

Silane 중합을 통한 면섬유의 개질에 관한 연구

오 경 화

중앙대학교 사범대학 가정교육학과

Modification of Cotton Fibers via In-Situ Polymerization of Silane Monomers

Kyungwha Oh

Dept of Home Economic s Education, Chung-Ang University
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요 약

다양한 유기관능기를 가진 Silane 가교제의 기능 양면성과 독특한 화학적 구조는 이들이 면섬유의 물성을 향상시키기 위한 in-situ 중합 및 가교처리의 단량체로 사용될 수 있는 가능성을 시사하므로, 본 연구에서는 이를 위한 기초 실험으로 수용액 상의 silane 단량체의 거동과 in-situ 중합의 가능성을 조사하였다. 관능기를 달리하는 methyltriethoxysilane (MES), vinyltriethoxysilane (VES), vinyltriacetoxysilane (VAS)과 epoxy (glycidoxy) propyltrimethoxysilane (EMS) 등이 silane 단량체로 선택되었다. Silane 수용액의 안정성과 용해도는 단량체의 농도가 증가함에 따라 감소하였으며, pH에 의해서도 크게 영향을 받아 pH 3과 4.5사이에서 가장 안정함을 나타내었다. 10분간의 증기 고차과정에 의해서 충분한 양의 단량체가 면섬유 안으로 확산되었으며, 섬유의 방추성은 반응성이 높은 organotin 촉매제를 사용하여 열처리한 후 증가되었다.

I. INTRODUCTION

Methods for improving easy-care properties of cotton fabrics involve the use of bifunctional or multifunctional reagents which can react with hydroxyl groups of cellulose in accessible region^{5,8,11}. As a consequence, crosslinking of cellulose restricts the molecular displacement of the cellulose and thus improves its resilience. The highly valued properties such as wrinkle recovery and dimensional stability, are improved according to the degree of crosslinking. At the same time, however, the extensibility of the fiber is significantly diminished. The fibers

become somewhat more brittle with consequent losses in abrasion resistance, tensile strength, and tear strength^{2,18,20}. Numerous studies have been devoted to improve the balance of fiber resilience and mechanical properties by modifying the crosslinking system. Tesoro¹⁹ stated that the performance properties of durable press finished cotton fibers were significantly affected by substrate, treatment condition, and the crosslinking resin.

Among various durable press finishing, in-situ polymerization and crosslinking (IPC) treatment with nonconventional wet or steam fixation process seems to be an effective technique. It facilitates the deposition of a polymeric resin within the fiber to

retain the stronger deconvoluted form and provides subsequent crosslinking between the fiber and resin to improve fiber resilience^{5,15}. Previous studies have shown that the success of IPC was significantly dependent upon selecting a suitable monomer as well as controlling treatment conditions.

N-methylacrylamide (NMA) has been widely used in IPC system^{5,9,16,18}. However, it was also noted that NMA had potential problems in terms of excessive crosslinking and formaldehyde release.

Recent studies^{1,6,13} on silane coupling agents indicated that they provided good crosslinking among silicone polymers, as well as with cellulose. It has been known that polysiloxanes are obtained from these silane monomers by hydrolyses followed by a condensation process^{1,6}. In textile finishing, silane monomers are generally used in form of polysiloxanes as softeners or water repellents^{3,7,11}. However it has been proposed that in-situ polymerization of silane monomers would provide more advantage, in terms of durability and reactivity than direct application of siloxane polymer¹⁷.

The general formula of an organosilane shows the two classes of functionalities, $R_nSiX_{(4-n)}$, where R is an organofunctional group attached to silicon in a hydrolytically stable manner, and X designates hydrolyzable groups which are converted to silanol groups on hydrolysis^{1,6}. The dual functionalities of organofunctional silane monomers and their unique chemical structure provide the potential use as monomers in the in-situ polymerization and crosslinking of cotton fiber.

