

Modification of Nylon 6 by Organochlorosilanes.

I. Chemical Reaction

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Synopsis

The reaction of nylon 6 with dimethyldichlorosilane and vinylmethyldichlorosilane was investigated. Bright, 20-denier monofilament, nylon 6 yarns with 12.83% nitrogen, 61.16% carbon, and 10.16% hydrogen content were taken. Benzene or toluene was used as solvent for the reagents. The extent of reaction was estimated from the increase in weight of the parent yarn. Reaction was carried in the presence of nitrogen or in atmospheric oxygen (air). The per cent weight gain increased with increase in concentration of reagents, time, and temperature of the reaction. Viscosity and dyeability of the modified samples were measured, and in some samples the percentage of carbon, hydrogen, and nitrogen was also determined.

INTRODUCTION

Chemical modification of nylon, by reacting it with suitable reagents, may lead to improvement in its various properties, e.g., increased ironing temperature, better thermal stability, improved wrinkle resistance, etc.

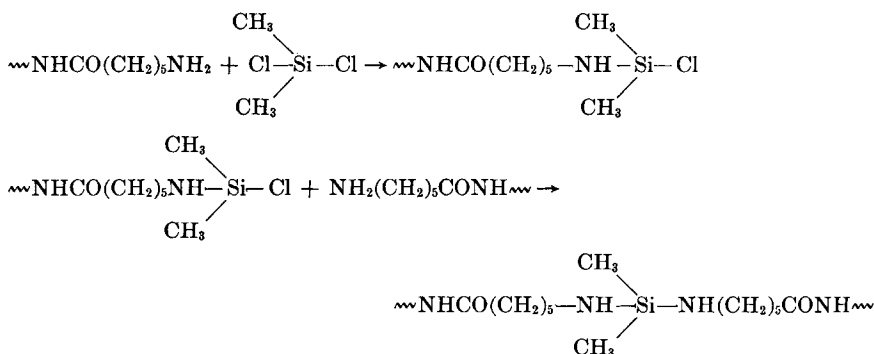
The reactions of nylon 66 with some difunctional reagents have been investigated in the last several years.¹⁻⁷ Thus, the reaction of some α - ω diacid chlorides and diisocyanates with nylon 66 yarn has been investigated,⁶ and the effect of such crosslinking reactions on the physical properties of yarn has also been reported.⁸ Cyanuric chloride,⁷ phosphorous chloride and sulfur monochloride⁹ are some of the other reagents that have been tried. Self-crimping and helical coiling can be achieved by introducing disulfide and alkylene sulfide crosslinkages.^{10,11} In the present paper, the reaction of nylon 6 with dimethyldichlorosilane and vinylmethyldichlorosilane is reported.

Extensive work has been reported on the use of silicones as water repellents in combination with a crease resistant resin on natural fibres as well as synthetic fibers.¹²

The high thermal stability of silicone compounds may also lead to an improvement in the thermal behavior of nylons. The aim of the present work was to investigate the possibility of crosslink formation with organochlorosilanes.

The organochlorosilanes undergo a SN_2 type of reaction at the silicon atom with the nucleophiles. Nylon 6 has a sufficient number of amine end-

groups, and these may displace the chlorine in dimethyldichlorosilane and vinylmethyldichlorosilane to form a crosslink as follows:



The carboxyl endgroups may also react in a similar manner. It has been reported that the carboxyl group is silylated more readily than the amino group.¹³ Such a reaction will increase the molecular weight of the sample considerably and a linear product will be obtained.

The amide nitrogen, though a much weaker nucleophile, may also react with organochlorosilanes. Crosslink formation will take place owing to the participation of amide nitrogen in the reaction. The reaction of organochlorosilane with the nucleophiles is distinctly a two-step reaction where the two chlorines are successively displaced by nucleophile. In the first step, one chlorine atom will be displaced from silicon. Since the reaction is a nucleophilic substitution, the reactivity of the second chlorine will be less, and so the second step should be slower than the first one.

The substitution of an electronegative vinyl group in place of methyl in dimethyldichlorosilane may also influence the reactivity of the silicon compound.

EXPERIMENTAL

Raw Materials

Dimethyldichlorosilane (BDH), bp 70°C, was kept in completely anhydrous condition. Vinylmethyldichlorosilane, bp 93°C, was distilled before use.

