

## Modification of Nylon 66 with Diisocyanates and Diacid Chlorides. II. Physical Properties

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### Synopsis

The physical properties of nylon 66 yarn treated with  $\alpha,\omega$ -diisocyanates (tetramethylene, hexamethylene, decamethylene, and eicosane) and diacid chlorides (succinyl, adipyl, pimeloyl, sebacyl, dodecane, and docosane) were compared to the properties of a control exposed to the same reaction conditions but without the reagent being present. Two types of yarn were used: (1) a highly ordered yarn, as judged by density and x-ray, from polymer of number-average molecular weight 21,000; and (2) a less-ordered yarn from polymer of molecular weight 14,800. Treatment was carried out with yarn in both constant-length and relaxed conditions. The properties were changed most by constant-length treatment and by the use of less-ordered yarn. Treatment with diisocyanates resulted in an increase in the tenacity and modulus simultaneously. The strength properties often went through a maximum as a function of the degree of reaction. Treatment with diacid chlorides degraded the physical properties as a result of polymer chain scission and weakening of the interchain forces. Treatment with either type of reagent lowered the zero strength temperature, but had little effect on the moisture regain or ability of the yarn to dissipate static electricity.

### INTRODUCTION

In a previous paper<sup>1</sup> the reaction of nylon 66 yarn with diisocyanates and diacid chlorides was described. The present paper is concerned with the effect of these crosslinking reactions on the physical properties of the yarns.

Of major interest was the determination of the critical factors in the treating process (e.g., treatment with the yarn held at constant length, CL, versus treatment in a relaxed, R, condition). It was expected, also, to learn something about the relative importance of the physical as well as the chemical changes which were occurring during the treating process.

The control yarn, subjected to identical conditions as the treated yarn but in the absence of the treating agent, is taken as the standard of comparison for the physical properties which were measured. The original untreated yarn does not represent a good standard because the constraints used in carrying out the treatment in the absence of a treating agent bring about a significant change in the yarn properties.

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## EXPERIMENTAL

### Yarns

Nylon 66 yarns A and B were described previously.<sup>1</sup> In addition, some of Yarn A was relaxed in boiling water before treatment, as follows: a 12-m. length was wound loosely onto a cylindrical core made from flexible polyethylene sheet, and the assembly was immersed in boiling water for 25 min. After air drying, the yarn finish was removed by extracting with petroleum ether (30–60°C. fraction) for 2 hr. These water-relaxed yarns were always treated chemically in a R condition.

### Reaction

Treatment of nylon 66 yarns, R, with organic diisocyanates and diacid chlorides has been described in a previous paper.<sup>1</sup> For treatment at CL, a 6-m. length of yarn was wound in a single layer onto a stainless steel core under constant tension such as to cause 5% elongation of the yarn. The yarn finish was removed by extracting with petroleum ether (30–60°C. fraction) in a Soxhlet apparatus for 2 hr. The finish-free yarn was dried for 24 hr. at 100°C. in a vacuum oven. All methods of handling and carrying out the reaction under moisture-free conditions were described previously.<sup>1</sup>

The weight gain of the yarn treated at constant length, CL, was assumed to be the same as for yarn treated under relaxed conditions, R, under the same treating conditions. This assumption was necessary because of the small weight gain of the single layer of yarn wound on heavy stainless steel cores. In reality, the weight gain will be less, which fact only reinforces the conclusion below that treatment at constant length modifies the yarn properties more drastically than relaxed treatment for a given weight gain.

Some of the yarns which were treated chemically with diacid chlorides were washed for 5 hr. at 25°C. in 0.25*N* sodium hydroxide solution to reduce the chlorine content. These yarns were washed further with distilled water until the wash water was neutral.

### Test Procedures

Tenacity, elongation, modulus, and energy were measured with an Instron tensile tester at 21°C. 65% R.H., on 5-in. gage lengths at 100%/min. extension rate. At least five samples were tested and the average value was used. The initial modulus, ultimate tenacity, ultimate elongation, and energy were reported. The energy, taken as the area under the stress-strain curve, was reported as gram-centimeters per denier-centimeter. The standard deviations,  $\sigma$ , for these tests were: tenacity,  $\pm 0.075$  g./den.; elongation,  $\pm 1.4\%$ ; modulus,  $\pm 1.2$  g./den.; energy,  $\pm 0.05$  g.-cm./den.-cm.

The boiling water shrinkage represented the average of ten specimens for each sample held in 100°C. water for 5 min.

Zero strength temperature determinations were carried out with a load of 0.1 g./den. at a heating rate of 5°C./min. in an atmosphere of nitrogen.

