Chemical Modification of Viscose Rayon by Dimethyl and Methylvinyl Diacetoxysilanes

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Synopsis

Crosslinking of viscose rayon filament with dimethyl and methylvinyl diacetoxysilanes in benzene has been studied. The extent of crosslinking appears to depend on the nature of the reactant, material-to-reactant ratio, time, and temperature of the reaction. An increase in the breaking stress, initial modulus, and recovery properties was observed with increase in the crosslink density. Birefringence values as well as orientation index decrease in the treated samples. Thermal behavior of the crosslinked viscose was also studied by TGA and DTA, and it was found that *IPDT* (integral procedural decomposition temperature) and D_{max} (maximum decomposition temperature) values of the crosslinked samples are higher than those of the untreated viscose.

INTRODUCTION

Crosslinking reactions on viscose rayon by various N-methylol compounds,[1-6] epimines,[7] epoxides,[8] and other functionalscompounds have been investigated for imparting wash-wear finish. Yowever, it has been observed that cotton after crosslinking is invariably weakened, whereas viscose almost always gains somewhat in dry strength and substantially in wet strength.[9] Nuessle and co-workers[10] have related this difference in behavior with the fine structures of the two fibers.

Organosilicon compounds have also been used in dyeing and finishing of cotton and wool fabrics.[11,12] But in these reactions functional silanes, e.g., acetoxy, fluoroalkoxy, organoisocyanato, and aminosilanes are partially polymerized prior to their application or condensed to form polysiloxanes on the fibers themselves to render them water and oil repellent[13] or for improving the crease recovery of wash-wear fabrics. Fluorosilicon compounds have been incorporated along with dimethylol dihydroxyethyleneurea in the finishing bath and applied to blends of polyester with cotton and rayon for imparting soil-release finish with improved handle.[14] Organosilicon derivatives of cellulose with bifunctional organic siloxanes, i.e., α,ω-dichlorodimethylsiloxane, have been synthesized which had high water repellency and improved elasticity and crease resistance.[15] Polysiloxanes having end acetoxy groups have been used for obtaining crease-resistant finishes with inappreciable loss of strength and resistance. So far, the work reported on the application of silicon compounds in finishing has dealt with polysiloxanes only. The object of the present study is to investigate the crosslinking reactions of organoacetoxysilanes on viscose rayon and their influence on the physicomechanical properties and the thermal behavior of crosslinked material.

EXPERIMENTAL

Raw Materials. Dimethyldichlorosilane (BDH) and methylvinyldichlorosilane (Pierce Co.) were purified by distillation. Benzene was dried over sodium wire and distilled before use.

Preparation of Dimethyl and Methylvinyl Diacetoxysilane. Dimethyl and methylvinyl diacetoxysilanes were prepared by treating the corresponding chlorosilanes with acetic anhydride in 1:2 molar ratio[16] and purifying by distillation.

Yarn. Viscose rayon yarn with a specification 300/66 (300 denier and 66 filaments) was supplied by J. K. Rayon, Kanpur, India. The yarn was Soxhlet extracted with petroleum ether for 6 hr to remove the finish. After drying at 100° ± 2°C for about 6 hr, the yarn was weighed and kept in a desiccator. A known amount of the dried sample was treated with organoacetoxysilane in benzene under anhydrous conditions at a bath temperature of 100 ± 2°C. After the reaction had progressed for the desired time, the treated filament was removed and washed with benzene to remove the unreacted silane. Samples were then soxhlet extracted with benzene and dried in the oven at 100°C. The extent
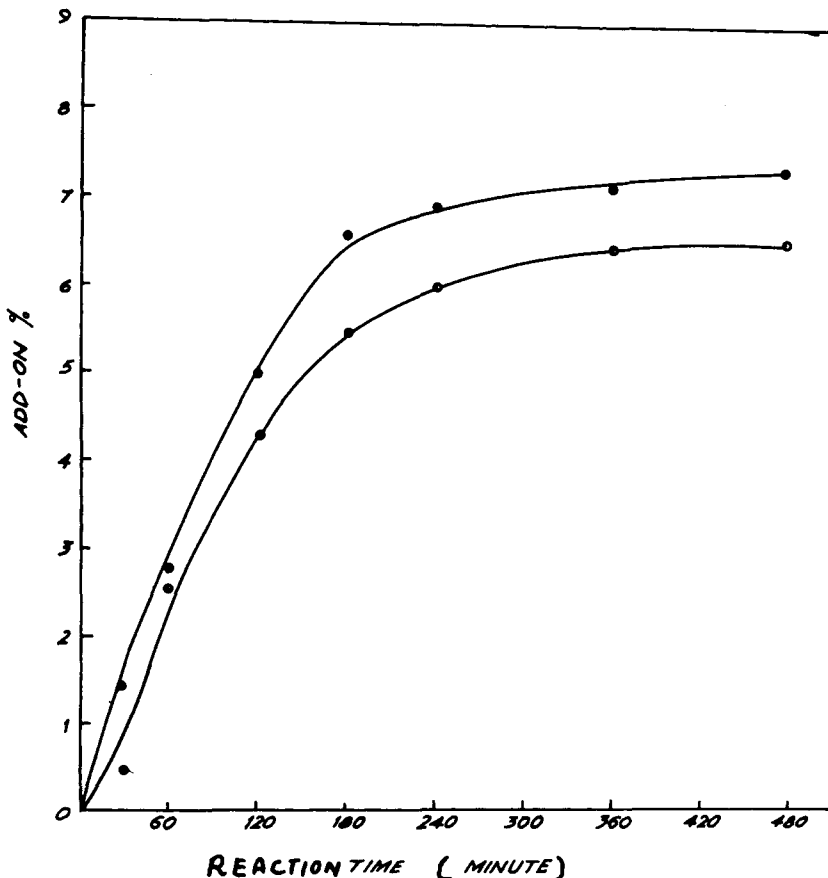