The objective of this study is to investigate the feasibility of using silane coupling agents as monomers in the in-situ polymerization and crosslinking with cellulose were investigated. These parameters included monomer and initiator concentration, steam fixation time and temperature, catalyst type and curing temperature and time. Treated fiber samples were evaluated in terms of retention of mechanical properties and improvement of fiber

resilience. In addition, scanning electron microscopic analysis (SEM) and x-ray electron probe microanalysis (EPMA) were utilized to evaluate the effect of treatment on the fiber morphology and the location of silicon in the fiber.

II. EXPERIMENTAL PROCEDURES

1. Materials

A desized, scoured, and bleached 100% cotton fiber web weighing 98.4 g/m², was used as a substrate in this study. This web, obtained from the cotton Inc., were prepared with a hydro-entanglement method at 2.41×10^6 Pa water pressure. Silane monomers selected were vinyltriethoxysilane (VES) from Union Carbide, methyltriethoxy-silane (MES), vinyltriacetoxysilane (VAS), and epoxy (glycidoxy) propyltrimethoxy silane (EMS) from Dow Corning. Organotin catalyst containing dioctyltin bis (isooctyl-mercaptoacetate) as active material, was obtained from Dow Corning. Potassium persulfate (KPS) obtained from a commercial source, was used as a free radical initiator. A nonionic wetting agent and all other chemical used were reagent grade.

2. Rate of Hydrolysis/polymerization

The determination of the relative rates of hydrolysis or polymerization of silane monomers was carried out following the modified method of Plueddemann¹³. Aqueous solution of silane was prepared by shaking silane monomer vigorously with 100 ml of Elenmeyer flask. The pH of the solution was adjusted with hydrochloric acid, acetic acid, or sodium hydroxide as measured with a pH meter standardized with standard buffer solutions (pH=4, pH=10). Clarity of the solution was checked periodically by placing a printed page under the flask. Rate of the reaction was determined as the time when the printed page could not be read through the flask because of the haze. All experiments were carried at room temperature.

3. Fiber Web Treatment

Samples of the cotton fiber web, 45.7 cm×30.5 cm were treated with the two-step steam fixation technique¹⁷⁾. The steam treatment was carried out in a padder-steamer range at specified temperature and time. The steam fixed sample was mounted on a pin flame and dried at specified temperatures and times in Despatch oven. It was then conditioned and weighted to determine % pick-up. The web sample was placed in a 100% cotton fabric bag and washed in warm water (about 30°C) for 20 minutes. The sample were then dried in the fabric bag for 10 minutes at 120°C, followed by conditioning and weighing to determine % add-on. Percent fixation was then calculated as the ratio of % pick-up to % add-on. Curing of fiber samples was carried out by padding the treated samples through an aqueous bath containing catalyst, then air-dried, and cured at 140°C for 1.5 minutes.

4. Evaluation of the Treated Fiber Webs

1) Tenacity and Elongation

Tenacity and elongation of the treated fiber were measured with a High Volume Instrument (HVI) at the cotton Incorporated Testing Lab (U.S.A).

The comber/brusher technique was used as specified in ASTM D-4604-86.

2) Compression Recovery

A modified method⁵⁾ of ASTM D-612-82 was used to measure the resilience of the cotton fiber web. Compression recovery was measured as:

$$\begin{aligned} \% \text{ Compression Recovery} \\ = [H_2 - H_1 / H_0 - H_1] \times 100 \end{aligned}$$

were, H_0 , H_1 , and H_2 are, respectively the initial, compressed and recovered heights of the sample. In addition, modified compression recovery (CR/work) was calculated from compression recovery value divided by toughness index (work) of fiber.