The reaction was carried out in the presence of either benzene or toluene. Variations in time, temperature, and concentration of the reagents were tried. Up to a temperature of 80°C benzene (BDH) was used, and above, it toluene (BDH) was used. Both benzene and toluene were purified by refluxing for 6 hr over metallic sodium and then distilled under anhydrous condition. These solvents were stored over metallic sodium.

Yarn

Nylon 6, 20-denier, bright monofilament, having a density of 1.152 g/cc, nitrogen content of 12.83%, carbon content of 61.16%, and hydrogen content of 10.16%, was supplied by M/S J. K. Synthetics Ltd. The yarn was

Soxhlet extracted for 6 hr with petroleum ether to remove the finishing agents. After drying at 100°C for 24 hr, the material was kept in a desiccator and handled thereafter carefully under anhydrous conditions.

The reaction with organochlorosilanes was carried out in benzene or in toluene, in nitrogen as well as in atmospheric oxygen, and in the presence or absence of an acid absorbant. In a typical experiment, about 1 g ether-extracted yarn was placed in a two-necked, round-bottom flask fitted with a reflux condenser and a CaCl₂ drying tube and containing 30 ml benzene or toluene. Depending upon the molar ratio of nylon 6 and organosilane compound, desired quantities of the latter were introduced into the reaction flask, dropwise and with shaking of the flask to ensure thorough mixing. The temperature was then raised to the desired value by keeping the flask in an oil bath. After the reaction had progressed for the desired time, the yarn was removed and washed several times with solvent (benzene or toluene) and then dried in an oven at 100°C and kept in a desiccator.

Treatment in atmospheric oxygen in the presence of trimethylamine was carried out in a similar way. The amine was added to the solution in the flask before the addition of silane.

Reaction in nitrogen atmosphere was carried out by bubbling nitrogen through the flask during the entire course of reaction. The extent of the reaction was judged by the increase in the weight of the yarn after the treatment.

Measurement of Viscosity

The viscosity of the samples was measured in Ubbelohde's suspended-level viscometer at 30° ± 0.1°C using *m*-cresol as solvent. *m*-Cresol was distilled (bp 202°C) before use.

Measurement of Dyeability

Dyeing was carried out with a disperse dye, Cibacet Turquoise Blue G, at 100°C for 1 hr by the usual method. Finish-free parent yarn and some of the modified samples were dyed at 2% shade (on the weight of the material) at a material-to-liquor ratio of 1:300. The amount of the dye absorbed was found by measuring the optical density by the colorimetric method at 578m μ .

Firstly, a graph of optical density versus concentration was standardized with the solution of pure dyestuff in formic acid (90% BDH). The dyed samples were also dissolved in the same solvent at a known concentration, and the optical density was determined under similar condition. Comparing the results with the standard, the dye uptake was calculated.

RESULTS AND DISCUSSIONS

Effect of Concentration of Organochlorosilane on Weight Gain of Nylon

The results on the per cent weight gain with varying molar concentration of yarn to silane are given in Table I, for samples treated with dimethyl-

TABLE I
Effect of Concentration of Organochlorosilanes on Per Cent Weight
Gain of Nylon 6 in Nitrogen Atmosphere at 80°C^a

Sample no.	Reagent	Yarn:silane Molar ratio	Weight gain, %
T ₁	DMCS	1:0.5	2.463
T ₂	DMCS	1:1.0	2.900
T ₃	DMCS	1:1.5	3.195
T ₄	DMCS	1:2.0	3.377
V ₂	VMCS	1:0.5	1.685
V ₃	VMCS	1:1.0	2.073
V ₄	VMCS	1:1.5	2.160
V ₅	VMCS	1:2.0	2.253

^a Solvent: benzene; time: 2 hr.

TABLE II
Effect of Concentration of DMCS on Per Cent Weight Gain
of Nylon 6 in Oxygen Atmosphere at 80°C^a

Sample no.	Yarn:silane molar ratio	Silane:amine molar ratio	Weight gain, %
O ₁	1:0.1	1:0.01	0.45
O ₂	1:0.5	1:0.05	1.00
O ₃	1:1.0	1:0.10	1.30
O ₄	1:1.5	1:0.15	1.45
O ₅	1:2.0	1:0.20	1.60
O ₁₄	1:0.1	0	0.62
O ₁₅	1:0.5	0	1.25
O ₁₆	1:1.0	0	1.56
O ₁₇	1:2.0	0	1.79

^a Solvent: benzene; time: 2 hr.

