

Modification of Nylon 6 with Organochlorosilanes. II. Physical Properties

I. K. VARMA, R. MANDAL, and D. S. VARMA, *Indian Institute of Technology, Delhi, India*

Synopsis

The physical properties of nylon 6 yarn treated with dimethyldichlorosilane (DMCS) and vinylmethyldichlorosilane (VMCS) in nitrogen atmosphere or air in the presence and absence of an amine have been compared with those of ether-extracted parent yarn. Treatment with DMCS in nitrogen resulted in marginal improvement in breaking stress, considerable increase in breaking elongation, and elastic behavior, whereas initial modulus was decreased. A decrease in density, birefringence, and moisture regain with increase in per cent weight gain was observed. Mechanical damping was decreased considerably up to an optimum weight gain after which it was increased. Thermal properties were also determined, and results are discussed in relation to mechanical properties. The results indicate that the overall thermal stability has decreased in the chemically treated yarns. Treatment with organochlorosilanes in the presence of air results in a chain-scission reaction and a decrease in mechanical properties.

INTRODUCTION

In the previous paper,¹ the reactions of nylon 6 with dimethyldichlorosilane and vinylmethyldichlorosilane under suitable conditions were shown. The effect of such reactions on viscosity and dyeability of the material has also been reported. This paper deals with the effects of the chemical reaction on various physical properties of the yarn.

Special interest was given to determination of the thermal behavior of the yarn treated with organochlorosilanes in nitrogen atmosphere and in air. Thus, the parent as well as some modified samples were heated at different temperatures and the tensile behavior of the heat-treated samples was then observed. The physical properties have been compared with those of the parent yarn which was subjected to Soxhlet extraction with ether and then used as standard for comparison.

EXPERIMENTAL

The parent nylon 6 yarn and the chemically treated yarn were the same as reported in previous paper.¹ Ether-extracted yarns were allowed to react with the organochlorosilanes under different conditions of time, temperature, and concentration of reagents and kept in anhydrous conditions. The various physical properties of these yarns were then measured.

Test Procedures

Denier. Deniers of the yarns were measured by cutting fixed length of yarns and weighing in a bundle on a sensitive balance. These denier values were used in determining the tensile behavior of the corresponding yarns.

Density. Density of the samples was determined by the density gradient column method, as described by Preston and Nimkar.² The liquid mixture used was prepared from xylene ($\rho = 0.866$) and carbon tetrachloride ($\rho = 1.595$). The density measurements were carried out at 20°C and 65% R.H.

Birefringence. The birefringence of the yarn was measured by the immersion method,^{4,5} using paraffin oil ($n = 1.471$) and α -monobromonaphthalene ($n = 1.660$).

Moisture Regain. The moisture regain was determined by vacuum desiccator method as described by Urquart and co-workers,³ using phosphorus pentoxide as dehydrating agent at 65% \pm 2% R.H. and 21° \pm 1°C.

Tensile Properties. Tenacity and elongation of the yarns were measured by Instron at 21°C and 65% R.H., on 2.5 cm gauge length. The cross-head speed was maintained at 5 cm/min and a chart speed of 50 cm/min on a full-scale load of 200 g. Twenty samples were tested for each quality of yarn and the mean was then taken. The load-elongation value was reduced to stress-strain, and results are reported. The initial modulus was calculated from the initial slope of the stress-strain curves.

Elastic Recovery. The method used to determine the elastic recovery was that of Guthrie and Norman.⁶ An extension of 5% was given to the yarn of gauge length 5 cm on the Instron at 21°C and 65% R.H. It was held for 30 sec after 5% extension for relaxation to take place, then contracted to the original gauge length, and then kept at this position for 1 min, to allow recovery from deformation. A cross-head speed of 5 cm/min and a chart speed of 100 cm/min were used, while a full-scale load of 20 g was calibrated.

Dynamic Mechanical Properties. Elastometer: a direct reading instrument was used to measure the dynamic mechanical properties of the parent and modified samples. The statically prestressed fibers were subjected to generate simple harmonic longitudinal oscillation of small amplitude at medium frequency. The amplitude of the alternating force generated in the fiber was kept at constant level during the stress.

In the resonance condition achieved by frequency variation, it is possible to simplify the equation valid for the oscillating motion of the system. The dynamic modulus and loss modulus were determined, and hence the loss tangent or mechanical damping was calculated. A load of 1 g was used for all samples, and forces of 50, 100, 150, 200, and 300 dynes were used to find the corresponding value of elongation and resonance frequency. Standard relations were used to find the value of storage modulus E^1 and loss modulus E^{11} whereby $\tan \delta = E^{11}/E^1$ has been calculated.