3) Degree of Crosslinking

Cuene Solubility test⁴⁾ was used for the quantita-

tive determination of the degree of crosslinking of the treated fibers. The regenerated soluble portion of cellulose were measured and the degree of crosslinking was then calculated as follows:

$$W_s = [2S/C_0] \times 100$$

$$\text{Degree of crosslinking (\%)} = 100 - W_s$$

were W_s is the percentage of the soluble cellulose, S is the weight found for the regenerated cellulose, and C_0 is the weight of the original cellulose sample employed.

4) Location of Silicon

JEOL JSM-5400 Scanning Electron Microscope (SEM) was employed to analyze the effects of IPC treatment on the cotton fiber morphology. JEOL JXA-840 A Electron Probe Microanalyzer (EPMA) was also used to confirm the location of silicon within the fiber interior. An associated electron microscope was used to locate the area to be bombarded. Finally, X-rays produced by the electron beam were collimated, dispersed by a single crystal and detected and analyzed with an wavelength dispersive spectrometer. The data from the detector was reduced using a Tracor-Northern 5500 series II, and the imaging program used was Vista. The X-ray intensity map had a resolution of 128×128 pixels.

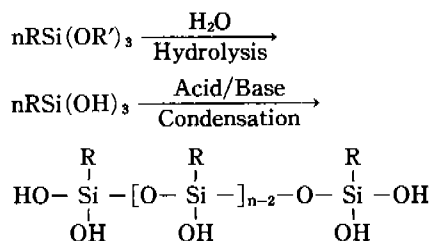
III. RESULTS AND DISCUSSIONS

1. Behavior of Silanes in Aqueous Solutions

In order to select proper bath conditions for in-situ polymerization and crosslinking treatment, the study was first devoted to investigate the behavior of silane monomers in an aqueous bath. Three types of commercial silane monomers were selected based on the solubility, molecular weight, reactivity, boiling point as well as commercial availability. The treatment parameters such as bath pH, monomer concentration were first investigated in an aqueous homogeneous system.

1) Effects of Monomer Concentration

Trialkoxysilanes, $\text{RSi}(\text{OR}')_3$, is known to hydrolyze stepwise in water to give the corresponding silanols, which ultimately condense to polysiloxane as follows¹³⁾:



In consequence, both the rate of hydrolysis and that of condensation are crucial factors affecting the stability of silane monomers in an aqueous solution.

In order to examine the influence of monomer concentration upon the rate of hydrolysis and that of condensation, aqueous solutions containing various concentration of monomers were prepared with acidified water of pH 2.5. For VAS solutions, pH was self-adjusted without addition of acid, since acetic acid was formed as by-product of the hydrolysis of the acetoxy groups on VAS. The rate of hydrolysis was determined as the time necessary for

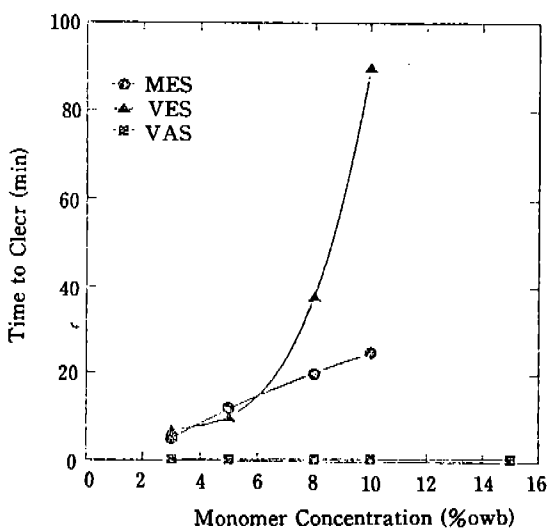


Fig. 1. Rate of Hydrolysis of Silane Monomers.

