory, which is easy to purchase in our local corporation. We chose it as its molecular formula is apt to our experiment requirement.

PPT (65.9 g) and IPDI (13.2 g) (PPT : IPDI = 1 : 3.15M ratio) were added in a four-necked round-bottomed flask equipped with a stirrer, an N₂ inlet, and a cooler/heater.⁵ After the reaction temperatures were increased to 100°C, 0.05 g dibutyltin dilaurate (DBTDL) dropped into the flask. The mixture was stirred for about 1 h at 100°C to form a NCO-group ended prepolymer (Scheme 1). The reaction end was decided by the content of NCO-group that was measured by titration with di-*n*-butylamine. After cooling the prepolymer to ambient temperature, stoichiometric amounts of 3-aminopropyltriethoxysilane (APTES) (NCO : APTES = 1 : 1.05, molar ratio) were added and mixed into prepolymer by stirring and was heated at 60°C for 30 min. So that the NCO-group ended prepolymer was blocked by 3-aminopropyltriethoxysilane and a precursor PPT-[Si(OEt)₃]₃ was synthesized (Scheme 2).

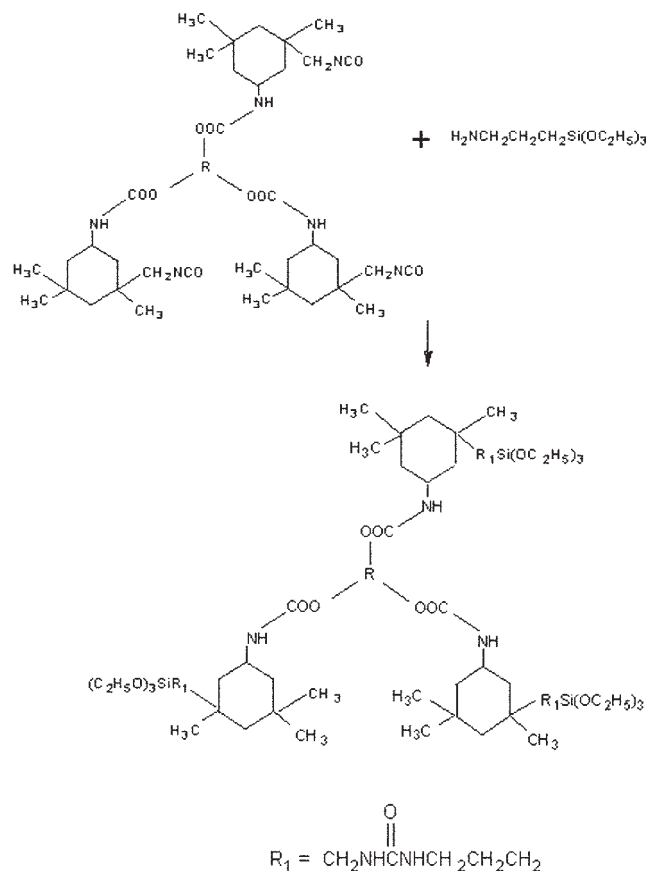
chometric amounts of 3-aminopropyltriethoxysilane (APTES) (NCO : APTES = 1 : 1.05, molar ratio) were added and mixed into prepolymer by stirring and was heated at 60°C for 30 min. So that the NCO-group ended prepolymer was blocked by 3-aminopropyltriethoxysilane and a precursor PPT-[Si(OEt)₃]₃ was synthesized (Scheme 2).