Moisture regain was measured at 21°C., 65% R.H. on 2-3 g. samples by reweighing the conditioned samples until the weight change was less than 0.001 g. Dry weight was found by treatment in a vacuum oven for 24 hr. at 105-110°C.

The melting point, found by observation under crossed polars at a heating rate of 1°C./min., represented the temperature at which birefringence disappeared.

X-ray pictures were taken on flat plates with a Norelco x-ray diffractometer. The crystallite perfection was compared on the basis of the relative sharpness of the spots on the film. Crystallite orientation, or  $\beta$  value, was reported as the half-width of an azimuthal diffractometer scan by using the (1, 3, 14) reflection.

## RESULTS

Diisocyanate modification of nylon 66 can raise simultaneously either the tenacity and elongation or the tenacity and modulus. The conditions of treatment must be chosen carefully because, as will be seen, the properties often pass through a maximum as a function of the degree of treatment. The data in Table I illustrate the type of property change which is obtained and how it depends on the treating conditions.

The exact value of the physical property depends on the extent of reaction and on the length of the crosslinking unit, as illustrated by the typical data shown in Figures 1-4. While the effect of the length of the crosslinking chain is of obvious importance, the data are insufficient to allow generalizations to be drawn. With reagents containing 10-20 atoms, high crosslinking densities (expressed as gain in weight of fiber) require

TABLE I  
Effect of Diisocyanate Treatment on the Properties of Nylon 66 Yarn

	Hexamethylene diisocyanate yarn A, R			Hexamethylene diisocyanate yarn A, CL		
	Treated <sup>a</sup>	Control	% change over control	Treated <sup>b</sup>	Control	% change over control
Tenacity, g./den.	5.3	4.9	8	5.8	4.4	32
Elongation, %	31	34	-10 <sup>c</sup>	23	12	92
Modulus, g./den.	28	31	-11 <sup>c</sup>	43	40	7 <sup>c</sup>
Energy, g.-cm./ den.-cm.	1.1	1.1	0	0.92	0.33	180

<sup>a</sup> 0.787 mole/l. of reagent, in xylene, 137°C., 24 hr., 0.3% triethylenediamine,  $\Delta$ wt. = 2.5%.

<sup>b</sup> 0.525 mole/l. of reagent, in xylene, 110°C., 24 hr., 0.2% triethylenediamine,  $\Delta$ wt. = 2.3%.

<sup>c</sup> Of borderline significance at the 95% confidence level.

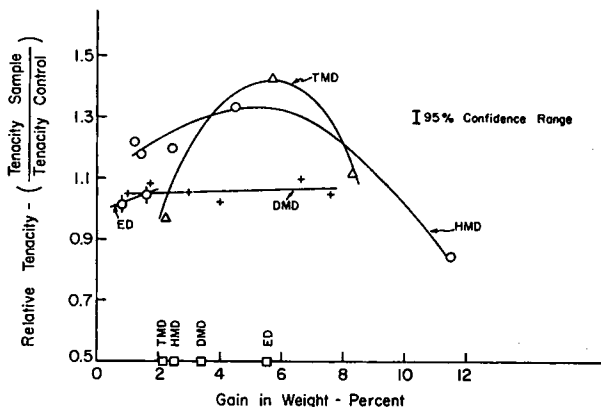


Fig. 1. Effect of diisocyanate treatment at constant length on the tenacity of yarn A: ( $\Delta$ ) tetramethylene diisocyanate (TMD); ( $\circ$ ) hexamethylene diisocyanate (HMD); (+) decamethylene diisocyanate (DMD); ( $\odot$ ) eicosane diisocyanate (ED); ( $\square$ ) calculated gel point for each reagent as shown.

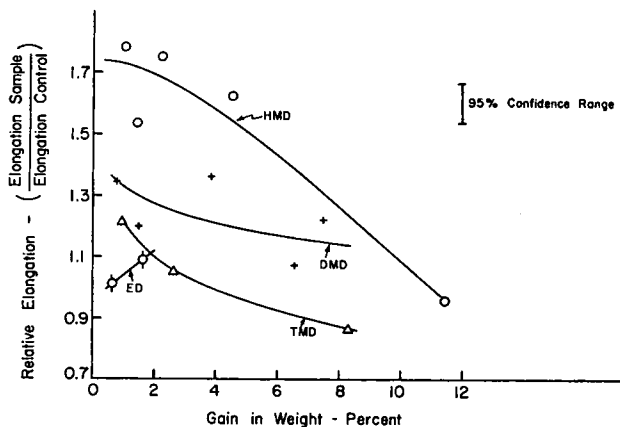


Fig. 2. Effect of diisocyanate treatment at constant length on the elongation of yarn A. Key as in Fig. 1.

such large increases in yarn weight that difficulty in forcing the reaction arises. Moreover, at these high crosslinking densities the crosslinking unit becomes a significant fraction of the total weight of the sample (>10%) and may influence the properties over and above its role of effecting crosslinking.