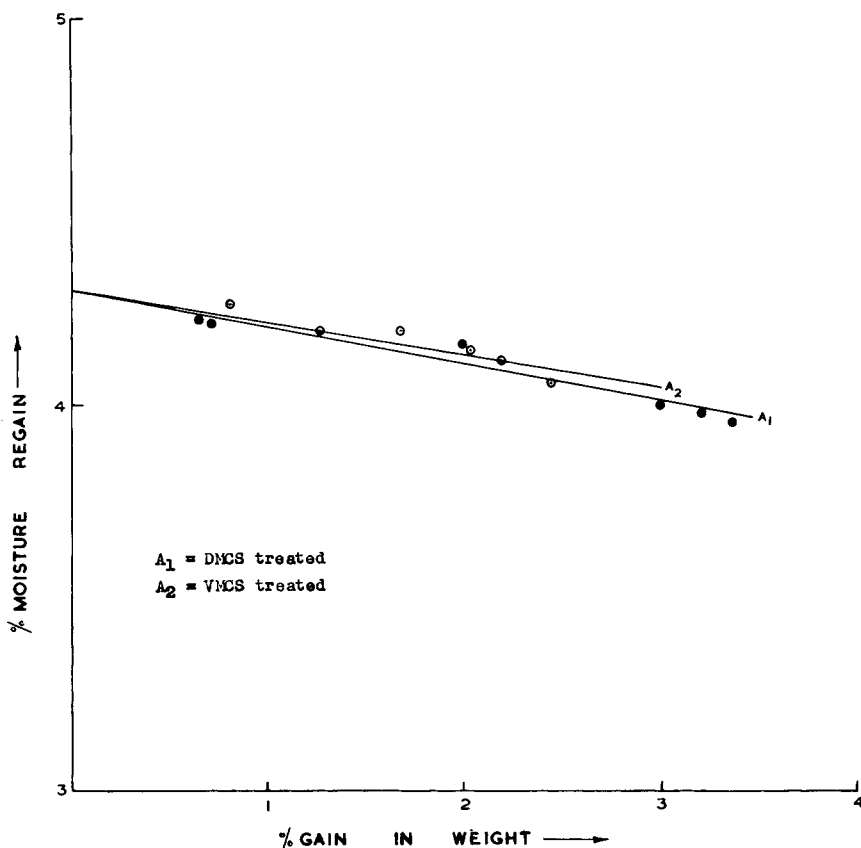


Fig. 1. Plot of per cent weight gain vs. moisture regain of samples treated with DMCS and VMCS in nitrogen.

Thermal Behavior. The thermal stability of both parent and modified yarns was measured by two methods. In the first method, the various samples of nylon were heated for 2 hr at 140°C and 185°C. The temperature during the heat treatment was controlled by using a vapor jacket. Xylene (140°C) and decalin (185°C) were used as the boiling solvents. The stress-strain behavior of the heated samples was then investigated.

The second method for comparing the thermal behavior of modified and parent nylon 6 was to investigate the overall thermal stability by the use of a Stanton thermogravimetric balance. The heating rate was 6°C/min, and the samples were heated from room temperature to 550°C in air. A sample weight of 50 ± 2 mg was taken. The primary thermograms were obtained by plotting the per cent residual weight versus temperature. By this technique, change in weight of the samples as a function of temperature was evaluated. The initial decomposition temperature and the temperatures of 10%, 20%, 30%, 40%, 50%, and 70% decomposition were evaluated.

lated from the TGA trace, and a qualitative idea regarding thermal behavior of various samples was obtained.

RESULTS AND DISCUSSIONS

In Table I, the denier, density, and birefringence of nylon 6 as a result of treatment with DMCS in nitrogen atmosphere are given. An increase in the denier and decrease in density with an increase in per cent weight gain was observed. The denier of the yarn is expected to increase since the mass of the material increases as a result of treatment. The decrease in density with increase in weight gain may be due to the fact that some swelling takes place as a result of chemical treatment. The increase in mass may, however, be smaller compared to the increase in volume. The resultant effect is a decrease in density. The birefringence of the treated samples decreased with an increase in weight gain. The marginal fall in birefringence is probably attributable to some disorientation taking place owing to slack swelling during treatment with silanes.