Preparation of sol from PPT-[Si(OEt)₃]₃

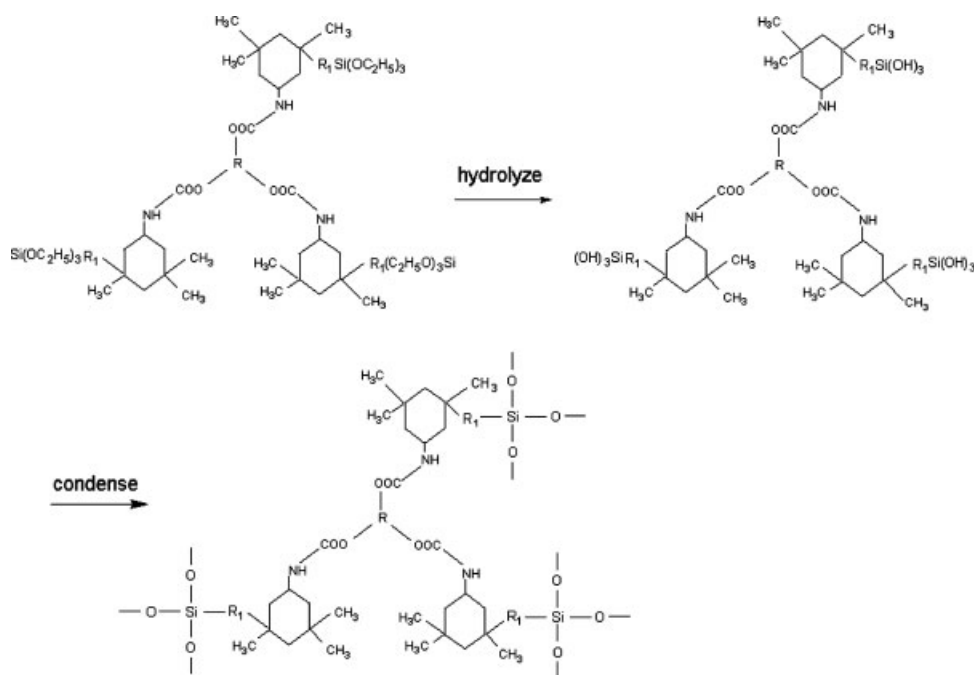
To prepare a sol from precursor PPT-[Si(OEt)₃]₃ (hydrolyzing reaction in Scheme 3) for antifelting agent, the precursor PPT-[Si(OEt)₃]₃, water, and ethanol (PPT-[Si(OEt)₃]₃ : H₂O : C₂H₅OH = 0.01 : 1.78 : 3.47, molar ratio, weight concentration 20%) were added into a four-necked round-bottomed flask, while adjusting pH value to 5–6 with stoichiometric amounts of 0.1M HCl, then violently stirring at ambient temperature for 2 h and then stored for 10 h.

Preparation of an organic-inorganic hybrid film

An organic-inorganic hybrid film was produced the sol from PPT-[Si(OEt)₃]₃ by dropping on a glass plate. After drying at ambient temperature for 1 day, the gelation was achieved and a sticky plate was



Scheme 2 NCO group ended prepolymer blocked by APTES.



Scheme 3 Hydrolysis and polycondensation reactions of PPT-[Si(OEt)₃]₃ to form organic-inorganic hybrid materials.

obtained. The translucent and solid film of an organic-inorganic hybrid material was formed after the plate was heated from 40 to 100°C and then kept at 100°C for 3 h (condensing reaction in Scheme 3). To investigate the thermal characteristics of the hybrid material, PROTOLAN 367 was selected as the reference, the film was prepared by the aforementioned methods.

Treatment on wool fabrics

Wool sample was treated by the sol from PPT-[Si(OEt)₃]₃ with pad-dry-cure process (bath ratio 20 : 1, pH value of 5–6, and pick up of 70–80%). Then the samples were dried at 80°C for 3 min and cured separately at different temperatures (120, 140, and 160°C) for 3 min.

Characterizations

FTIR spectra meter (Avatar 380 FTIR, American Nicolet Instrument Co.), SEM (JSM-5600LV, Japan JEOL Co.), and thermogravimetry analyzer (TGA-209F₁, NETZSCH Instruments Co., under a N₂ flow and heating rate of 10°C/min) were employed to characterize the properties of materials.

Measurements

The content of NCO group was measured by titration with di-*n*-butylamine. Shrinkage ratio tests were carried out with a standard washing machine Wasicator FOM71 CLS, Electrolux, using the ISO 6330

3*5A wash cycles program, as described in IWS Test Method 31. The shrinkage was measured by the standard procedure except that the sample size (20 × 20 cm) differed from that specified in the test (50 × 50 cm). The area shrinkage was measured as follows:

Area dimensional change (%)

$$= WS + LS - (WS \times LS)/100$$

where WS is the mean width direction size (%) and LS is the mean length direction size (%).