Treatment at constant length brings about a greater change in properties than does treatment at relaxed conditions, especially for yarn A (Figs. 2 and 5). Differences in constant-length and relaxed treatment are expected because the control yarns themselves react differently to constant-length and relaxed treatments (Table II). Changes due to heat treatment precede the chemical changes in time. There is no major difference in the

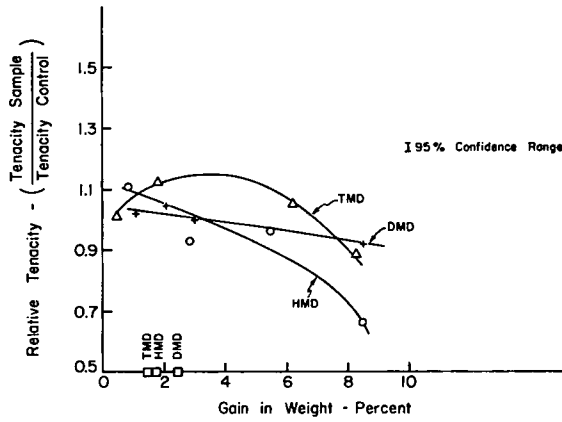


Fig. 3. Effect of diisocyanate treatment at constant length on the tenacity of yarn B. Key as in Fig. 1.

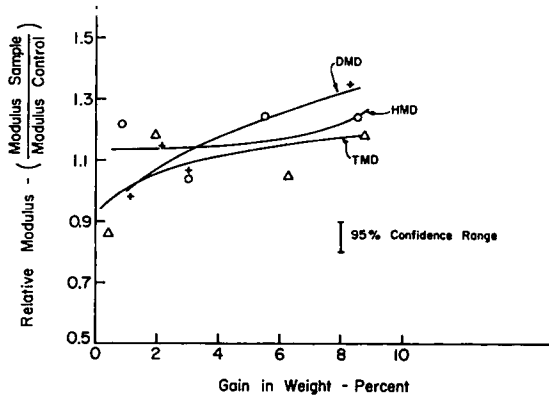


Fig. 4. Effect of diisocyanate treatment at constant length on the modulus of yarn B. Key as in Fig. 1.

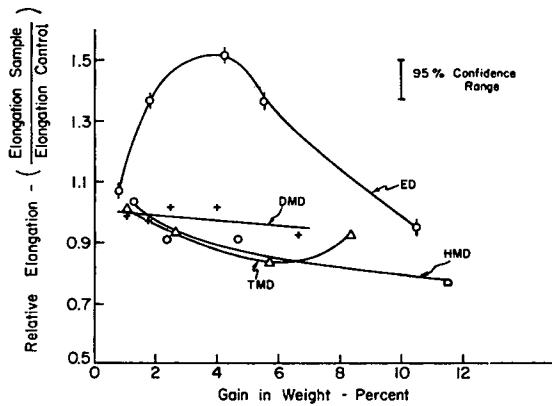


Fig. 5. Effect of diisocyanate treatment, relaxed, on the elongation of yarn A. Key as in Fig. 1.

TABLE II  
Effect of Treating Conditions on the Physical Properties of the Controls\*

	Yarn A			Yarn B		
	Original yarn	R	CL	Original yarn	R	CL
Tenacity, g./den.	5	4.7	4.4	7.7	7.2	7.7
Elongation, %	29	31	15	19	26	19
Modulus, g./den.	30	30	41	36	33	40
Energy, g.-cm./den.-cm.	1.1	0.95	0.45	0.9	1.15	1.0

\* Properties of relaxed (R) and constant-length (CL) yarns were taken as the average for samples treated over a time period of 4-66 hr., and a temperature range of 100-137°C. For the controls, the physical properties were not sensitive to the time or temperature of treatment within these ranges.

properties of controls which are treated for either 2 or 48 hr. Chemical treatment as carried out usually required more than 10 hr.

The less oriented and less ordered the yarn, the greater the effect of the chemical treatment (Figs. 1-4, 6). Thus, for a given weight gain, the properties of yarn A are changed more than the properties of yarn B.

A given yarn normally exhibits ultimate tenacity and ultimate elongation properties which vary inversely in magnitude. Points on this curve result from variations in drawing and/or heat treatment. Treatment with diisocyanates represents one method for displacing the ultimate tenacity-ultimate elongation curve (Fig. 7). Constant-length treatment causes movement toward the origin and relaxed treatment causes movement away from the origin. In Figure 7 the data are absolute and not relative to a control.