Fig. 1. Change of silane add-on, expressed in millimoles silane per 100 g viscose, vs time of reaction, in min, at a viscose-to-silane reactant ratio of 1:1.5: (●) MVDAS- and (⊙) DMDAS-treated samples.

of the reaction was found by determining the silicon content gravimetrically[17] from the treated samples.

Evaluation of Physical Properties. Tensile properties (load–elongation characteristics) of the viscose filaments were measured by Instron at $25 \pm 2°C$ and $65 \pm 2\%$ R.H. on 2.5-cm gauge length. The cross-head speed was maintained at 5 cm/min and a chart speed of 100 cm/min on a full-scale load of 20 g. At least 20 samples were tested for each set of treated filaments, and the mean was then taken. The load–elongation curves were reduced to stress–strain curves. Initial modulus, breaking stress and breaking strain were calculated from these stress–strain curves.

Recovery from 10% Extension. An extension of 10% was given to the yarn of gauge length 5 cm on the Instron. It was held for 1 min after giving 10% extension, then contracted to the original gauge length and again kept for 1 min at this position to allow recovery from deformation. In other words, a dwell period of 1 min was allowed both in the relaxed and extended conditions. A cross-head speed of 5 cm/min and a chart speed of 100 cm/min were used with a full-scale load of 20 g.

Moisture Regain. The moisture regain at 65% R.H. was determined by the vacuum desiccator method as reported by Urquhart and co-workers[18] using P_2O_5 as a desiccant.
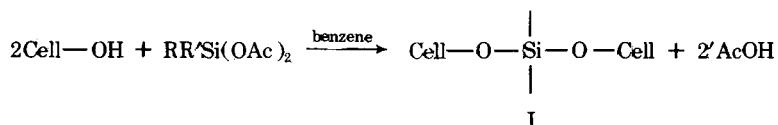
Birefringence was measured by the immersion method[19] using liquid paraffin ($\eta = 1.482$) and α-bromonaphthalene ($\eta = 1.659$). The refractive indices of various samples in the parallel ($\eta_\parallel$) and perpendicular ($\eta_\perp$) directions to the fiber axis were measured, and the difference between ($\eta_\parallel$) and ($\eta_\perp$) yielded the birefringence value.

X-ray diffraction patterns were recorded with a Philips Norelco x-ray diffraction unit using a flat film x-ray camera.

Thermal Analyses. Thermogravimetric analysis was carried out with a Stanton Model HT-D thermobalance in static air. The thermograms were run from room temperature to 500°C at a heating rate of 6°C/min. Primary thermograms were obtained from TGA traces by plotting the percentage residual weight against temperature. The integral procedural decomposition temperature as proposed by Doyle[20] was obtained from the summation of the whole shape of the normalized data curve. Differential thermal analysis (DTA) of the powdered samples was studied on a Stanton Redcroft differential thermal analyzer with the use of calcined alumina as reference and at a heating rate of 5°C/min in static air.