Dry wrinkle recovery angles were measured according to AATCC test method 128-1985. Tensile strength and tear strength were measured according to ASTM 5034-95 and the Elmendorf method (ASTMD 1424-96). The fabric whiteness was measured by using a WSB-2 d/o whiteness meter. The whiteness and wrinkle recovery angles (WRA) of the treated samples were measured before washing, and all samples were conditioned for 24 ± 4 h at 65 ± 2% relative humidity and 21 ± 1°C before measuring.

RESULTS AND DISCUSSION

Synthesis of precursor PPT-[Si(OEt)₃]₃

Scheme 1 is a hydrogen shift reaction between IPDI and PPT, resulting in urethane coupling between their molecules. Since the molar ratio between IPDI and PPT is 3.15 : 1, an isocyanate (—NCO) group

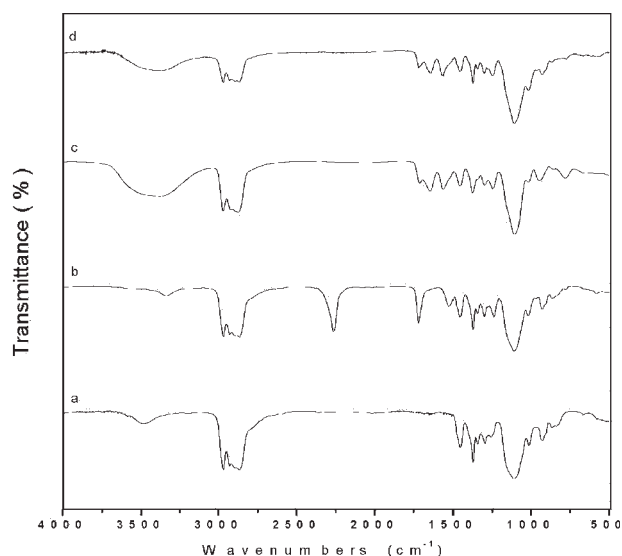


Figure 1 FTIR spectra of a PPT (3500) b Prepolymer c PPT-[Si(OEt)₃]₃ d the organic-inorganic hybrid materials.

ended prepolymer was gained. Scheme 2 is a blocking reaction of NCO-group on prepolymer by 3-aminopropyltriethoxysilane. In this reaction, —NCO groups of prepolymer with the amino-groups of 3-aminopropyltriethoxysilane form carbamido linkage and a precursor PPT-[Si(OEt)₃]₃ was synthesized.

To confirm the above reactions, the prepolymer and precursor were characterized with FTIR.^{19,20} The FTIR spectra of PPT (a) and prepolymer (b) were shown in Figure 1. Graph (a) shows a distinct absorption peak at 1100 cm⁻¹ in the region of —C—O—C stretching for ether groups and the peak at 3480 cm⁻¹, which confirms the existence of —OH groups. The peak at 2265 cm⁻¹ in Graph (b) of Figure 1 proved an existence of —NCO groups' and the peak at 3336 cm⁻¹ (ν_{NH}) and 1718 cm⁻¹ ($\nu_{\text{C=O}}$) confirms the existence of urethane groups. The FTIR spectra of PPT-[Si(OEt)₃]₃ is in Graph (c) of Figure 2. In Graph (c), it can be seen the characteristic bands of carbamido groups at 1644 cm⁻¹ appears and the peak at 2265 cm⁻¹ of —NCO groups disappears' which proves —NCO group was blocked with 3-aminopropyltriethoxysilane.

FTIR spectra and thermal stability of the hybrid materials

Figure 1(d) shows the FTIR spectra of the organic-inorganic hybrid film. It seems that there is no considerable change in the intensity of this absorption band between the hybrid films [Fig. 1(d)] and the precursor PPT-[Si(OEt)₃]₃ [Fig. 1(c)]. This is possibly due to the complexity of the spectra: $\nu_{\text{Si-O-Si}}$, $\nu_{\text{Si-O-C}}$, and $\nu_{\text{C-O-C}}$ which are all in the region of 1050–1150 cm⁻¹, so that the contribution of newly formed Si—O—Si bands and organic C—O—C