TABLE III
Effect of Concentration of DMCS on Per Cent Weight
Gain of Nylon 6 at 60°C in Nitrogen^a

Sample no.	Yarn:silane Molar ratio	Weight gain, %
T ₁₃	1:0.5	0.7147
T ₁₄	1:1.0	0.8028
T ₁₅	1:1.5	1.2480
T ₁₆	1:2.0	1.9750

^a Solvent: benzene; time: 2 hr.

dichlorosilane (DMCS) and vinylmethyldichlorosilane (VMCS) in nitrogen atmosphere at 80°C for 2 hr. In Table II, the weight gain with concentration in the presence of atmospheric oxygen is given, while Table III gives the effect of concentration of DMCS on the per cent weight gain in nitrogen at 60°C for 2 hr.

Effect of Time of Reaction on Per Cent Weight Gain of Nylon 6

The trend of results obtained by treating samples for different times is shown in Figure 1. It is noted that increase in sample weight is high in the initial periods in nitrogen atmosphere, whereas in the presence of oxygen there is almost a linear increase with time. The overall weight gain is less in oxygen atmosphere and more in nitrogen atmosphere.

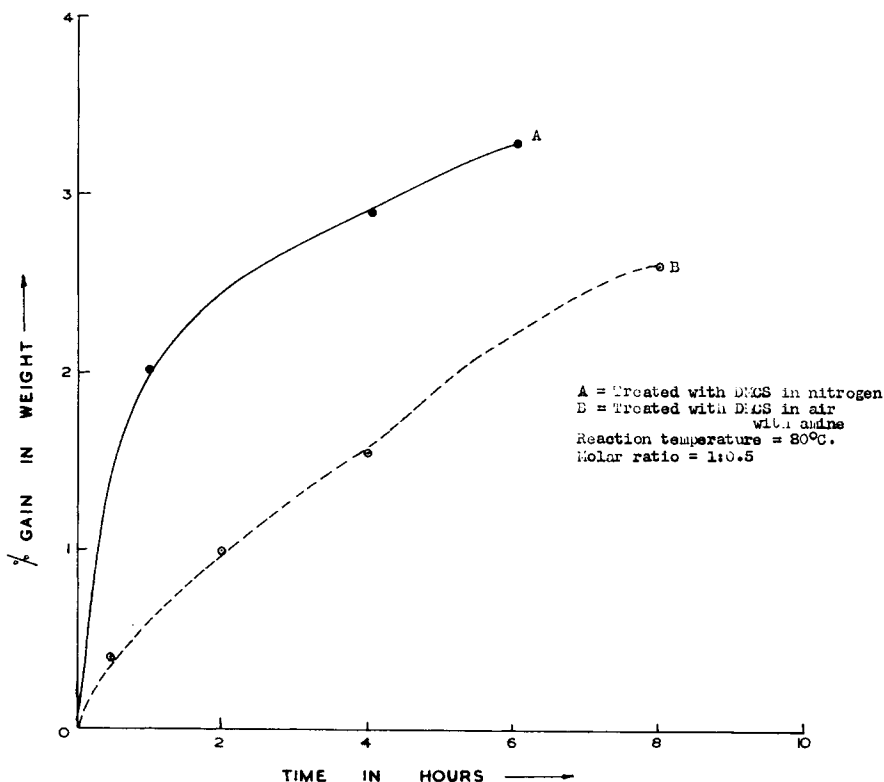


Fig. 1. Effect of time on per cent weight gain of nylon 6 treated with DMCS.

Effect of Temperature of Reaction on Weight Gain of Nylon 6

The results obtained by treatment with DMCS in nitrogen and in oxygen atmosphere are given in Figure 2. The temperature has a sharp influence on the rate of reaction.