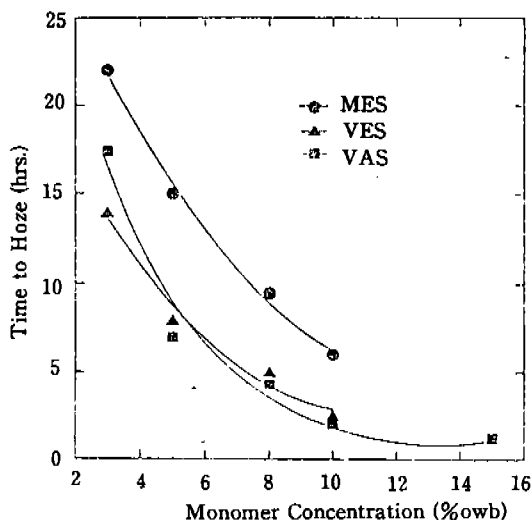
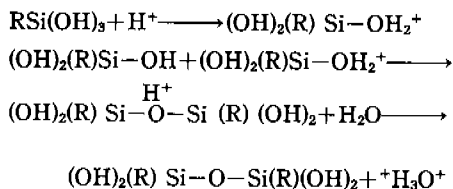


Fig. 2. Stability of Silane solutions at Various Monomer Concentration levels.

the mixture to become a clear solution (time to clear), since the solubility of monomer increased as it was hydrolyzed in aqueous solution. And time to become a hazy solution (time to haze) indicated the stability of trialkoxysilane in an aqueous solution since, on aging a trialkoxysilane ultimately condensed to insoluble oligomer. As shown in Fig. 1 & 2, both the rate of hydrolysis and the stability of silane monomers decrease with increasing monomer concentration. Furthermore, it is noted that acyloxy-substituted silane such as VAS, is far more susceptible to hydrolysis than alkoxy silane. It hydrolyzed in seconds in water, whereas other alkoxy silanes required much longer time to be hydrolyzed. It is believed that this greater rate of hydrolysis of acyloxy silane is attributed to the acidic character of by-product and relatively higher reactivity of acetoxy groups in water^{1,13)}.

2) Effects of Bath pH

In general, acid promotes the condensation of silanol groups as well as the hydrolysis of alkoxy or acyloxy groups due to the catalyzing effect of acid on the condensation process as follows.



Therefore, the stability of monomers in the solution is expected to be strongly affected by the pH of the solution. As shown in Table 1, the stability of alkoxy silane is a function of pH with maximum stability at pH 3.0~4.5. This result is consistent with the observations by Plueddemann¹⁹⁾ on vinyltrimethoxysilane. The result also indicate that the rate of condensation to polysiloxane is greatest at a pH range of about 8.0 to 9.0. Of perhaps greater significance, it was also observed that a stable solution was obtained at pH above 12. This is probably due to the fact that the alkylsilanetriol is permanently soluble as siliconate ion in strong base.

Table 1. Stability of Silane Monomers in Water at different pH levels (3% solution)

pH	Time to Haze		
	VAS	VES	MES
1.5	1 hrs.	37 min.	100 min.
2.0	6 hrs.	2 hrs.	11 hrs.
2.5	10 hrs.	10 hrs.	22 hrs.
3.0	41 hrs.	33 hrs.	69 hrs.
3.5	—	38 hrs.	>100 hrs.
4.0	44 hrs.	40 hrs.	>100 hrs.
4.5	22 hrs.	9 hrs.	>100 hrs.
5.0	4 hrs.	4 hrs.	53 hrs.
5.5	—	48 min.	6 hrs.
6.0	—	15 sec.	5 min.
6.5	10 sec.	—	—
7.0	—	1 sec.	—
8.0	1 sec.	5 sec.	12 sec.
9.5	5 sec.	20 sec.	15 sec.
10.0	21 sec.	22 sec.	—
11.0	—	>100 hrs.	1 min.
12.0	>100 hrs.	>100 hrs.	>100 hrs.
13.0	>100 hrs.	—	>100 hrs.