RESULTS AND DISCUSSION

Acetoxysilanes, though less reactive than corresponding chlorosilanes, react with hydroxyl groups of cellulose without catalyst:

$$2\text{Cell}-\text{OH} + \text{RR}'\text{Si}(\text{OAc})_2 \xrightarrow{\text{benzene}} \text{Cell}-\text{O}-\underset{|}{\overset{|}{\text{Si}}}-\text{O}-\text{Cell} + 2'\text{AcOH}$$

$$\text{I}$$

where $R = R' = CH_3$ or $R = CH_3$, and $R' = H_2C = CH$—. The reaction of silanes
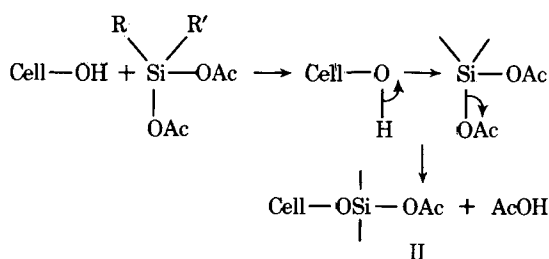
TABLE I

Crosslinking of Viscose Rayon Filament (300/66) with DMDAS in Benzene at 100°C Bath Temperature

Sample no.	Material: Reactant, (w/w)	Reaction time, hr	% Silicon	Silane combined, mmoles/ 100 g viscose	Moisture regain, %	Bire-fringence
1	1:0.25	4	0.1281	4.57	—	—
2	1:0.50	4	0.1734	6.19	12.24	0.02604
3	1:0.75	4	0.1828	6.45	12.15	0.02572
4	1:1.0	4	0.2082	7.40	11.75	0.02492
5	1:1.5	4	0.2323	8.20	11.30	0.02492
Parent	—	—	—	—	12.98	0.02811

TABLE II

Crosslinking of Viscose Rayon (300/66) with MVDAS in Benzene at 100°C Bath Temperature

Sample no.	Material: Reactant, (w/w)	Reaction time, hr	% Silicon	Silane combined, mmoles/ 100 g viscose	Moisture regain, %	Bire-fringence
1	1:0.25	4	0.1344	4.80	—	—
2	1:0.50	4	0.1880	6.69	11.75	—
3	1:0.75	4	0.2134	7.62	11.82	0.02504
4	1:1.00	4	0.2223	8.12	11.29	—
5	1:1.50	4	0.2436	8.90	11.00	0.02496
Parent	—	—	—	—	12.98	0.02811

is probably of the S_{N^2} type and proceeds through the formation of a pentavalent silicon complex as shown below:

$$Cell-OH + \underset{\underset{OAc}{|}}{\overset{R \quad R'}{\underset{\diagdown \diagup}{Si}}}-OAc \longrightarrow Cell-O \longrightarrow \underset{\underset{OAc}{}}{\overset{\diagdown \diagup}{Si}}-OAc$$

$$Cell-\underset{|}{OSi}-OAc + AcOH$$
$$II$$

In a similar manner, the acetoxy group of II reacts with another hydroxyl group of cellulose to form a crosslink (I) which could be intermolecular, intramolecular, or both depending upon the availability of accessible sites for the reaction.

On the basis of the silane fixed (weight add-on of the treated sample) (Fig. 1), it may be seen that methylvinyl diacetoxysilane (MVDAS) is more reactive than dimethyldiacetoxysilane (DMDAS). The higher reactivity of MVDAS may be attributed to the more electronegative vinyl group which would make the silicon atom more electropositive and facilitate the nucleophilic substitution reaction.

TABLE III
Crosslinking Reaction at Different Bath Temperatures[a]

| Reactant | Silane fixed, mmoles silane per 100 g viscose | |
	40°C	100°C
Dimethyl diacetoxysilane (DMDAS)	3.33	6.40
Methylvinyl diacetoxysilane (MVDAS)	3.65	7.25

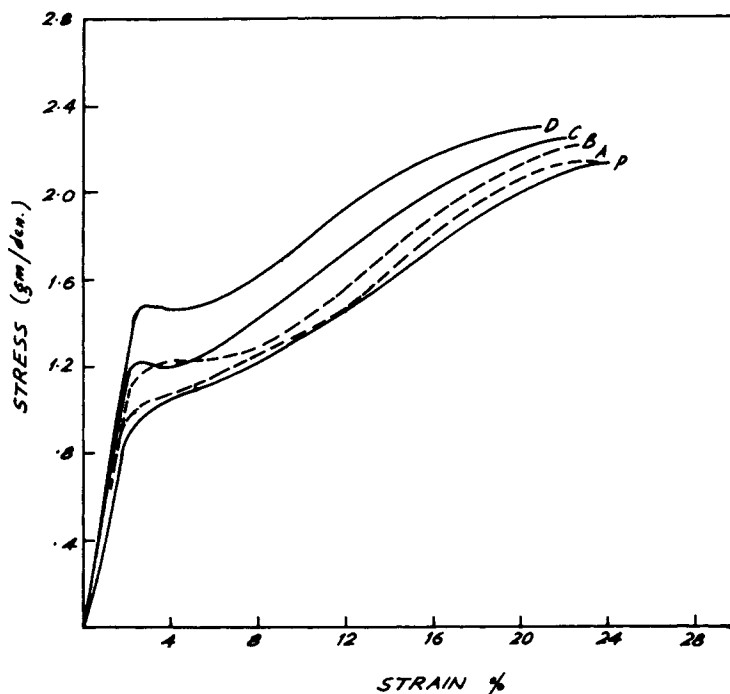[a] Material:reactant ratio, 1:0.5 (w/w); reaction time, 8 hr.