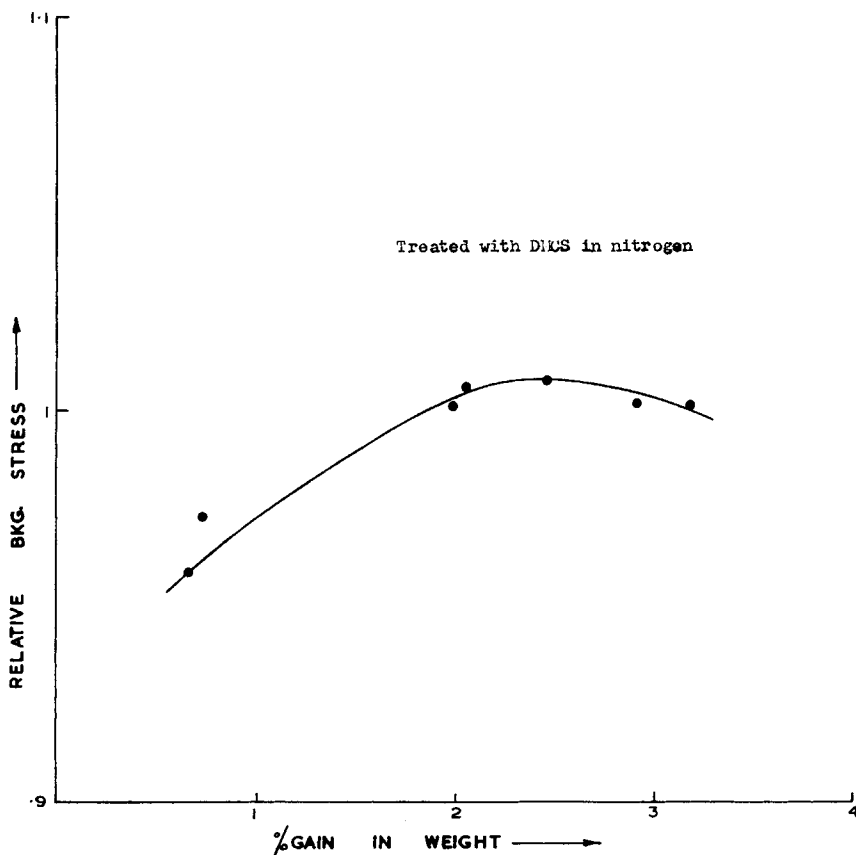


Fig. 2. Relative results of breaking stress of samples treated with DMCS in nitrogen.

TABLE I
Effects of Treatment of Nylon 6 with Dimethyldichlorosilane in
Nitrogen on Denier, Density, and Birefringence of the Fibers

Sample no.	Weightgain, %	Denier	Density, g/cc	Birefringence
P	—	20.000	1.152	0.05151
T ₉	0.6454	20.1290	1.149	0.05141
T ₁₀	0.7147	20.1429	1.149	0.05066
T ₁₄	0.8028	20.1606	1.149	0.05065
T ₁₅	1.248	20.2496	1.148	0.05022
T ₁₆	1.975	20.3958	1.146	0.04697
T ₅	2.046	20.4292	1.146	0.04331
T ₁	2.463	20.4929	1.145	0.04223
T ₂	2.900	20.5800	1.144	0.03998
T ₇	2.901	20.5802	1.144	0.03977
T ₁₂	2.910	20.5820	1.144	0.03969
T ₃	3.195	20.6390	1.143	0.03934
T ₈	3.327	20.6654	1.142	0.03906
T ₄	3.377	20.6754	1.141	0.03892

TABLE II
Effect of Treatment of Nylon 6 with DMCS in
Nitrogen on Mechanical Properties

Sample no.	Weight gain, %	Breaking stress, g/d	Breaking elongation, %	Initial modulus, g/d
P	0.0000	4.800	34.0	20.0
T ₉	0.6454	4.600	41.0	16.7
T ₁₀	0.7147	4.670	43.0	16.7
T ₁₄	0.8028	4.755	48.0	16.7
T ₁₅	1.2480	4.805	55.7	16.7
T ₁₆	1.9750	4.880	58.5	16.7
T ₅	2.0460	5.040	62.6	16.7
T ₁	2.4630	5.180	68.0	11.5
T ₂	2.9000	4.930	63.0	14.3
T ₇	2.9010	4.845	59.0	10.2
T ₁₂	2.9100	4.836	58.2	19.5
T ₃	3.1950	4.880	58.5	16.7
T ₈	3.3270	4.825	75.0	12.5
T ₄	3.3770	4.660	48.7	11.8

The effect of chemical treatment on mechanical properties is shown in Table II. There is practically no change in breaking stress, but the breaking elongation is considerably increased. The considerable increase in breaking elongation of the material treated in nitrogen atmosphere may be due to the high stretchability of the intermolecular N-Si bonds which are introduced by the chemical reaction with silanes. In those cases where the degradation is high, the breaking elongation is decreased, as seen in the case of treatment in air in the absence of any amine. Further, the results show a decrease in the initial modulus. The initial modulus

is measured from the initial slope of the stress-strain curve; and as extension behavior is always improved, the stiffness of the material will decrease.

In Figure 1, the effect of weight gain on moisture regain is shown. The lowering in moisture regain can best be explained from the fact that since the chemical reaction generally takes place mainly with the groups available in the noncrystalline region, the sites for water absorption are thus blocked causing a decrease in moisture regain.