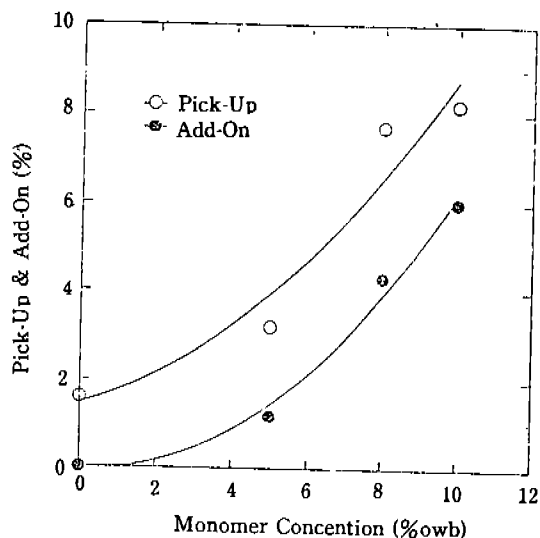


Fig. 3. Effect of Monomer Concentration on % Pick-Up and % Add-On.

Based on above observations, pH of the bath was adjusted to 4.0 for all subsequent experiments with fiber web treatment.

2. In-Situ Polymerization and Crosslinking Treatment

Vinyltriethoxysilane (VES) was selected as a monomer for in-situ polymerization and crosslinking treatment of cotton fiber. It was expected that the two functional groups, silanol and vinyl, could be controlled independently to undergo condensation and addition polymerization respectively. Initially, vinylsilanes were hydrolyzed in the acidified bath containing free radical initiator. Adsorption and diffusion of the hydrolyzed monomers onto/into the fiber were facilitated during impregnation and steam fixation. During the drying process, vinyl polymerization was expected to occur to form a linear homopolymer. Finally, acid condensation reactions among silane polymers and the crosslinking reaction between silane polymers and cellulose molecules were expected to take place during the curing process. However, the occurrence

Table 2. Effect of Steam Fixation Time on the Monomer Inclusion and the Strength of Cotton Fiber: VES (8.0% owb)

Steam Time (min)	PU ^a (%)	AO ^b (%)	FN ^d (%)	Rten ^d (%)	Rtough ^e (%)
2	7.7	4.3	55.8	99.4	105.3
5	8.3	4.6	55.4	102.4	95.5
7	8.0	5.0	62.5	95.3	95.5
10	8.1	5.6	69.1	96.2	90.4
15	8.4	5.7	67.9	96.3	88.3
20	8.0	5.5	68.8	96.3	89.8

a. Pick-Up. b. Add-On. C. Fixation.

d. Retention of tenacity of control value.

e. Retention of toughness of control value.

of the condensation/crosslinking reaction during steaming or drying, and vinyl polymerization during curing could also be possible, due to high reactivity of silanol groups and low reactivity of KPS, the free radical initiator, under acid conditions. The effects of major experimental parameters, such as monomer and initiator concentrations, treatment time and temperature, and catalyst type and curing conditions, on each treatment process were thus investigated in order to obtain optimum treatment conditions.

1) Effects of Monomer Concentration

The effect of VES concentration on % pick-up and % add-on of cotton fiber was examined and results were shown in Fig. 3. In general, % pick-up as well as % add-on increase with an increase in monomer concentration.

2) Effects of Steam Fixation Time

The steam fixation process is expected to facilitate the swelling of the cotton fiber to increase its accessibility. However, diffusion of monomer into fiber interior is also affected by the nature of the monomer, as well as the treatment time and temperature. In addition, due to the competing nature of the two processes, the diffusion and the polymerization, the control of treatment temperature and time is crucial in obtaining an optimum treatment



(a) Untreated Control Cotton Fibers



(b) VES Treated Cotton Fibers

Fig. 4. Effect of IPC Treatment on the Morphology of Cotton fibers (Magnification: 1,500)

efficiency^{5,17,20}.