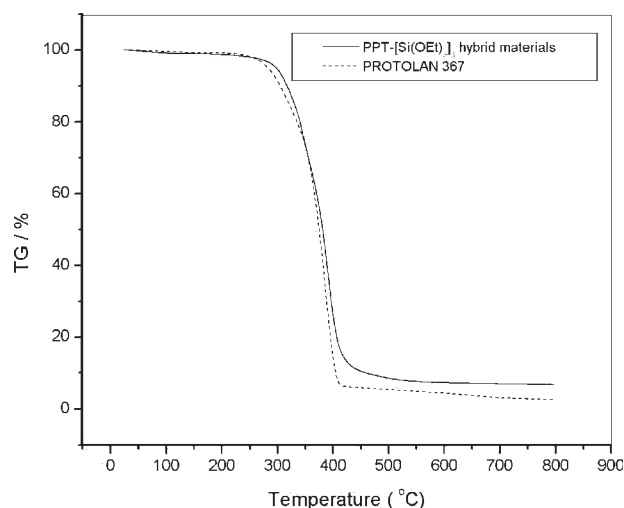


Figure 2 TGA of the organic-inorganic hybrid materials and PROTOLAN 367.

bands among the hybrid films cannot be clearly distinguished.

To compare the thermal stabilities of the organic-inorganic film with organic material of PROTOLAN 367, thermogravimetry analyzer (TGA) was used and the analyzed results are shown in Figure 2. It can be seen in Figure 2 that the PPT-[Si(OEt)₃]₃ residual mass was 6.69% while that of PROTOLAN 367 was 2.68% at 800°C.

TGA thermogram of the hybrid films reveals that the thermal degradation behavior of the hybrid materials and PROTOLAN 367 with one stage and the start thermal degradation temperature is 343.4 and 339.5°C. To show this stage more clearly, DTG results of the hybrid films shows that the weight loss peak of hybrid materials is 391.0°C (Fig. 3) whereas the weight loss peak of PROTOLAN 367 is 383.5°C (Fig. 4). Consulting the thermogravimetric

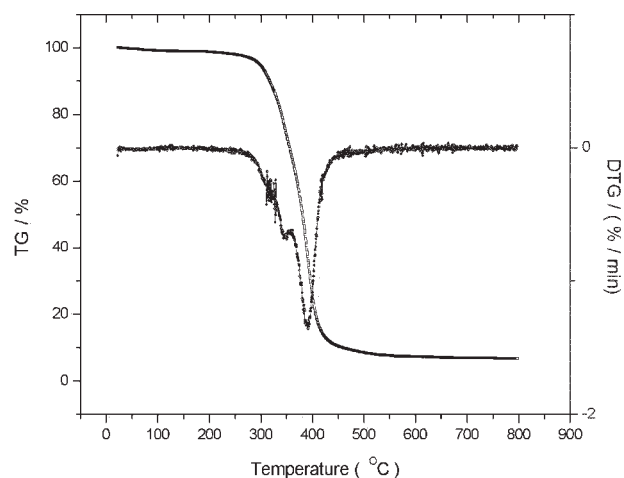


Figure 3 TGA and DTG of PPT-[Si(OEt)₃]₃ hybrid materials.

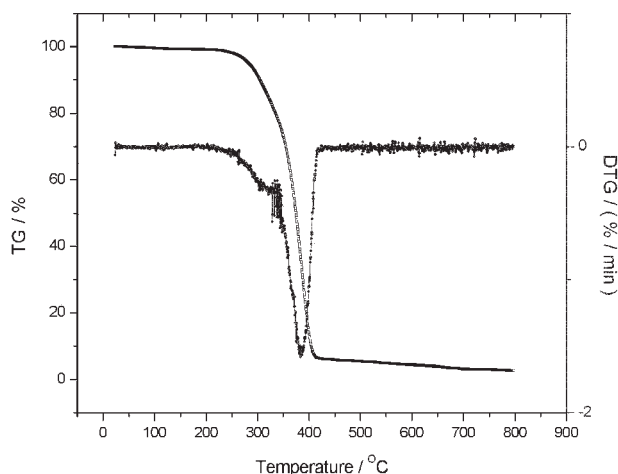


Figure 4 TGA and DTG of PROTOLAN 367.

observations of hybrid films, the degradation stage of the hybrid materials may be caused by the cleavages of relatively unstable groups such as the urethane groups of the hybrid materials. With the results of the thermogram information about the hybrid materials, it is clear that the thermal stabilities of the organic–inorganic hybrid film and organic material of PROTOLAN 367 are similar. This means the thermal property is changed greatly when inorganic ceramic is modified with organic groups. Comparing with the application of PPT-[Si(OEt)₃]₃ sol coatings in lower temperature of 120–160°C and by a simple technique of pad-dry-cure process, the coating with ceramic requires huge technical effort and very high temperature (>900–1000°C).

