Chemical Modification of Nylon 6 by Organoacetoxy- and Ethoxysilanes

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Synopsis

Chemical crosslinks were introduced in nylon 6 filament by means of organoacetoxy- and ethoxysilanes in benzene under anhydrous conditions. A comparison of the relative reactivities of these silanes toward nylon was made on the basis of the weight add-on calculated from silicon analysis. Application of acetoxysilanes on preswollen nylon caused an increase in the breaking stress and extensibility. However, a decrease in the initial modulus, birefringence, and moisture regain was observed. An improvement in the thermal stability has also been observed in the crosslinked samples.

INTRODUCTION

Use of silicones as water repellents in combination with crease-resistant compounds both on natural[1-4] and synthetic fibers[5,6] has been reported. A number of other polymeric siloxanes have been examined as soil release agents.[7,8] Isocyanate functional siloxanes[9] have been used for improving the tear strength, abrasion, and water resistance of nylon 66. Silicone oils are considered to be better lubricants for spraying onto nozzles in the spinning of polyamide because of their high thermal stability and good releasing property.[10]

Ethoxylated silicones have been used in the texturing finish also as they combine thermal stability with self-dispersity and antistatic property.[11,12] Recently, crosslinking of nylon 6 with chlorosilanes[13] has been reported. In this process hydrochloric acid is liberated as a byproduct which might impair the mechanical properties. In order to overcome this problem, an attempt has been made to modify nylon 6 with organoacetoxy and ethoxysilanes. Similar studies were reported previously on modification of viscose rayon by organoacetoxysilanes.[14]

EXPERIMENTAL

The nylon 6 filament with specification 40/13 (40 denier and 13 filaments) supplied by Modipon Ltd. (India) was used in this investigation. The filament was Soxhlet extracted with petroleum ether (bp 40–60°C) for 4 hr to remove the spin finish. The samples were then dried at 90–95°C for 4 hr before silylation.

Preparation of dimethyl- and methylvinyldiacetoxysilanes (VMDAS) was described previously.[14] Ethoxysilanes were obtained from Aldrich Chemical Co. (U.S.A.) and purified by distillation. Benzene (BDH) India was dried over sodium wire and distilled before use. Silylation with organoacetoxysilanes was carried out as reported for viscose yarn. In one set of the reactions nylon filament

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was preswollen in dimethylformamide for 4 hr and then silylated with acetoxysilanes in benzene under anhydrous conditions at a bath temperature of 100°C.

Reaction with Ethoxysilanes

A known amount of the dry nylon 6 filament was taken in a round-bottom flask containing 50 ml dry benzene. To this flask was added the same amount of the ethoxysilane [nylon:silane ratio 1:1 (w/w)] and a small drop of trifluoroacetic acid as catalyst. The reaction was carried out in a constant-temperature bath at 100 ± 2°C. As the reaction proceeded, ethanol was liberated as a binary azeotrope of ethanol/benzene at 68.4°C. The reaction was continued till the inner temperature reached 80°C; then the treated filament was washed with fresh benzene and Soxhlet extracted. The weight add-on was calculated from the silicon content determined gravimetrically as silicon dioxide. The ethanol liberated during the reaction was estimated by the potassium dichromate oxidation method.[15]

Evaluation of Physicomechanical Properties

Tensile properties of silylated nylon were measured by Instron at 25°C and 65 ± 2% R.H. on 5 cm gauge length. The cross-head speed was maintained at 5 cm/min and the chart speed at 50 cm/min, on a full-scale load of 50 g.

Elastic recovery was measured using an Instron with the following experimental details: gauge length, 5 cm, cross-head speed, 5 cm/min; chart speed, 100 cm/min, with a maximum load of 20 g. The sample was held for 1 min after giving 15% extension, then contracted to the original gauge length, again kept for 1 min at this position to allow recovery from deformation, and then recycled.

The experimental details for measuring birefringence and the moisture regain were described previously.[14]
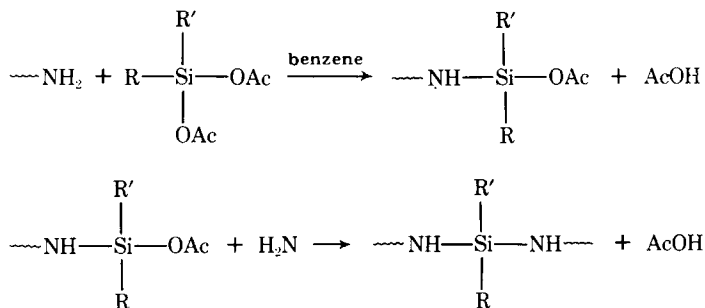
Thermal Analysis