However, steam temperature was fixed at 95°C to facilitate maximum diffusion without significant polymerization since it was anticipated that the rate of polymerization was relatively low at this temperature^{5,18}.

As tabulated in Table 2, % pick-up was independent of the steam treatment time, since % pick-up was mostly determined by the adsorption of monomer in the treatment bath during impregnation. However, both % add-on and % fixation increased with an increase in steam time at a given temperature. The results indicated that sufficient

amount of monomer diffusion was achieved in a 10 minute treatment time.

In addition to the gravimetric determination, the analysis of the treated fiber by scanning electron microscopy and X-ray electron probe microanalysis further support the evidence of the diffusion of silane monomer into the fiber interior. In Fig. 4, SEM micrograph of cotton fiber cross-section showed sufficient swelling of the treated fibers after 10-minute steam fixation process. X-ray electron probe microanalysis also confirmed the location of silicon. Silicones were detected from the interior of the fiber as well as on the surface of the fiber as shown in Fig. 5. Furthermore, no apparent change in the strength of the treated fibers would also indicate that no extensive crosslinking occurred during the steam process.

3) Effects of Initiator Concentration and Curing

In general, the rate of addition polymerization is proportional to the square root of free radical initiator Concentration. The concentration of initiator required for a given polymerization depends upon the type of initiator and the nature of monomer. Furthermore, the rate of initiation, thus the rate of polymerization is governed by the rate of decomposition of the initiator, which is generally affected by the pH and reaction temperature^{5,17,20}.

Potassium persulfate (KPS) was selected as a free radical initiator for addition polymerization of vinyltriethoxysilane. As shown in Table 3, % add-on increased with increasing initiator concentration from 0% owm to 0.75% owm and then levels off. This accounts for the increase in the rate of polymerization, as well as subsequent grafting or crosslinking induced by free radical initiator^{5,20}. Due to the acidic nature of persulfate initiator, it is expected that acid-catalyzed crosslinking of cellulose can also occur. Previous studies^{5,20} have shown that the degree of crosslinking of treated fibers

Table 3. Effect of curing and Initiator concentration on the Strength and the Resilience of Cotton Fiber: VES (8% owb)

Initiator ^a (%owm)	PU (%)	AO (%)	FN (%)	Rten (%)	Rtough (%)	CR/work ^b
uncured						
0.00	6.9	4.9	71.0	95.3	95.5	0.88
0.50	6.8	5.1	75.0	94.4	86.2	1.02
0.75	7.4	5.8	78.4	93.1	92.3	0.92
1.00	7.4	5.6	75.7	96.2	90.4	0.93
1.50	7.7	5.8	75.3	92.4	88.0	0.96
Cured						
0.00	—	—	—	88.7	87.3	1.00
0.75	—	—	—	80.8	80.7	1.14
0.75	—	—	—	89.1	90.2	0.95
1.00	—	—	—	85.1	87.4	0.99
1.50	—	—	—	83.8	83.7	1.04

a. Potassium Persulfate.

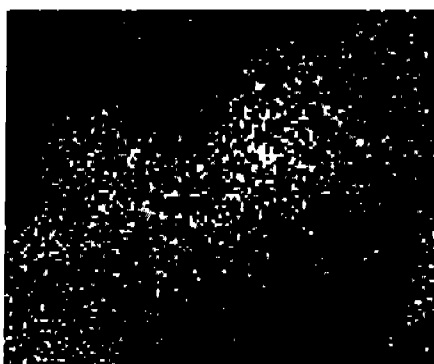
b. compression Recovery/Work (Toughness Index).
Control value is 0.74.

increased with an increase in persulfate concentration. However, current results did not show apparent increase in fiber resilience as a function of increasing initiator concentration, suggesting that significant crosslinking of cellulosic chains did not take place. Furthermore, high add-on (almost 5%) could also be obtained without the presence of initiator. It is thus believed that extensive condensation and/or crosslinking would create steric hinderance for addition polymerization and, would also deplete silanol groups available for crosslinking the cellulosic chains.