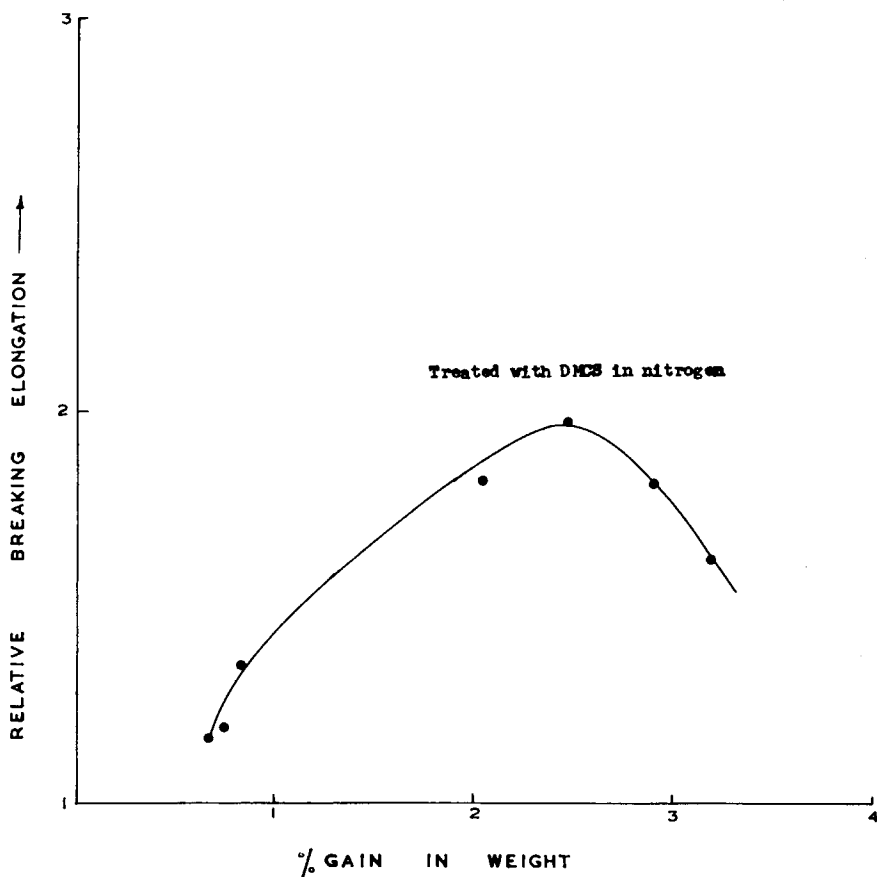


Fig. 3. Relative results of breaking elongation of samples treated with DMCS in nitrogen.

The values of relative breaking stress and breaking elongation were calculated from the results given in Table II. These results are shown in Figures 2-5. The improvement in breaking stress may be due to the formation of covalent bonds which are stronger than the hydrogen bonds present in the parent yarn. This, however, is dependent upon the uniformity of distribution of the silylating agents. If the crosslinking is not uniform in the structure, the stress of the material falls. In the presence of air, however, the breaking stress always falls. It may be due to the degradation that may

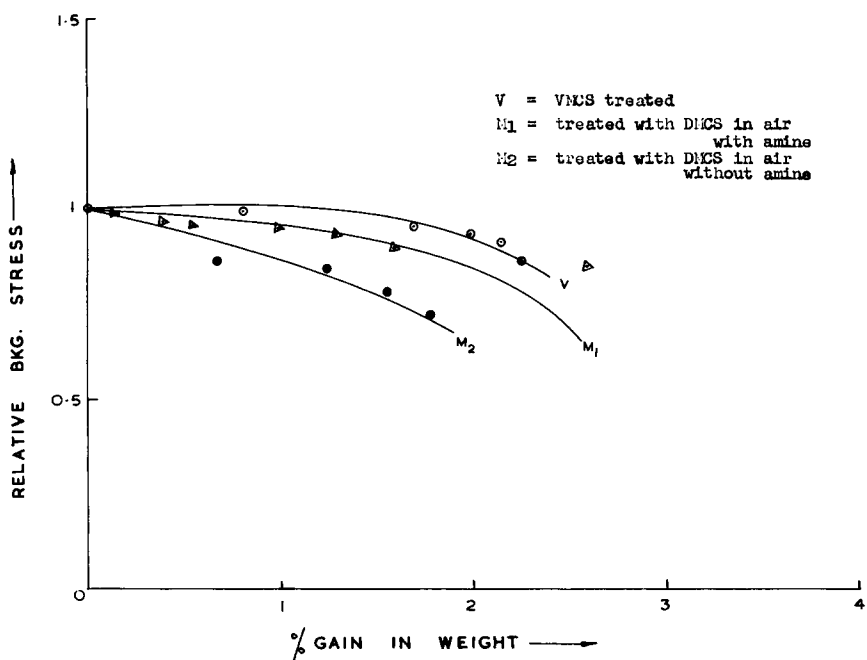


Fig. 4. Relative results of breaking stress of samples treated with DMCS in air and VMCS in nitrogen.