Fig. 2. Stress–strain curves for DMDAS-treated viscose: (P) parent; (A) 2.53 mmoles; (B) 4.27 mmoles; (C) 6.20 mmoles; (D) 8.20 mmoles silane fixed per 100 g viscose.

Optimization of Conditions for crosslinking of Acetoxysilanes

Effect of Silane Concentration. The material-to-reactant ratio was varied from 1:0.25 to 1:1.5 (w/w); and from the weight add-on (Tables I and II) it is evident that the fixation of the silane increases linearly with increase in the silane content in the reaction bath. With both silanes, the trend is similar, however, it tends to level off when the material-to-reactant ratio is greater than 1.

Effect of Reaction Time on Crosslinking. The effect of time on the extent of crosslinking was also investigated (Fig. 1), and it was found that fixation of the silane increases with increasing the reaction time in both DMDAS- and MVDAS-treated samples. However, after 4 hr of reaction period, the increase in the extent of crosslinking is not appreciable.

Effect of Bath Temperature. All the reactions were carried out at a bath temperature of $100 \pm 2°C$, except for one set at 40°C to compare the efficiency of the reactions at two temperatures. From the amount of silanes fixed (Table III), it may be seen that the rate of reaction is much higher at 100°C for both si-
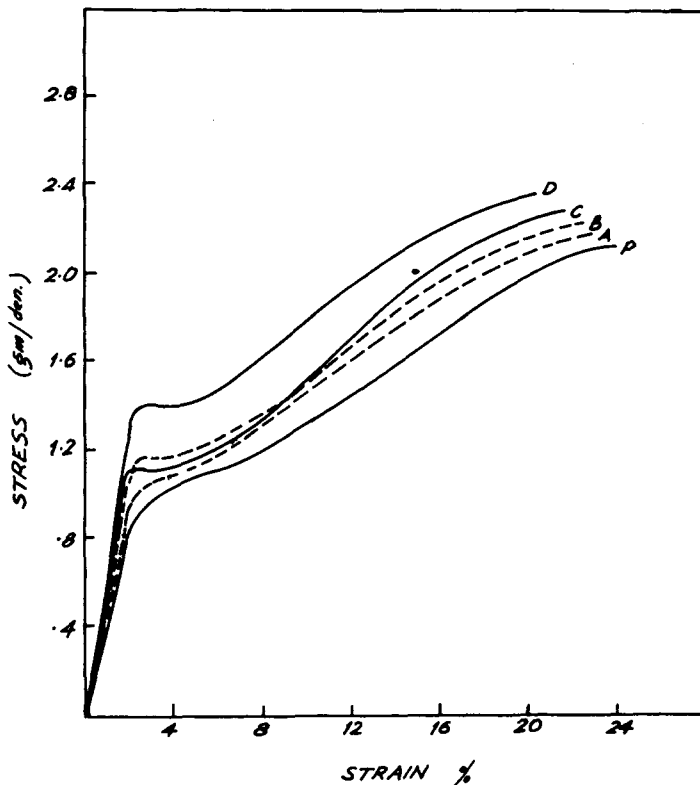
Fig. 3. Stress–strain curves for MVDAS-treated viscose: (P) parent; (A) 1.44 mmoles; (B) 2.8 mmoles; (C) 7.25 mmoles; (D) 8.9 mmoles fixed per 100 g viscose.

lanes, and weight add-on is nearly twice that of the reaction carried out at 40°C.

The overall extent of reaction toward viscose rayon is low, the maximum add-on for both silanes being 8–9 mmoles silane per 100 g viscose. A lower combination of the silanes may be attributed to a smaller number of accessible hydroxyl groups as the reaction was carried out under anhydrous conditions after drying the viscose yarn at 100 ± 2°C in the oven for about 6 hr.

Physicomechanical Properties

Stress–strain curves of the untreated control and viscose filament treated with different concentrations of the silanes are compared in Figures 2 and 3. Initial modulus increases with increase in the crosslink density irrespective of the chemical nature of crosslinks. In untreated viscose, the initial modulus is 43 g/den; whereas in DMDAS-treated (8.2 mmoles) and MVDAS-treated (8.9 mmoles silane per 100 g viscose) samples it increases to 61 and 63 g/den, respectively (Tables IV and V). Introduction of covalent bonds would increase the rigidity of the matrix, and the work required for stretching the chain molecules will be high. Therefore, work recovery values as well as yield stress are higher in crosslinked viscose.