Effect of Chemical Treatment on Viscosity

The viscosity of the samples was measured in *m*-cresol at $30^\circ \pm 0.1^\circ\text{C}$ (Fig. 3); results are given in Table IV. The significant observation is that the change in viscosity is not dependent on the gain in weight but is dependent on the way the reaction was carried out. Thus, a 2.90% gain in weight was

TABLE IV
Intrinsic Viscosities of Nylon 6 and Organochlorosilane-
Treated Nylon 6 in *m*-Cresol at 30°C

Treated with DMCS in nitrogen		Treated with DMCS in air		Treated with VMCS in nitrogen	
Sample no.	η_{sp}/c	Sample no.	η_{sp}/c	Sample no.	η_{sp}/c
P	1.315	P	1.315	P	1.315
T ₁	1.580	O ₁	1.275	V ₁	1.310
T ₂	1.395	O ₂	1.245	V ₂	1.255
T ₃	1.362	O ₃	1.230	V ₃	1.234
T ₄	1.280	O ₄	1.210	V ₄	1.200
T ₅	1.482	O ₁₄	1.145	V ₅	1.198
T ₇	1.334	O ₁₆	1.035	—	—
T ₉	1.257	O ₁₇	0.925	—	—
T ₁₀	1.285	—	—	—	—
T ₁₂	1.325	—	—	—	—

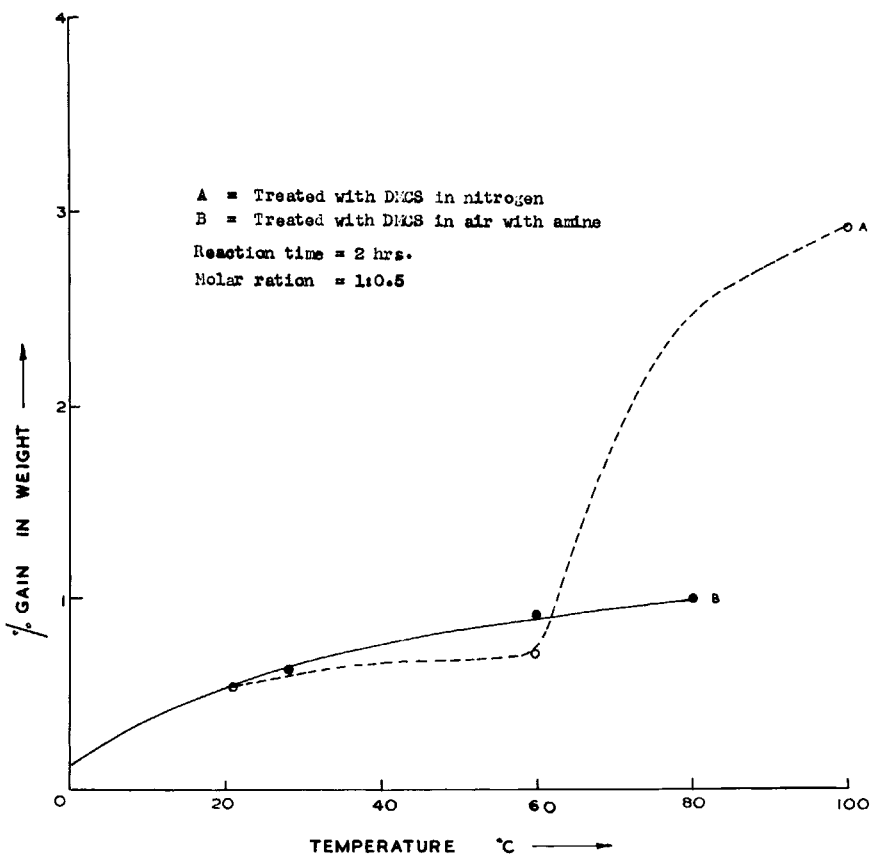


Fig. 2. Effect of temperature on per cent weight gain of nylon 6 treated with DMCS at a yarn-to-silane ratio of 1:0.5.