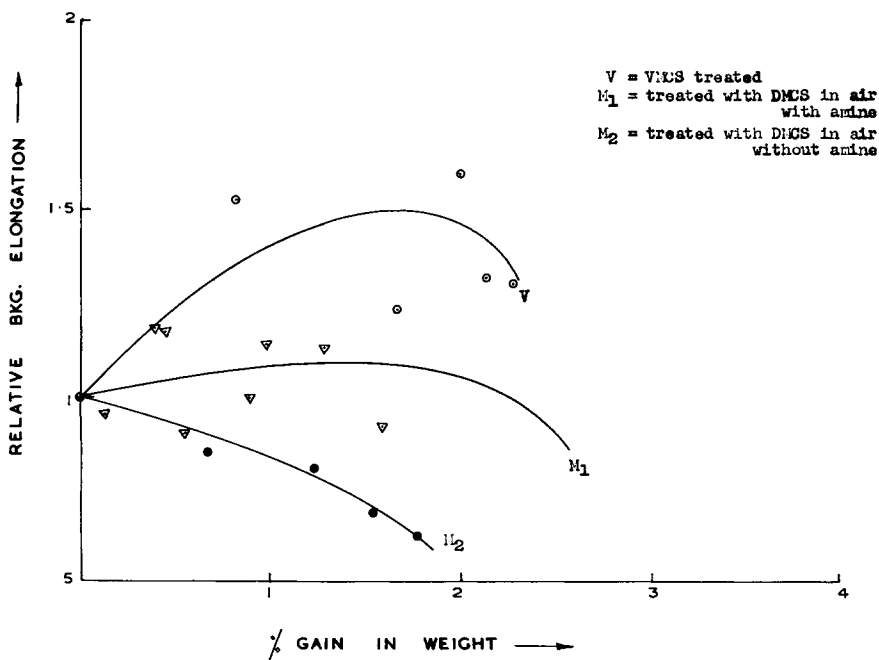


Fig. 5. Relative results of breaking elongation of samples treated with DMCS in air and VMCS in nitrogen.

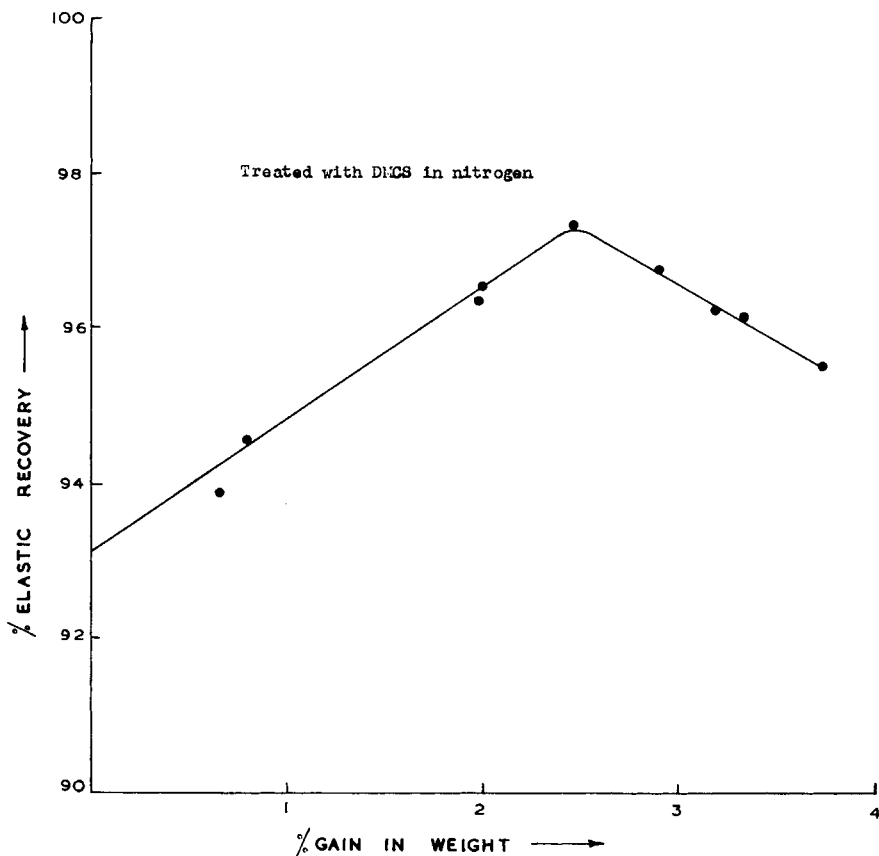
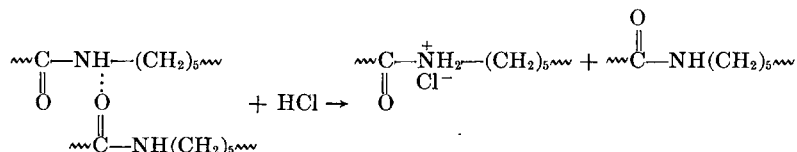