Antifelting effect of treated wool fabrics

The antifelting effect of wool treated with PPT-[Si(OEt)₃]₃ sol is shown in Table I. Under weak acid condition, the treatment with PPT-[Si(OEt)₃]₃ sol at curing temperature 120°C and 3 min can endow an obvious antifelting effect with the area-shrinking rate of 1.469% while the untreated fabric has a area-shrinking rate of 12.738%. The treatments with the

sol have also good effects with an area-shrinking rate of 1.225% and 0.982% under curing temperature 140 and 160°C, respectively.

The method according to ISO6330 was used to determine dimensional changes in treated fabric samples. The fabrics were washed in an Electrolux Wascator FOM71 washing machine, wash program 5A for felting shrinkage testing at 40°C with a standard detergent, and the 5A wash cycle was repeated three times to Woolmark Total Easy Care standards. In the light of the above washing tests, the felting shrinkage of treated samples and references was determined. In Table I, the values of shrinkage in width and length after third washing are shown. For all the fabrics, the felting behavior is improved by the agent treatment and a degree shrinkage of the treated sample after the third washing is less than 3%, the value was measured according to IWS TM 31 and satisfied the standard washing test (IWS TM 31) demand. With the antifelting effect, the fabrics with better durability are achieved inevitable.

According to the Ref. 3, wool fibers are covered by a layer of overlapping scales (the cuticle), which have their exposed edges pointing toward the tip of the fiber. This cuticular structure results in frictional constraints on fiber movement in the direction of the fiber tip but not in the direction of the root; therefore, the effect of random forces transmitted to the fibers during washing causes fibers to slip over each other and move preferentially in the root direction. PPT-[Si(OEt)₃]₃ sol as a reactive agent is capable of undergoing self-crosslinking reaction at curing temperature, i.e., the function group of the agent is Si—OH group, which can condensate or gel under acid conditions to crosslink each other during curing, which form a thin layer on the surface of wool fibers and cover the scales. Moreover, the Si—OH group of the sol can also react with the active groups of the wool fabric, such as —NH₂, —OH, —SH, etc., to form firm covalently bonds. With the above analysis, we can conceive of the results that the fiber migration during washing will be inhibited in the manner described earlier for the agent treatment and

TABLE I
The Area-Shrinking Rate, Bending Length, and Whiteness of the Wool Fabrics^a

Sample	Curing temperature (°C)	The area-shrinking rate (%)			Bending length (cm)	Whiteness (%)
		Total	LS	WS		
Untreated ^b	— ^c	12.738	7.766	5.391	2.18	49.6
	120	1.469	1.096	0.373	3.24	47.7
Treated ^d	140	1.225	1.104	0.121	3.30	46.3
	160	0.982	0.884	0.098	3.38	44.2

^a Applied by pad-dry (3 min, 80°C), cure (3 min).

^b Untreated wool fabric.

^c Temperature corresponding to ISO 6330 3*5A wash cycles program required.

^d Treated wool sample with concentration 20% sol.

TABLE II
The Physical Performance of the Wool Fabrics^a

Sample	Curing temperature (°C)	Dry WRA degree (°)	Tensile strength		Tear strength (N × 10 ⁻²)	
			E (mm)	W + F (N)	W	F
Untreated ^b	— ^c	266.0	100.712	492.0	14,309.9	28,808.8
	120	289.0	110.795	470.3	17,448.0	24,477.4
Treated ^d	140	287.0	107.594	499.2	15,188.5	27,615.5
	160	294.5	112.642	501.2	11,297.3	24,602.9

^a Applied by pad-dry (3 min, 80°C), cure (3 min).