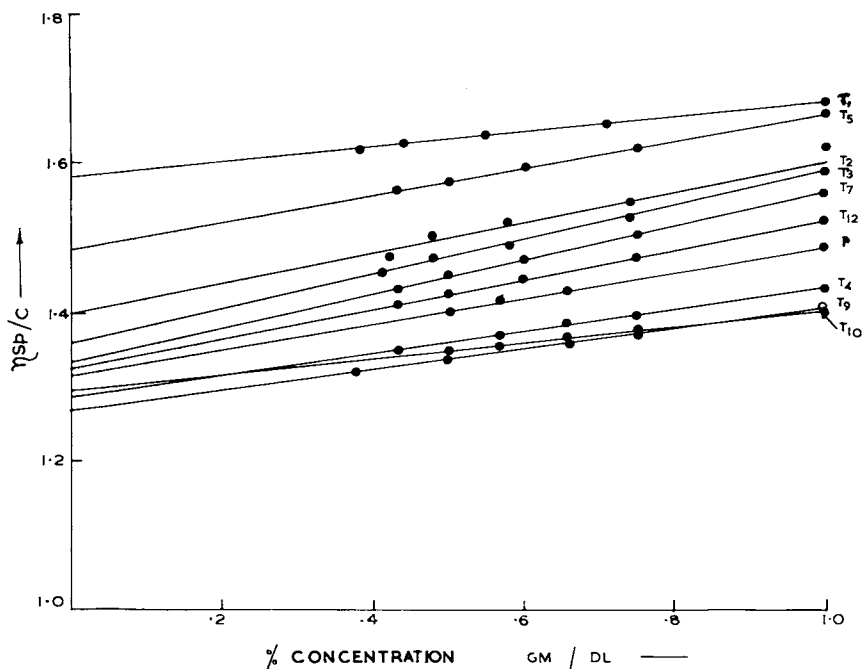


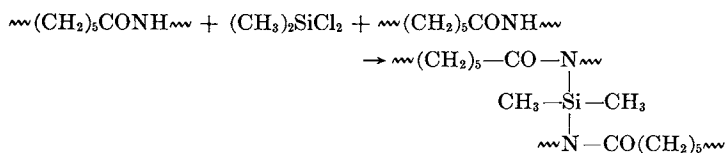
Fig. 3. Plot of intrinsic viscosity of nylon 6 and DMCS-treated nylon 6.

obtained for samples T_2 and T_7 , but the viscosities were 1.395 and 1.334, respectively. The intrinsic viscosities of the samples treated in air were always less than in nitrogen, and the decrease was more in the absence of amine.

Effect on Dyeability

The effect on dyeability of the parent and some of the modified samples was measured by dyeing with a disperse dye, and the results are given in Figure 4. The trend indicates a decrease in dye uptake with increase in the per cent weight gain of the samples.

It is evident from Tables I-III that the gain in weight is high at a low molar ratio of yarn to silane. At higher molar ratios, though the gain in weight is greater, it is not in the same proportion. Thus, an increase in the yarn-to-silane ratio from 1:0.5 to 1:1 results in a weight gain from 2.463 to 2.900%. Another significant observation of these experiments is that even at a very high molar ratio of yarn:silane (i.e., 1:2) the gain in weight is only 3.4% approximately. If silylation of all the —NH groups of nylon were taking place and both —Cl of silane were replaced, then one could calculate the expected increase in weight by the following method:



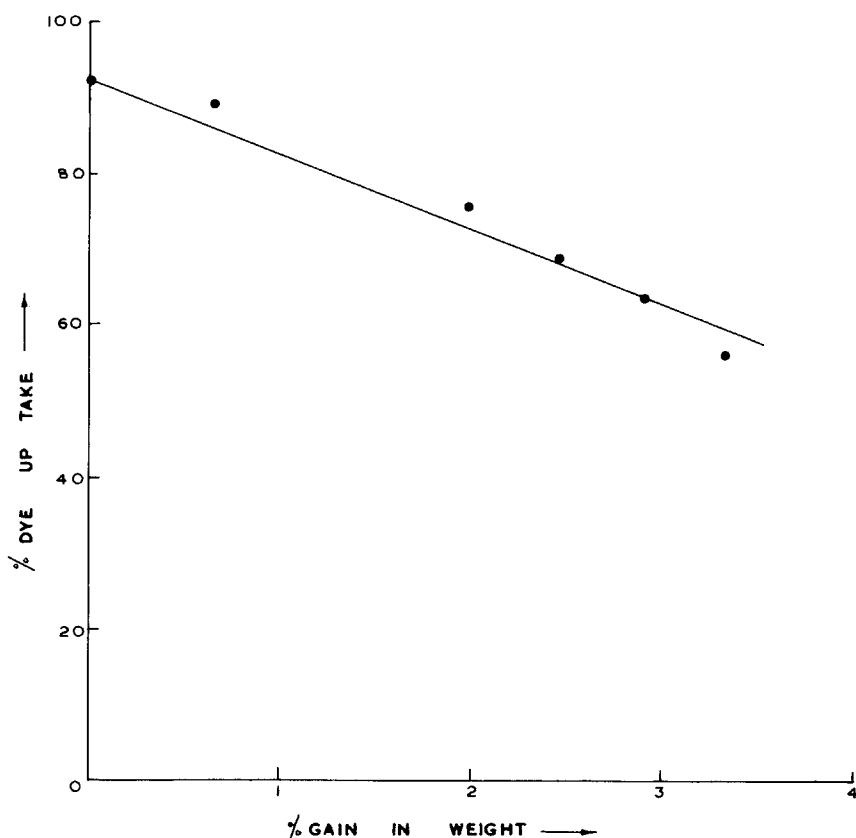
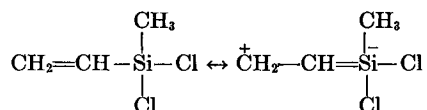