The thermogravimetric analysis was carried out with a Stanton Model TG-750 thermobalance in static air at a heating rate of 10°C/min. The differential thermal analysis (DTA) of the powdered samples was done on a Stanton Redcroft differential thermal analyzer using calcined alumina as reference at a heating rate of 10°C/min.
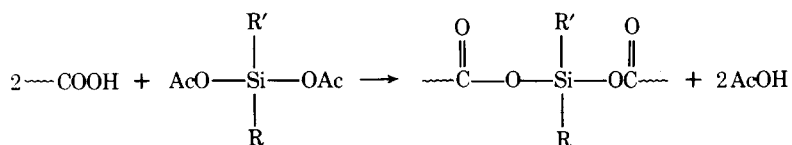
RESULTS AND DISCUSSION

Reactions of Acetoxysilanes with Nylon

There are three reactive sites, i.e., —NH$_2$, —OCNH, and —COOH groups, which can interact with functional silanes:
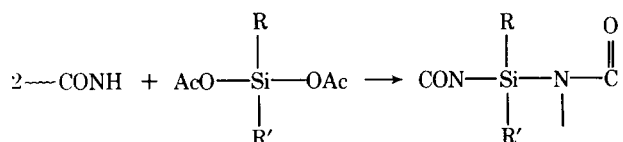
Reaction at the —NH$_2$ Endgroup

Reaction at —COOH Group

$$2\text{—COOH} + \text{AcO—}\underset{\underset{R}{|}}{\overset{\overset{R'}{|}}{Si}}\text{—OAc} \rightarrow \text{—}\overset{\overset{O}{\|}}{C}\text{—O—}\underset{\underset{R}{|}}{\overset{\overset{R'}{|}}{Si}}\text{—O}\overset{\overset{O}{\|}}{C}\text{—} + 2\,\text{AcOH}$$

Reaction with —CONH Group

$$2\text{—CONH} + \text{AcO—}\underset{\underset{R'}{|}}{\overset{\overset{R}{|}}{Si}}\text{—OAc} \rightarrow \text{CON—}\underset{\underset{R'}{|}}{\overset{\overset{R}{|}}{Si}}\text{—N—}\overset{\overset{O}{\|}}{C}$$

where R = R' = CH_3 or C_6H_5, or R = CH_3 and R' = $CH_2\text{=}CH$—. Since the amount of silane fixed is not high, one may assume that a small fraction of these sites are available for silylation.

Effect of Silane Concentration on Weight Add-on

In changing the material:silane ratio from 1:0.5 to 1:2 (w/w), a little increase in the weight add-on has been observed only up to a 1:1 ratio; thereafter, higher reactant ratio did not increase the silylation of nylon.

Effect of Swelling Agent on Weight-Add-on

An attempt was made to increase the accessible sites for silylation by pre-swelling the nylon filament with dimethylformamide for 4 hr. As expected, the amount of silane fixed in case of VMDAS-treated sample was found to be 15.4 mmole/100 g nylon instead of 10.7 mmole as shown in Tables I and II. Silylation of nylon was also carried out with dimethyl- and diphenylsilane after preswelling. From the weight add-on (Table II), the relative reactivity of these silanes toward nylon is

$$VMDAS > DMDAS > DPDAS$$

On the basis of the reaction mechanism as suggested for silylation of viscose,[14] the reactivity of a silane is increased by attaching an electron-withdrawing group. The vinyl group, therefore, being more electronegative than the methyl group,

TABLE I
Effect of VMDAS Concentration[a] on Weight Add-on

| Material:reactant ratio, w/w	SiO_2, g/100 g nylon	Silane combined, mmole/100 g nylon
1:0.5	0.60	10.0
1:1	0.644	10.7
1:2	0.648	10.8

[a] Reaction conditions: 4 hr in benzene at 100°C bath temperature.

TABLE II
Crosslinking of Preswollen Nylon with Acetoxysilanes

Reactant	SiO_2, g/100 g nylon	Silane combined, mmole/ 100 g nylon
t6rl20Dimethyldiacetoxysilane (DMDAS)	0.751	12.5
Diphenyldiacetoxysilane (DPDAS)	0.720	12.0
Vinylmethyldiacetoxysilane (VMDAS)	0.925	15.4

will make VMDAS more reactive than DMDAS. However, poor reactivity of
DPDAS as compared to VMDAS or DMDAS may be related to steric factors.