Breaking stress also increases by about 7.6% and 10.4%, respectively, in DMDAS- and MVDAS-treated samples at maximum add-on. Increase in
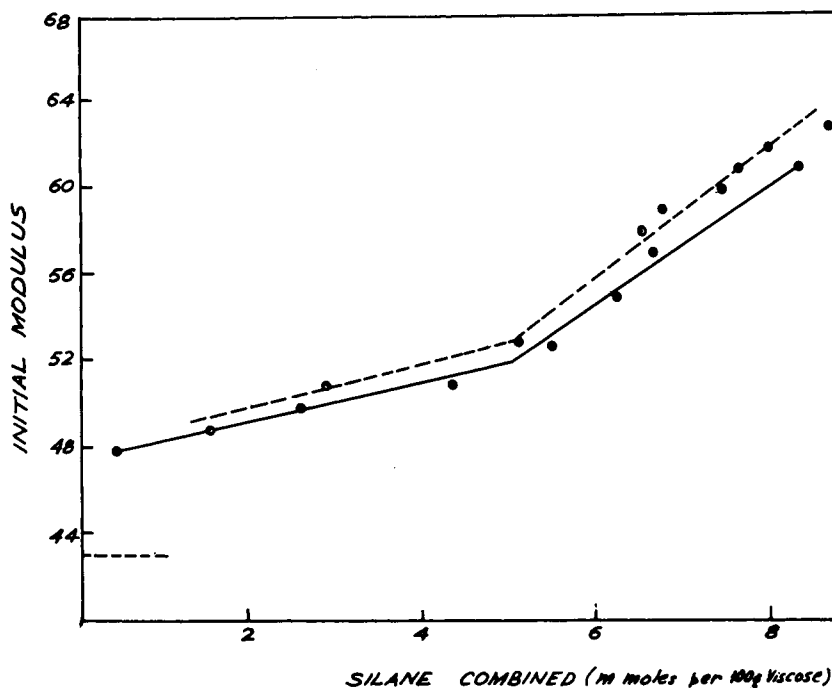
Fig. 4. Effect of weight add-on initial modulus: (●) DMDAS- and (○) MVDAS-treated sample.

breaking stress of crosslinked samples may be attributed to the increase in the points which serve as stress transfer points as explained by Rebenfeld.[21]

An interesting and distinctive feature of the curves for initial modulus, work recovery, and recovery at 10% (Figs. 4 and 5) is that at low levels of crosslink density, i.e., up to 4–6 mmoles silane per 100 g viscose, the increase in initial modulus and work recovery values is small but that above this level, a significant improvement in the properties is noticeable with increase in crosslink density. It is, therefore, apparent that with both silanes a minimum level of crosslink density is necessary before any appreciable response in tensile properties can be expected. The influence of crosslinking on breaking strain is marginal; however, one notices a consistent drop at higher levels of crosslinks. This may be attributable to resistence to chain slippage with increase in tie points.

Moisture Regain

Moisture regain decreases with increase in crosslink density, as shown in Tables I and II. Moisture regain of the parent sample is 12.98%, which decreases to 11.3% and 11.0% in DMDAS- and MVDAS-treated samples, respectively, at maximum add-on. Lowering in the moisture sorption may be related to two factors: (i) reduction in the number of accessible hydroxyl groups because of crosslinking reactions, and (ii) hydrophobicity of the silicon compounds.
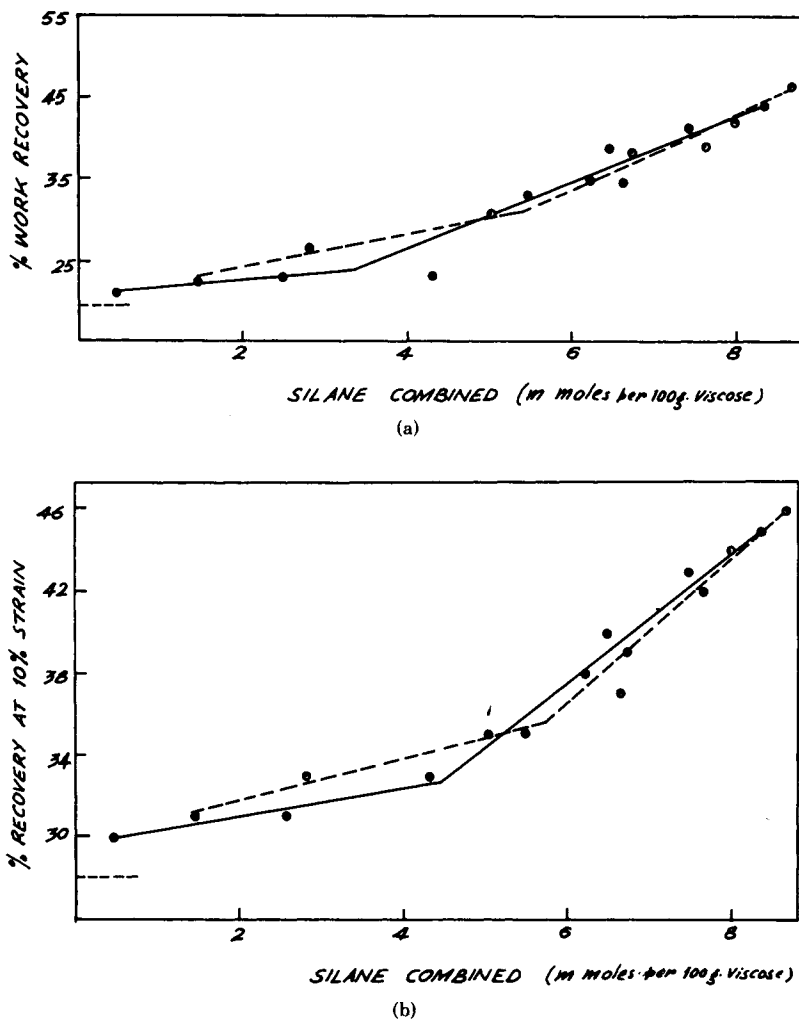
Fig. 5. Effect of weight add-on on recovery properties: (a) work recovery at 10% strain; (●)
DMDAS- and (⊙) MVDAS-treated sample.