As shown in Table 3, the strength of the uncured samples did not show any appreciable reduction. For the cured samples, however, a slight decrease in tenacity and toughness was observed. This may be attributable to acid hydrolysis of the fibers. Resilience of the treated fibers, as represented by normalized compression recovery data (CR/work) did not show significant improvement after curing with acid catalyst at elevated temperature,



(a) Cotton Fiber Image



(b) Silicon X-ray Intensity Map

Fig. 5. Silicon Distribution in VES Treated Cotton Fibers.

indicating that little crosslinking of cellulose took place.

4) Effect of Reactive Functional Group

Due to difficulties experienced with vinyl silane as discussed above, epoxy functional silane coupling agent (EMS) was then used. Cotton fiber web was impregnated in the bath containing monomer of 8 % owb, organotin catalyst and wetting agent, and then treated by one step steam fixation process. Performance properties of cotton fibers treated with epoxy silane (EMS) were compared to those treated with vinyl silane (VES).

Since epoxy silane contains silanol and epoxy functional groups, it is expected to undergo polymerization only through condensation process. Due to inductive effect and difference in electronega-

Table 4. Effect of Reactive functional Group on the Degree of Crosslinking and the Resilience of Cotton Fiber.

Monomer	PU (%)	AO (%)	DC ^a (%)	Rten (%)	Rtough (%)	CR/work (%)
Control ^b	1.6	0.0	0.6	100.0	100.0	0.74
VES ^c	7.4	5.6	9.7	85.1	87.3	0.99
EMS ^d	8.1	5.9	15.3	83.4	81.1	1.16

a. Degree of Crosslinking.

b. Mock Control.

c. Vinyltriethoxysilane.

d. Epoxy (glycidoxy) propyltrimethoxysilane.

tivities of silicon and carbon, however, the reactivities of these functional groups and the stability of crosslinks with cellulosic chains are expected to be different¹²⁾. Accordingly, it is anticipated that after monomers diffused into the fiber interior, silanol condensation would take place immediately and followed by crosslinking between epoxy groups in EMS and hydroxyl groups in cellulose.

As shown in Table 4, fiber samples treated with epoxy silane (EMS) provides better compression recovery than those treated with vinyl silane (VES). This could account for the higher stability of crosslink between epoxy groups of EMS and hydroxyl groups of cellulose. As mentioned earlier, owing to difference in electronegativities of silicon and carbon, silicon-oxygen-carbon links are more susceptible to hydrolysis than carbon-oxygen-carbon links, in the presence of water¹⁴⁾. It is also confirmed by the degree of crosslinking values.

IV. CONCLUSIONS

The feasibility of using silane coupling agents as monomers in the in-situ polymerization and crosslinking of cotton fibers was investigated. In a homogeneous system, the stability and the solubility of silane were strongly dependent upon the pH of the bath and monomer concentration. They de-

creased as the monomer concentration increased. Alkoxysilane showed the maximum stability in a pH range of 3.0 to 4.5 and the greatest condensation rate at pH 8.0 to 9.0. It was also found that sufficient diffusion of silane monomers into fiber interior could be facilitated by a steam fixation process. The gravimetric results (% add-ons) were further confirmed by scanning electron microscopic analysis and x-ray electron probe microanalysis.

However, retention of silane polymers in the treated fibers was believed due to condensation polymerization, rather than vinyl polymerization of silane monomers. Treated fibers did not show significant degree of crosslinking of cellulosic chains, thus little improvement in fiber resilience. Under the current treatment conditions, in-situ polymerization is believed to have proceeded predominately via silanol condensation and thus depleted available silanol groups for subsequent crosslinking with the cellulose hydroxyl groups. For future study, therefore, it is suggested that the effects of the different types of functional groups as well as treatment conditions should be investigated to improve treatment efficiency.

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