Fig. 6. Per cent weight gain vs. elastic recovery of samples treated with DMCS in nitrogen.

take place due to the presence of HCl that is evolved during the reaction. In the chemical modification of nylon 66 with acyl halides, a decrease in physical properties was observed, and this was attributed to breakage of intermolecular hydrogen bonds by HCl:



However, the intrinsic viscosity measurements¹ indicated a decrease in the viscosity of the fiber treated with DMCS in the presence of air. Thus, chain scission along with breakage of intermolecular hydrogen bonding may be a possibility here.

Elastic behavior was found to be improved, unless there was a severe degradation of the material. Elastic recovery with respect to per cent

weight gain and with respect to breaking elongation is shown in Figures 6 and 7, respectively. The improvement is probably a result of the more elastic nature of the N-Si intermolecular bond that brings the molecular chain back to its original position after removal of the load of deformation. The elastic intermolecular bond is due to the action of organochlorosilane.

The effect of chemical treatment on the dynamic mechanical behavior is shown in Figure 8. It was found that the mechanical damping is decreased considerably with an optimum weight gain, after which it is found

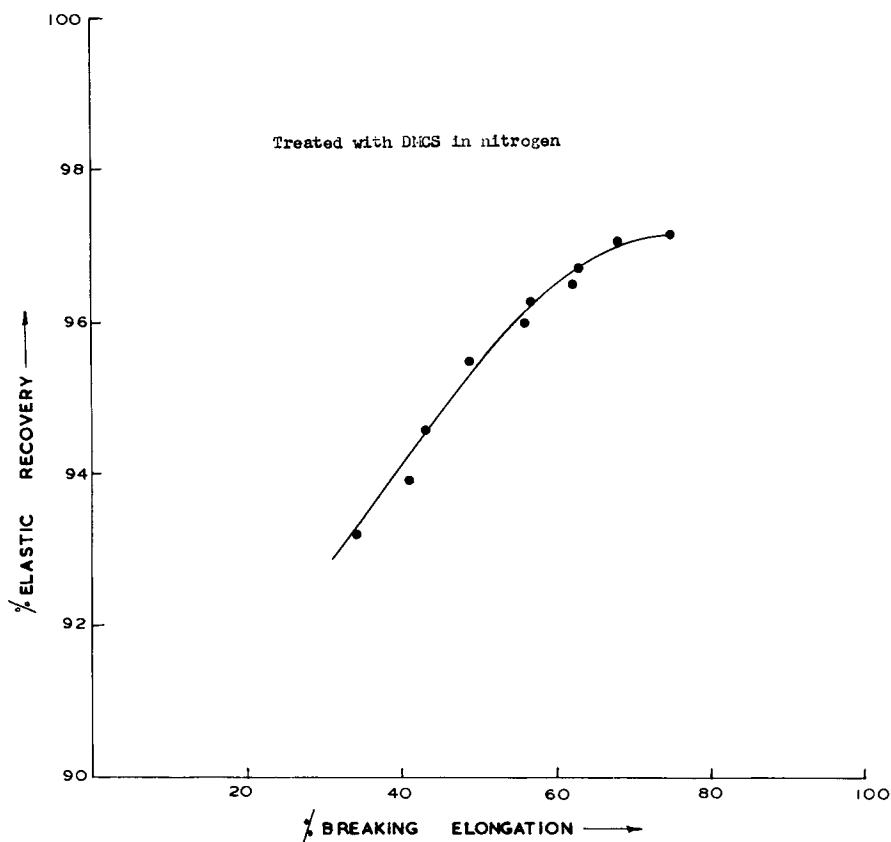


Fig. 7. Breaking elongation vs. elastic recovery of samples treated with DMCS in nitrogen.

to increase. As the elastic behavior of the material improved as a result of treatment with DMCS in nitrogen, the damping is expected to increase. A highly elastic material will have a higher damping since most of the energy lost during deformation can be recoupled on removal of the load. However, if the degradation takes place, it will break the bonds causing a lowering of the damping value.