Birefringence and Orientation Index

A decrease in both the birefringence (Tables I and II) and orientation index
values (Table VI) is observed with increase in crosslink density. The decrease
in birefringence in treated samples may be due to the disorder introduced in the
matrix during crosslinking reactions. It is anticipated that even in an anhydrous
state the introduction of silanes into the amorphous regions of viscose fibers
would induce some shrinkage due to the lowering of hydrogen bonding.

Thermal Behavior

The DTA curves for the control sample and the two crosslinked samples are
shown in Figures 6 and 7. They display an endothermic dip with a minimum
between 52° and 65°C due to moisture evaporation. Decomposition of the vis-
cose, as shown by TGA, begins at about 280°C, whereas in MVDAS-treated

TABLE IV
Effect of DMDAS Crosslinking on Mechanical Properties of Viscose Rayon

Sample no.	Silane combined, mmoles/ 100 g viscose	Breaking stress, g/den	Breaking strain, %	Initial modulus, g/den	Elastic recovery, %	Work recovery, %
1	0.485	2.15	23.7	48	30	21.0
2	2.530	2.19	23.0	50	31	22.8
3	4.270	2.21	22.7	51	33	23.1
4	5.450	2.215	22.5	53	35	33.3
5	6.190	2.25	22.2	55	38	35.1
6	6.450	2.26	21.9	58	40	38.5
7	7.400	2.28	21.5	60	43	41.2
8	8.20	2.31	21.0	61	45	43.8
Parent	—	2.145	24.0	43	28	19.5

TABLE V
Effect of MVDAS Crosslinking on Mechanical Properties of Viscose Rayon

Sample no.	Silane combined, mmoles/ 100 g viscose	Breaking stress, g/den	Breaking strain, %	Initial modulus, g/den	Elastic recovery, %	Work recovery, %
1	1.44	2.180	23.0	49	31	22.1
2	2.81	2.210	22.6	51	33	26.5
3	5.02	2.215	22.5	53	34	31.2
4	6.58	2.260	21.8	57	37	34.2
5	6.69	2.280	21.6	59	39	38.3
6	7.62	2.300	21.4	61	42	39.0
7	7.94	2.320	21.1	62	44	42.0
8	8.90	2.370	20.3	63	46	46.0
Parent	0	2.145	24.0	43	28	19.5