Reactions of Ethoxysilanes with Nylon

Reactivity of ethoxysilanes as compared to acetoxysilanes is poor. The re-
actions of the former were accelerated in the presence of trifluoroacetic acid as
catalyst. The relative reactivity of ethoxysilanes was found from the amount
of ethanol liberated azeotropically:

$$2 \text{---NH}_2 + \text{EtO---Si---OEt} \xrightarrow{C_6H_6} \text{---NH---Si---NH---} + 2\,\text{EtOH}$$
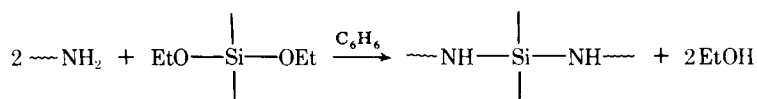
Although the liberation of ethanol is much faster in the initial stage in case of
the phenyltriethoxysilane reaction toward nylon, completion of reaction takes
a much longer time as compared to methyl- and vinyltriethoxysilane. On the
basis of the reaction time required to liberate 1.7–1.87 mole of ethanol as against
2 moles required for the introduction of a covalent bond (Table III), the relative
reactivity of ethoxysilane is

VTES > MTES > PTES

TABLE III
Crosslinking of Nylon with Ethoxysilanes

Silane	Reaction time, hr	Ethanol liberated, moles/mole silane	SiO_2, g/100 g nylon	Silane combined, mmole/ 100 g nylon
Dimethyldiethoxysilane (DMDES)	5.5	1.8	0.684	11.4
Methyltriethoxysilane (MTES)	6.0	1.85	1.095	18.23
Vinyltriethoxysilane (VTES)	4.5	1.87	0.812	13.52
Phenyltriethoxysilane (PTES)	8	1.7	0.602	10.2

Physicomechanical Properties

The effect of silylation on the mechanical properties of nylon 6 is summarized in Tables IV and V, and the stress–strain behavior of the treated nylon is shown in Figures 1 and 2. An increase in the breaking stress in all the crosslinked samples except the one treated with vinylmethyldiacetoxysilane without preswelling has been observed. Lowering of breaking stress in sample 4 (Table IV) may be due to the localization of crosslinks only on the surface which will cause nonuniform distribution of stress. Preswelling, therefore, helps in getting the uniform distribution of crosslinks and consequently more favorable distribution of stress. However, an increase in the breaking stress in case of ethoxysilane-treated samples may be attributed to the greater diffusion of ethoxysilanes vis-à-vis better distribution of crosslinks during long reaction period.

An increase in the extensibility due to crosslinking, except for sample 4 (Table IV), has been observed. In acetoxysilane reactions, preswelling of nylon was carried out in a relaxed state, which caused some disorientation in the amorphous region. Further stabilization of this structure with crosslinks might help in easier slippage of the chain molecules. In ethoxysilane-treated nylon, however, an increase in the extensibility may be related with the size and nature of the crosslinks which might affect the orientation of the chain molecules. Maximum extensibility has been shown in the samples treated with diphenyldiacetoxy- and phenyltriethoxysilane. This effect may be attributed to the bulky phenyl groups in the crosslinks which cause greater disorientation, thereby leading to higher extensibility.

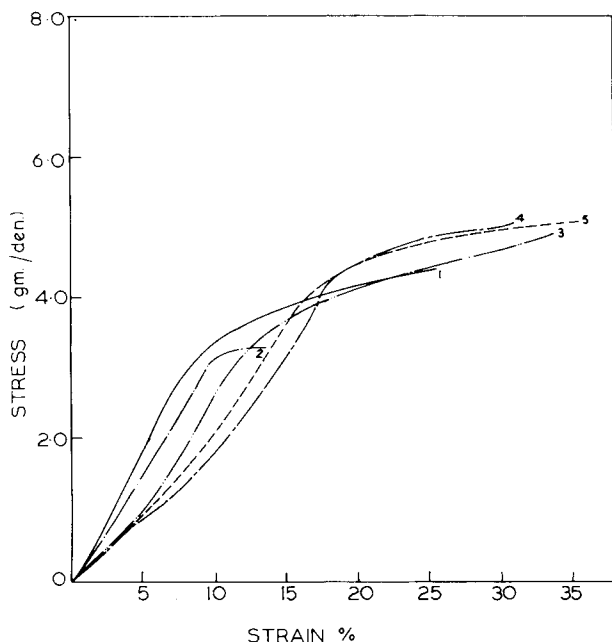Initial modulus was found to decrease in all the crosslinked samples, which

Fig. 1. Stress–strain curves of nylon treated with acetoxysilanes: (1) parent; (2) VMDAS-treated nylon; (3) VMDAS-treated nylon preswollen in DMF; (4) DMDAS-treated; and (5) DPDAS-treated nylon preswollen in DMF.