Fig. 4. Effect of per cent weight gain of DMCS-treated nylon 6 on per cent dye uptake.

Thus, an increase of 56 g will take place for an original weight of 226 g of nylon 6. This amounts to an increase in weight of 24.7%. Thus, it is obvious that complete silylation of nylon 6 is not taking place and approximately 12% of the —NH group of the polymer backbone are reacting to give products of silylation. Nylon 6 is about 50% crystalline, and one should not expect silylation of —NH groups in these regions. However, if this is taken into account, it may be concluded that —NH groups of amorphous regions are also not reacting completely and only 25% are reacting with organochlorosilane. Another noteworthy point is that the per cent gain in weight is larger in the presence of nitrogen atmosphere than in the presence of air. In presence of amine, the gain in weight is less, while in its absence the gain is more.

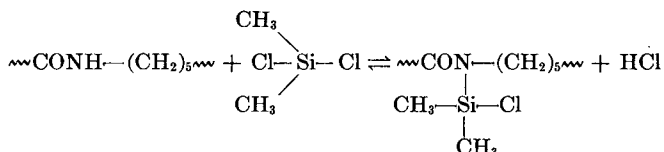
It has been reported that a 10- to 50-fold equivalent weight of silylating agent to functional group is required for complete silylation.¹³ An excess of reagent has been recommended to consume smaller traces of water which may be present even after repeated purification of the solvents. The low conversion of nylon 6 to the silylated product may then be explained on these grounds.

A comparison of the per cent weight gain of nylon 6 by DMCS and VMCS indicates that in the latter case less reaction has taken place. This is contrary to the expected reactivity of the two compounds. Generally, the reactivity of a silane is increased by attaching an electron-withdrawing group, and the vinyl group is definitely more electronegative than the methyl group. So, on the basis of inductive effect alone, it may not be possible to explain this observed phenomenon. The resonance and steric factors may also be influencing the reactivity. It is a known fact that $-\text{Si}-$ can accept an electron in its vacant d orbitals to give dative $d_{\pi} - p_{\pi}$ bonding. Perhaps the electrons of the vinyl group are donated to the $-\text{Si}-$ atom, increasing electron density around it in the following manner:



Also, a vinyl group is bulkier than a methyl group, and reactivity of organosilanes is greatly influenced by the steric requirements of the groups attached to it. On the basis of these observations, therefore, it may be concluded that DMCS is a better reagent for silylation than is VMCS.

It has been observed that per cent gain in weight of nylon 6 is greater in the presence of nitrogen than in air. As the yarns become very hard and brittle in air, the degradation is expected to be greater. In case of nitrogen, the gas was bubbled through the solution, and this might have removed the HCl which is formed as a result of reaction of nylon 6 and organochlorosilane:



Removal of HCl is necessary in this equilibrium reaction, as it may degrade the nylon 6. A base may remove the acid generated, and therefore, in air, based on the molar ratio of organochlorosilane, triethylamine was used. However, it was observed that in such a case the weight gain was slightly more in absence of base than in its presence. It may therefore be concluded that an inert atmosphere is needed to get a better yield of silylated product.

An increase in the duration of the reaction and the reaction temperature resulted in an increase in weight gain. In the initial period, the rate of reaction was high, and later there was a tendency for leveling off. This is due to the large number of $-\text{NH}$ groups available in the initial stage and later, as the number of $-\text{NH}$ groups decreases, the rate of silylation is also decreased.