TABLE VI
Effect of Crosslinking on Orientation Index

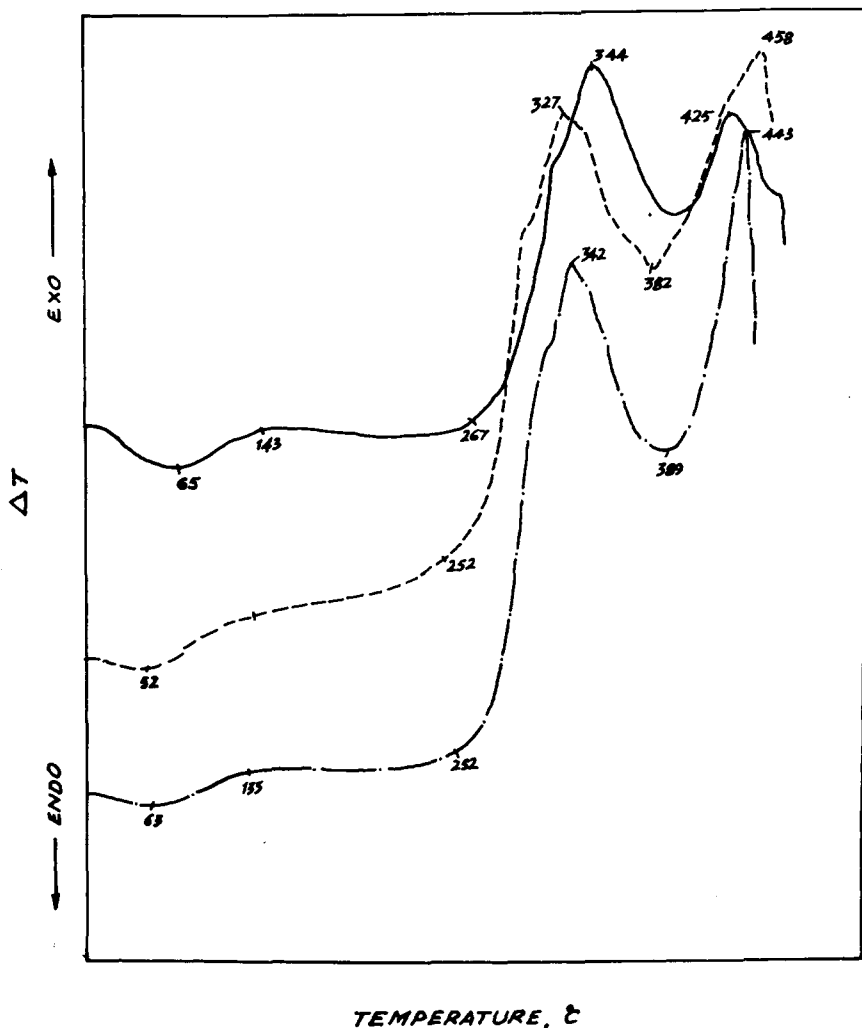| Experiment no. | MVDAS | | DMDAS | |
	Silane fixed, mmoles per 100 g viscose	Orientation index	Silane fixed, mmoles per 100 g viscose	Orientation index
1	2.81	4.424	4.27	4.237
2	5.02	4.149	6.20	4.065
3	7.94	3.990	8.2	3.80
Control		5.235		

Fig. 6. DTA curves for MVDAS-treated viscose: (—) parent; (-.-.-) 1.44 mmoles; (- - -) 8.9 mmoles silane fixed per 100 g vicose.

samples decomposition begins at 312°C (Fig. 8). Decomposition is accompanied by two exotherms, one beginning at about 267°C in control samples with a peak at 344°C, and associated with the main pyrolytic reaction of the cellulose, and the other with a peak at 425°C, associated with the final stages of decomposition of the char as observed in cotton.[22] However, in crosslinked samples, the first exotherm associated with the formation of volatiles is shifted toward lower temperature with a peak at 320°–342°C.

The shifting of the first exotherm toward the lower temperature side may be related to the disorder introduced because of the crosslinking. At higher temperatures, perhaps formation of some crosslinks takes place *in situ* due to the thermo-oxidation of the side substituents which might be responsible for shifting the second exotherm to higher temperatures.