TABLE IV
Physicomechanical Properties of Nylon 6 Treated with Acetoxysilanes[a]

Sample no.	Silane combined, mmole/100 g nylon	Breaking stress, g/den	Breaking strain, %	Initial modulus, g/den	Elastic recovery, %	Work of rupture	Moisture regain, %	Birefringence
1	DMDAS (12.5)	5.04	30.8	23.5	93.4	174.0	3.03	0.05695
2	DPDAS (12.0)	5.03	36.6	22.3	90.2	237.1	3.24	0.04874
3	VMDAS (15.4)	4.77	33.6	26.6	89.2	169.3	2.91	0.05443
4	VMDAS[b] (10.7)	3.36	13.26	32.5	—	—	3.29	0.05523
5	Parent Sample	4.43	25.2	37.6	86.1	157.0	3.69	0.06094

[a] DMDAS= Dimethyldiacetoxysilane, DPDAS = diphenyldiacetoxysilane, VMDAS = vinylmethyldiacetoxysilane.
[b] No preswelling in DMF.

TABLE V
Physicomechanical Properties of Nylon 6 Treated with Ethoxysilanes[a]

Sample no.	Silane combined, mmole/ 100 g nylon	Breaking stress, g/den	Breaking strain, %	Initial modulus, g/den	Elastic recovery, %	Work of rupture	Moisture regain, %	Birefringence
1	MTES (18.23)	5.03	31.2	30.0	88.6	158.1	2.89	0.05420
2	VTES (13.52)	4.94	33.4	28.2	87.5	184.0	3.30	0.05825
3	PTES (10.2)	5.25	37.6	26.6	89.3	227.5	3.36	0.05319
4	DMDES (11.4)	4.90	28.0	33.5	91.7	192.0	3.39	0.05830
5	Control Sample	4.43	25.2	37.6	86.1	157.0	3.69	0.06094

[a] MTES = Methyltriethoxysilane, VTES = vinyl triethoxysilane, PTES = phenyltriethoxysilane, DMDES = dimethyldiethoxysilane.
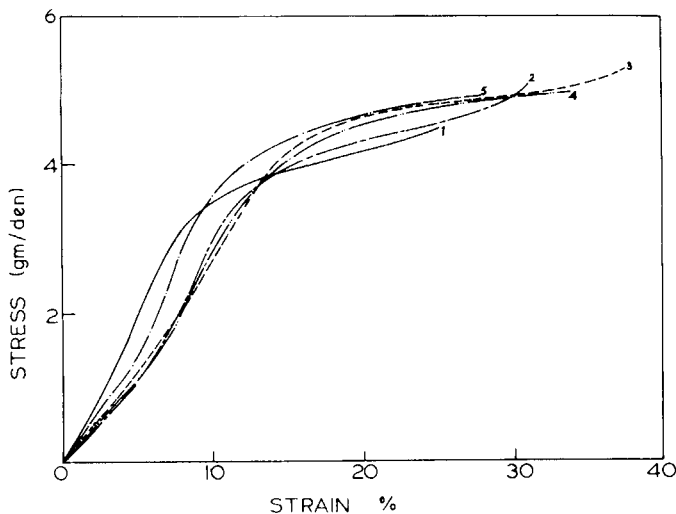
Fig. 2. Stress–strain curves of nylon treated with ethoxysilanes: (1) parent; (2) MTES-treated; (3) PTES-treated; (4) VTES-treated; (5) DMDES-treated nylon.
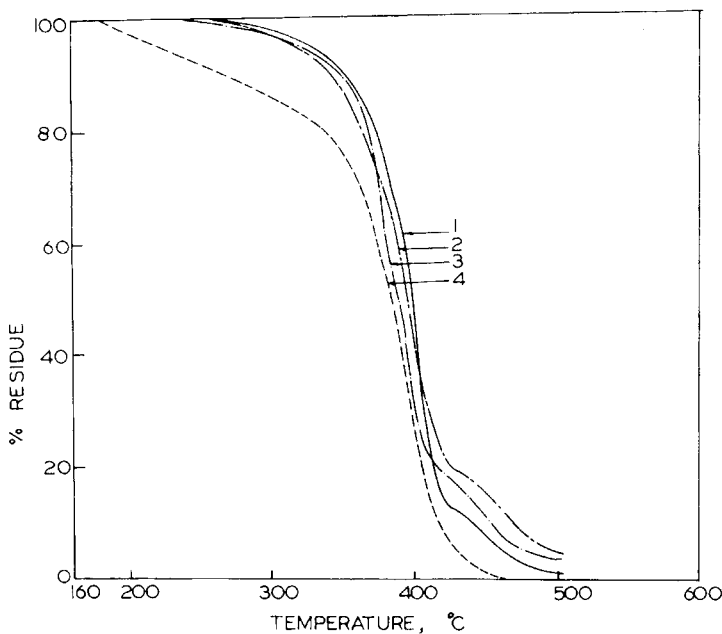