An examination of Table III reveals that there is always a decrease in breaking stress and breaking strain when the samples treated with DMCS in nitrogen are heated at 140°C for 2 hr. The fall in breaking extension is greater than that of the parent yarn. However, at 185°C the reverse is observed. The fall in breaking stress is less in modified samples than in parent samples, both at 140°C and at 185°C. The decrease in the stress and extension of parent yarn may be explained on the basis of the scission of covalent bonds of polycaprolactam. It has been suggested⁷ that

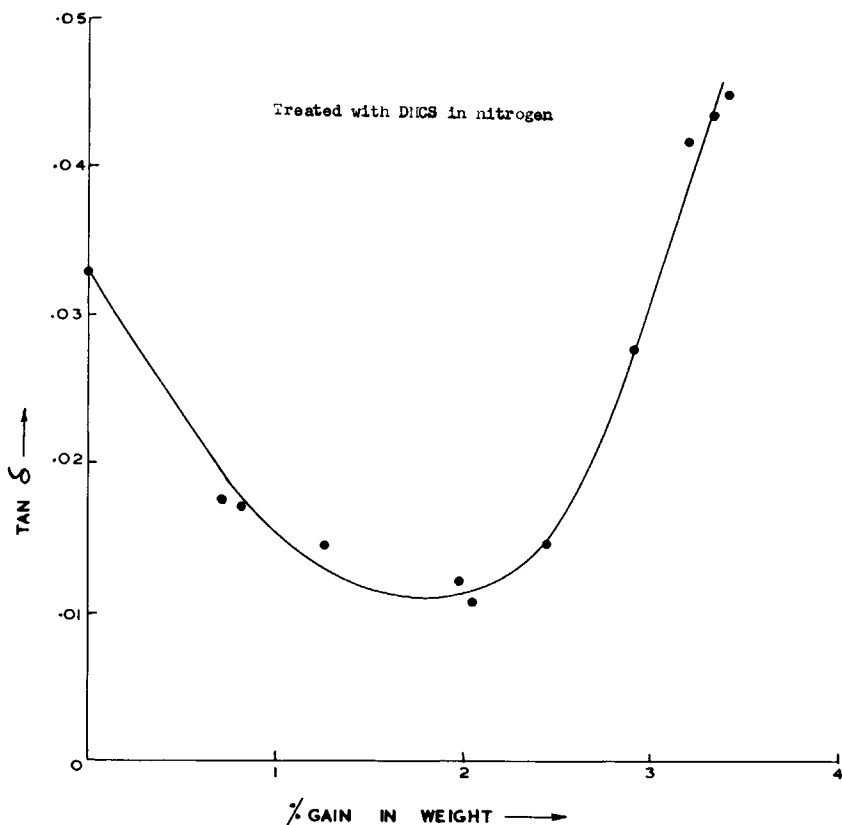


Fig. 8. Per cent weight gain vs. $\tan \delta$ of samples treated with DMCS in nitrogen.

homolytic fission of covalent bond and secondary reaction such as hydrolysis, etc., take place during the heat treatment of nylon 6.

By the introduction of silicon bonds, the stability at lower temperature may be improved. As a consequence, an improvement in the tensile properties may be expected. It has been mentioned that the Si-C bond has higher thermal stability than the C-C bonds in organic compounds. The Si-C bond dissociation energy is somewhat lower than the C-C bond energy, but the polarity of the Si-C bond and the shielding effect of the silicon atoms enhance the thermal stability of the bond. Same argument

TABLE III
Effect of Temperature on Mechanical Properties of Nylon 6 and DMCS-Treated Nylon 6^a

Sample no.	Weight gain, %	140°C				185°C			
		Breaking stress, g/d	Decrease, %	Breaking strain, %	Decrease, %	Breaking stress, g/d	Decrease, %	Breaking strain, %	Decrease, %
P	0	4.1	17	32.8	2.6	1.05	81.7	12	64.6
T ₁	2.463	4.93	4.6	62.8	7.6	3.71	27.3	42.6	37.3
T ₂	2.90	4.86	7.4	57.2	9.2	3.74	24.1	34.0	46.0
T ₃	3.195	4.66	4.5	53.0	7.2	2.95	39.5	32.8	42.0
T ₄	3.377	4.43	4.9	46.5	4.5	2.70	41.2	32.2	33.8
T ₅	2.046	4.89	3.1	57.7	7.9	3.66	28.4	40.4	35.4
T ₇	2.901	4.73	2.5	56.0	5.4	3.2	34.0	39.0	34.1
T ₈	3.327	4.67	3.3	70.7	5.7	2.78	42.5	54.4	27.5
T ₉	0.6454	—	—	—	—	2.41	47.6	29.0	29.3
T ₁₀	0.7147	4.46	4.5	38.6	9.8	2.49	46.7	26.2	39.1
T ₁₂	2.91	—	—	—	—	2.92	39.6	40.6	30.2
T ₁₄	0.8028	4.3	9.5	42.2	12.1	2.59	45.4	27.4	42.92
T ₁₅	1.248	4.57	5.3	49.4	11.5	2.86	40.5	30.3	45.6
T ₁₆	1.975	4.51	7.6	50.8	13.2	3.28	32.8	31.4	46.3

^a Heat treatment 2 hr.