^b Untreated wool fabric.

^c Temperature corresponding to ISO 6330 3*5A wash cycles program required.

^d Treated wool sample with concentration 20% sol.

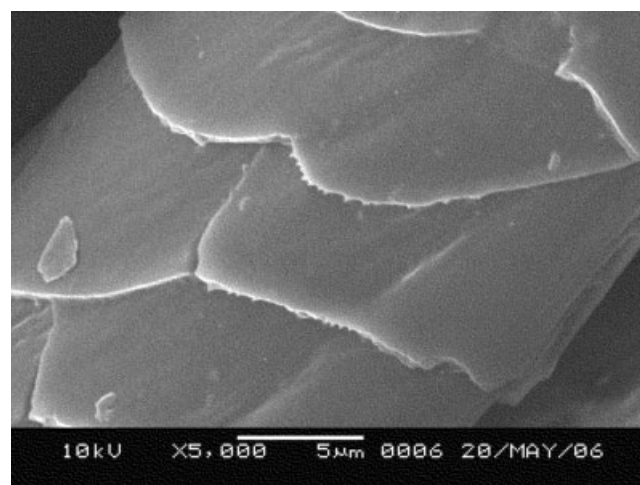
the antifelting effects will be reinforced by the inter-fiber connections of polymer.

The whiteness and mechanical properties of the treated wool

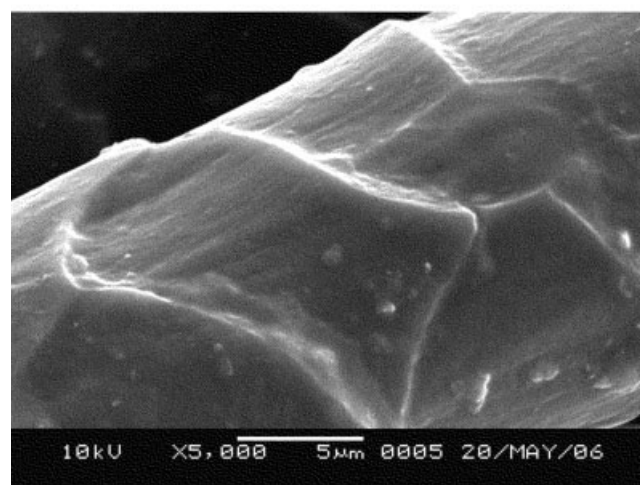
From Table I, the whiteness of the treated wool was decreased as the curing temperature increased and the treatment with curing temperature in 120°C has a minimum change in whiteness. Thermal oxidation during curing process is prone to decrease whiteness as the curing temperature increased, the reasons is due to tyrosine (a phenol), which may give rise to phenoxyl radicals, and thereby, to oxidative coupling, e.g., production of dityrosine, etc. Such a process is favored when the phenolic group is ionized and lead the fabrics yellow obviously with the increased curing temperature²¹ and therefore, the fabrics whiteness is decreased normally.

In Table II, the wrinkle recovery angles of wool fabric increase with the agent posttreatment, and the values are higher than the agent-only treated samples. In addition, the values are increased obviously with increasing the curing temperature from 140 to 160°C. The improved wrinkle recovery of the wool fabric obtained with the surface postapplication of a polymer is attributed to the formation of interfiber and interyarn connections. These elastic connections are believed to stretch when the fabric is deformed and then, during recovery, they help the fabric overcome the component of residual deformation. This severely restricts the fiber–fiber movement in bending, so that there is a rise in bending rigidity (in Table I). Such elastic interfiber connections contribute load-bearing elements to the fabric that not only inhibit fiber movement but also aid recovery from deformation and reduce the residual strain after deformation. The tensile strength increased slightly with increasing curing temperature can be attributed to the formation of an elastic network on the fiber surface. Moreover, due to the value of picks per inch less than ends per inch of the samples, so the tear strength results varied in W and F direction and the

former value is less than the later one. With the above analysis, the bending lengths of the treated fabrics are increased, which means the handle of the



(a)



(b)

Figure 5 SEM of the wool fabrics surface morphology (a) untreated wool fabrics and (b) treated wool fabrics (treating condition 20% concentration and curing temperature 120°C at 3 min).

treated wool fabrics becomes harder than that of the untreated fabrics. The value of the tensile strength, tear strength, and dry wrinkle recovery angles of the wool samples treated by the sol with different processes do not differ significantly (Table II), which indicates that different treating ways cannot affect the strength of wool fabric.