The DTA results are supported by TGA measurements. From the primary thermograms, the rate of decomposition in DMDAS-treated samples appears
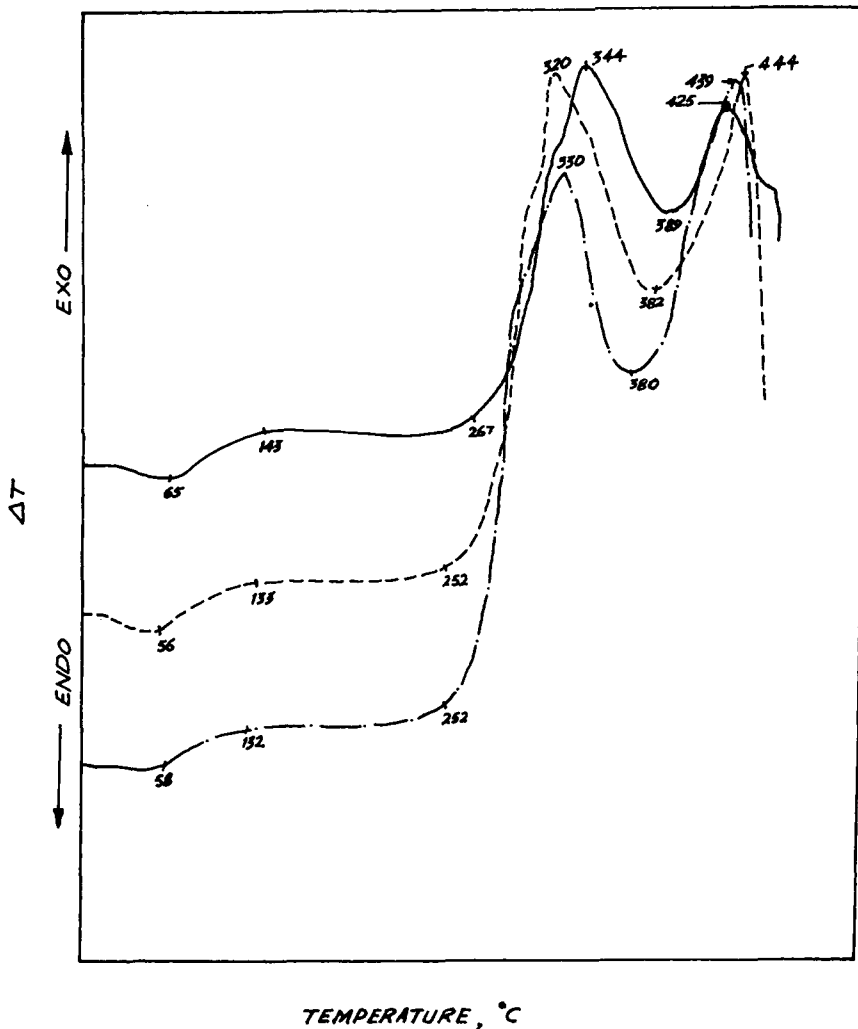
Fig. 7. D curves for DMDAS-treated samples: (—) parent; (-----) 2.53 mmoles; (- - - -) 8.2 mmoles silane fixed per 100 g viscose.

TABLE VII
Thermogravimetric Analysis of Crosslinked Viscose[a]

Sample no.	Sample	IDT, °C	T_D, °C, at weight loss of								$IPDT$, °C	D_{max} °C
			10%	20%	30%	40%	50%	60%	70%	80%		
1	Parent	280	300	312	320	328	342	374	416	444	370	365
2[b]	DMDAS crosslinked sample	280	300	310	320	328	344	386	424	452	374	368
3[c]	MVDAS crosslinked sample	312	324	334	342	354	362	408	454	480	396	410

[a] IDT = Initial decomposition temperature; T_D = decomposition temperature; $IPDT$ = integral procedural decomposition temperature; D_{max} = maximum decomposition temperature.
[b] 8.2 mmoles silane/100 g material.
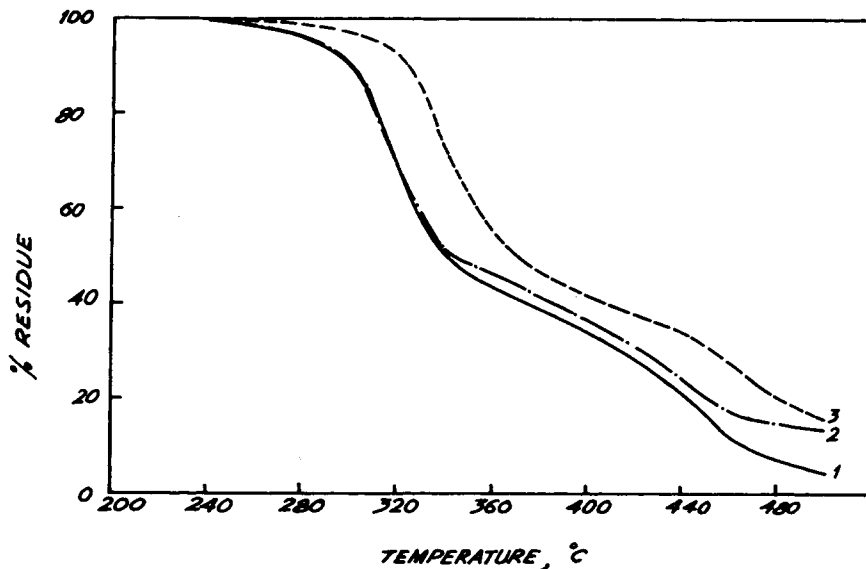[c] 8.9 mmoles silane/100 g material.

Fig. 8. Primary thermograms of crosslinked viscose: (1) parent; (2) DMDAS-treated (8.2 mmoles); (3) MVDAS-treated (8.9 mmoles per 100 g viscose) sample.

to be the same as that of the control up to 330°C; the trend then changes, i.e., the decomposition rate is low (Table VII). The crosslinks introduced by MVDAS, however, appear to enhance the thermal stability of viscose filament much more than the crosslinks introduced by DMDAS. Despite these differences, from $IPDT$ and D'_{max} values one may predict a higher thermal stability for crosslinked samples. Rodrig et al.[23] have also reported that substitution of strong chemical bonds for weaker hydrogen bonds stabilizes the cellulose thermally.

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