TABLE IV
Evaluation of Relative Thermal Stability of DMCS-Treated Nylon 6^a

Sample no.	Weight gain, %	10% DT	20% DT	30% DT	40% DT	50% DT	75% DT	90% DT
P	0	365.0	390.0	400.0	407.5	410.0	430.0	480.0
T ₅	2.046	350.0	372.5	382.5	390.0	395.0	410.0	450.0
T ₁₅	1.248	352.5	370.0	382.5	390.0	397.5	417.5	460.0
T ₁₆	1.975	360.0	372.5	380.0	387.5	395.0	413.0	447.5
O ₁₄	1.450	327.5	360.0	375.0	382.5	392.5	415.0	480.0
O ₁₂	1.560	347.5	380.0	395.0	402.5	407.5	425.0	465.0
O ₁₃	2.600	355.0	385.0	395.0	405.0	415.0	447.5	507.5
O ₁₅	1.250	320.0	367.5	380.0	392.5	400.0	420.0	442.5

^a DT = Decomposition temperature.

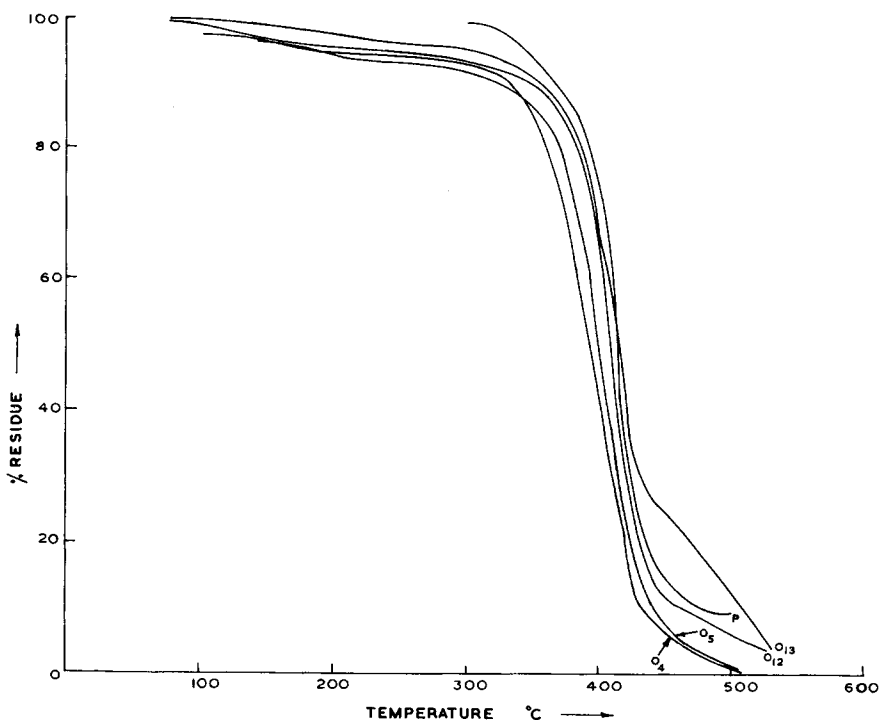


Fig. 9. Primary thermograms of nylon 6 and samples treated with DMCS in air.

may be put forward for Si-N bonds which may be introduced by the reaction of nylon 6 with organochlorosilanes.

A comparison of the overall thermal stability of the parent sample and yarns treated with DMCS in nitrogen is given in Table IV, and a comparison for samples treated with DMCS in air is given in Figure 9. The results show that the overall thermal stability has decreased in the treated yarns.

Thermal degradation of poly(dimethylsiloxane) has indicated that at 300°C the polymer decomposes partially and at 400°C the rate of decomposition is very high. This indicates that the N-Si bonds which have been introduced are undergoing scission along with the nylon at this temperature.

References

1. I. K. Varma, R. Mandal, and D. S. Varma, *J. Appl. Polym. Sci.*, **17**, 2097 (1973).
2. J. M. Preston and M. V. Nimkar, *J. Text. Inst.*, **41**, T446 (1950).
3. A. R. Urquart and A. M. William, *J. Text. Inst.*, **15**, T138 (1924).
4. J. L. Stoves, *Fiber Microscopy*, Interscience, New York, 1959, p. 52.
5. A. N. J. Heyn, *Fiber Microscopy*, Interscience, New York, 1954, p. 288.
6. J. C. Guthrie and S. Norman, *J. Text. Inst.*, **52**, 503 (1961).
7. E. M. Fettes, *Chemical Reactions of Polymers*, Interscience, New York, 1965, p. 612.

Received October 3, 1972

Revised December 7, 1972