SEM observation

Compared SEM photograph (a) with (b) in Figure 5, the surface of the treated wool fibers was coated with a thin layer and scales of wool fibers were covered. In addition, the scale edges of treated fibers are blunt obviously, which could decrease DFE of wool fabrics and a better antifelting effect was obtained (Table I).

CONCLUSIONS

A wool antifelting agent containing polyurethane modified with 3-aminopropyltriethoxysilane (APTES) was synthesized as a precursor PPT-[Si(OEt)₃]₃. A sol of the precursor was prepared for an antifelting agent. The agent could endow a better antifelting effect with the area-shrinking rate of 1.469% under curing temperature in 120°C and 3 min while the untreated fabric has an area-shrinking rate of 12.738%. The treatment with the agent has also a good effect with an area-shrinking rate of 1.225% and 0.982% under curing temperature 140 and 160°C, respectively. With the SEM observation, the cuticle of the treated wool fibers shows a thin polymer layer deposit. The thermal stabilities of the agent and PROTOLAN 367 are similar. As the curing temperature increased, the whiteness of the treated wool was decreased and the wrinkle recovery angles of wool fabric rised, especially, the wrin-

kle recovery angles increased obviously with the temperature from 140 to 160°C. Moreover, the increased tensile strength and the bending length can be attributed to the formation of an elastic network on the fiber surface. The tear strength results varied in *W* and *F* direction and the former value is less than the later one.

The authors acknowledge support for this work via a project titled "A new method of sol-gel technique for shrink-resist treatment" under the China Australia Wool Innovation Network (CAWIN) project.

References

1. Yan, K. L.; Song C. Proc 3rd China Int Wool Text Conf 2002, 2, 519.
2. Xu, P.; Wang, W.; Chen, S.-L. AATCC Rev 2005, 5, 29.
3. Lewin, M.; Sello, S. B. Handbook of Fiber Science and Technology; Marcel Dekker, Inc., NY, USA, 1984; Vol. 2, p 331.
4. Luo, M.; Zhang, X. L.; Kong, Y. K. Y. Text Res J 2003, 119, 297.
5. Jiang, W.-C.; Meng, W.-D.; Qing, F.-L. Text Res J 2005, 75, 39.
6. Onar, N.; Sariisik, M. J Appl Polym Sci 2004, 93, 2903.
7. Wu, C.; Xu, T.; Yang, W. J Solid State Chem 2004, 117, 1660.
8. Schumacher, K.; Heine, E. J Biotechnol 2001, 89, 281.
9. Pascual, E.; Julia, M. R. J Biotechnol 2001, 89, 289.
10. Liu, Y.-L.; Su, Y.-H.; Lai, J.-Y. Polymer 2004, 45, 6831.
11. Kang, T. J.; Kim, M. S. Text Res J 2001, 71, 295.
12. Wicks, D. A.; Wicks, Z. W., Jr. Prog Org Coat 2001, 41, 39.
13. Roberts, G. A. F.; Wood, F. A. J Biotechnol 2001, 89, 297.
14. Mahltig, B.; Böttcher, P. Text Res J 2004, 74, 521.
15. Guise, G. B. J Appl Polym Sci 1977, 21, 3427.
16. Textor, T.; Bahners, Th.; Schollmeyer, E. Proc 10th Int Wool Text Res Conf 2000, 12, 1.
17. Textor, T.; Bahners, Th.; Schollmeyer, E. Melliandtextilberichte 1999, 10, 229.
18. Ye, Z.-P.; Yan, K.-L. Dye Finish 2006, 4, 11.
19. Barikani, M.; Ebrahimi, M. V.; Mohaghegh, S. M. S. J Appl Polym Sci 2007, 104, 3933.
20. Subramani, S.; Park, Y.-J.; Lee, Y.-S.; Kim, J.-H. Prog Org Coat 2003, 48, 73.
21. Norton, G. P.; Nicholls, C. H. J Text Inst 1964, 55, 9.