The effect of temperature on the increase in weight gain is somewhat difficult to explain. In these reactions, DMCS was added to the solvent-

TABLE V
Elemental Composition of Nylon 6 and DMCS-Treated Nylon 6

Sample no.	Weight gain, %	Carbon, %	Hydrogen, %	Nitrogen, %
P	0.000	61.16	10.16	12.83
T ₁	2.463	62.12	10.41	12.46
T ₂	2.900	63.41	10.70	12.19
T ₇	2.901	59.22	9.56	12.08

fiber system at room temperature and then the temperature was raised to the desired value. The time of reaction was recorded when the required temperature was attained. Since the silanes are very reactive, it may be possible that the reaction takes place during this initial heating period and that at higher temperature some secondary reactions are also taking place. The T_g of nylon 6 is reported as 50°C. It is quite likely that the extent of silylation increases at a high temperature owing to the physical state of polymer.

The change in viscosity is not dependent on the extent of reaction but is dependent on reaction conditions. Thus, highest viscosity is obtained for a sample prepared in nitrogen atmosphere by treating yarn with DMCS at a molar ratio of 1:0.5 at 80°C for 2 hr. At the same molar ratio, if the duration of reaction is increased or decreased, the viscosity also decreases but is still higher than that of the parent yarn.

An increase in the concentration of silanes reduces the viscosity. So, in interpreting the results of viscosity, one has to consider two competing reactions: (a) silylation reaction and (b) hydrolytic cleavage of amide linkage by evolved HCl.

At optimum temperature, concentration, and duration of reaction, there is an increase in viscosity; otherwise viscosity decreases in all other cases. Results obtained in the presence of air indicate that the viscosity of the material is higher when reaction is carried out in the presence of amine. This again shows that the removal of HCl is one of the essential problems in this reaction.

The decrease in dyeability with disperse dye may be partly due to the lowering in the possibility of hydrogen bond formation due to lowering of the number of —NH groups and partly due to the steric effect of the bulky dyestuff employed. Steric factors, however, appear to be contributing more.

The analysis for the elemental composition of some of the chemically modified samples was also carried out, and the results are given in Table V. The carbon content of the parent nylon 6 is less than expected on a theoretical basis, and the hydrogen content is higher than the expected value. This may be due to the presence of some moisture in the nylon 6 samples. Since all the samples were placed under similar condition a comparison regarding the variation in C, H, and N content with silylation and increase in weight may be obtained. A comparison of T₁ and T₇ samples reveals that

an increase in the reaction time at 80°C results in an increase in per cent weight and a decrease in the C, H, and N content. In the initial periods of reaction, an increase in the C and H content takes place as compared with parent yarn. It has been suggested that in the presence of protonic acids, incipient gel formation takes place owing to amidine¹⁴ cyclization in nylon 6. Such a structure will increase the carbon (72.9%) and hydrogen (11.55%) content of the sample. Since in the reaction with DMCS, HCl is formed, it may be helping in the formation of such a structure. Another competing reaction is the crosslinking with DMCS. Such crosslink formation, if it occurs completely, should cause a change in the carbon (59.5%), hydrogen (9.2%), and nitrogen (9.9%) contents. Increase in the nylon-to-silane ratio (sample T₂) yields a further increase in carbon content, showing that cyclization reactions are more predominant at higher molar ratio of silane. An increase in reaction temperature (100°C) indicates that crosslinking with silanes becomes more predominant than cyclization reactions. The significant observation of the elemental analysis is that samples T₇, T₁₂, and T₂ showed nearly the same amount of gain in weight, but the carbon, hydrogen, and nitrogen contents, of all the samples are different. Thus, depending upon the reaction condition, different reactions may be taking place.

CONCLUSIONS

Nylon 6 can be crosslinked with organochlorosilanes. The weight gain of the yarn is a measure of the degree of crosslinking. Dimethyldichlorosilane is a better crosslinking agent than vinylmethyldichlorosilane. The increase in concentration of reagent, time, and temperature of the reaction resulted in an increase in crosslinking reactions. However, the extent of crosslinking is not very high, and the reaction may be taking place in the less ordered region of the yarn. The elemental analysis and viscosity measurements indicated that per cent weight gain does not necessarily mean similar structure in the fiber, but different reaction may be possible. The dyeability of the fiber with disperse dyes was decreased by silylation.

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