Fig. 3. Primary thermograms of crosslinked nylon: (1) DPDAS-treated; (2) VMDAS-treated; (3) DMDAS-treated nylon; (4) parent sample.

indicates disruption of hydrogen bonds due to bulky crosslinks. Disorientation in the amorphous region will also lead to poor initial modulus. As expected, the elastic recovery increases due to the introduction of crosslinks which brings the chain back to its position after removal of the load. Work of rupture also increases due to crosslinking, and a maximum value has been obtained for DPDAS-treated samples. In other words, toughness of the fiber increases, and modified fibers can therefore withstand sudden shocks.

TABLE VI
Thermal Analysis of Crosslinked Nylon

Sample no.	Silane combined, mmole 100 g nylon	Decomposition temperature, °C, at loss of						IPDT,[a] °C
		10 wt-%	20 wt-%	40 wt-%	60 wt-%	80 wt-%		
1	MDMAS (12.5)	347	366	382	396	418		389
2	VMDAS (15.4)	343	364	389	410	430		395
3	DPDAS (12.0)	350	370	393	402	415		386
4	PTES (10.2)	348	365	390	400	472		390
5	MTES (18.23)	360	376	395	408	485		410
6	Parent sample	300	336	370	392	409		365

[a] IPDT = Integral procedural decomposition temperature.

TABLE VII
Differential Thermal Analysis of Silylated Nylon 6

Sample no.	Silane combined, mmole/ 100 g nylon	Endotherm, °C		Exotherm (peak maxima), °C
		T_g	T_m	
1	DMDAS (12.5)	45	215	426	295
2	DPDAS (12.0)	47	214	414	290
3	VMDAS (15.4)	43	216	432	303
4	Parent sample	41	215	400	260

Moisture regain decreases with increase in the crosslink density irrespective of the nature of the crosslinks.

Birefringence values also decrease in the treated samples perhaps owing to the disorder introduced in the matrix because of the bulky crosslinks. This supports the maximum lowering in birefringence value in DPDAS-treated samples, consequently a decrease in the initial modulus and higher extensibility.

Thermal Properties of Crosslinked Nylon

As is evident from Figure 3, thermal stability of nylon 6 increases due to the introduction of crosslinks. Initial decomposition appears to be influenced by the nature of the crosslinks, e.g., at 10% weight loss the decomposition temperature in nylon is 300°C, whereas in DPDAS-, VMDAS-, and DMDAS-treated nylon, it is 350°, 343°, and 347°C, respectively. The major decomposition in the untreated nylon takes place between 330° and 410°C, whereas in treated nylons it occurs between 360° and 430°C.

The decomposition temperature in DPDAS-treated sample is higher up to 55% weight loss; thereafter the trend is reversed (Table VI). Overall thermal stability is dependent on the crosslink density as shown by the highest IPDT value in case of the methyltriethoxysilane sample. The higher thermal stability of nylon 6 crosslinked with silanes may be attributed to the higher bond energy and greater polarity of Si–N, Si–O, and Si–C bonds introduced.

DTA data (Table VII) also supports the trend observed in thermogravimetric analysis. A slight increase in T_g (43°–47°C) has been observed in the crosslinked samples. The increase in T_g may be related to the introduction of bulky crosslinks and also to the decrease in the moisture regain. The T_m is not shifted as crosslinking takes place in the amorphous region.

The differential thermal analysis also reflects at least two processes involving a broad exotherm with a peak at 260°C in the parent sample followed by an endothermic decomposition reaction with a peak at 400°C. These changes are associated with small weight loss in the range of 260°–330°C followed by rapid volatilization associated with a large endotherm. The initial degradation reaction shown by the DTA and involving minor weight loss is consistent with a secondary decomposition temperature. In the crosslinked samples the exo-

thermic decomposition reaction occurs between 290 and 303°C followed by endothermic decomposition in the range of 414° to 432°C.

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