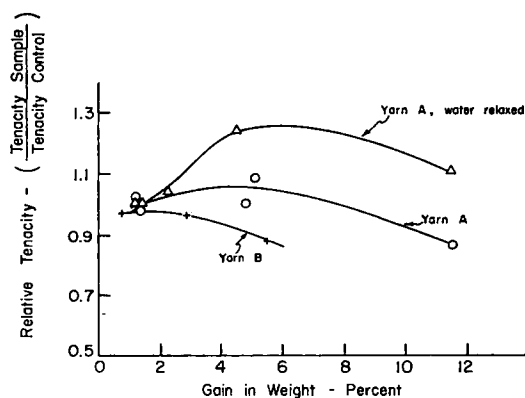


Fig. 6. Influence of order in the original yarn on the tenacity of yarns treated, relaxed, with hexamethylene diisocyanate. Order in the solid state decreases in the series yarn B > yarn A > yarn A, water relaxed.

Diacid chloride treatment degrades the physical properties of the yarn (Figs. 8 and 9). Part of the loss in properties is restored by means of a sodium hydroxide wash (Fig. 10). This wash removes most of the chlorine from the fiber. For example, a yarn was found to contain 0.25% chlorine

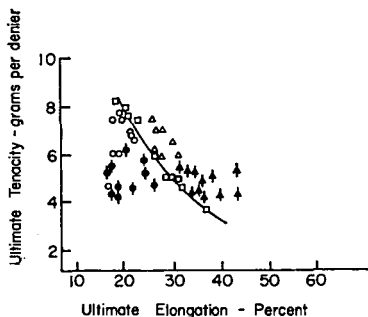


Fig. 7. Effect of diisocyanate treatment on the ultimate tenacity-ultimate elongation relationship of nylon 66 yarns: (□) original yarns A and B, and controls for yarn B; (●) yarn A treated at constant length; (▲) yarn A treated relaxed; (○) yarn B treated at constant length; (△) yarn B treated relaxed. These yarns were treated with diisocyanates of various chain lengths; weight gains ranged from 0.8 to 5.5%.

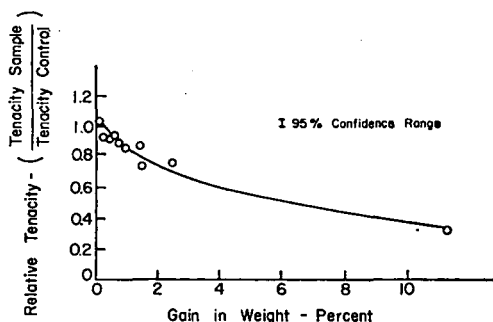


Fig. 8. Effect of treatment, relaxed, by adipyl chloride on the tenacity of yarn B.

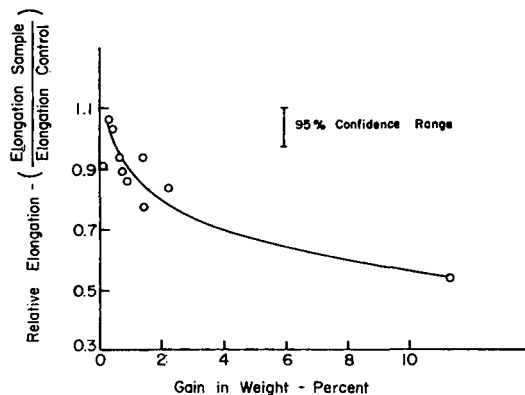


Fig. 9. Effect of treatment, relaxed, by adipyl chloride on the elongation of yarn B.

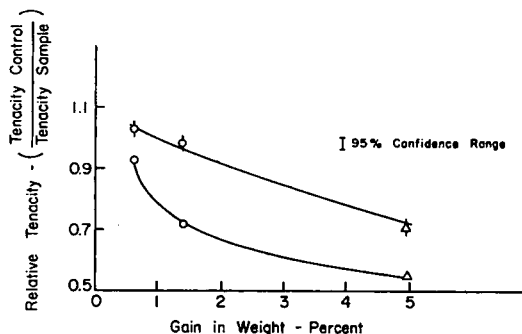


Fig. 10. Effect of caustic wash on the tenacity of yarns treated, relaxed, with diacid chlorides: (O) yarn B, as treated with adipyl chloride; ( $\Phi$ ) yarn B, after caustic wash; ( $\Delta$ ) yarn A, as treated with sebacyl chloride; ( $\Delta$ ) yarn A, after caustic wash.

after treatment with adipyl chloride. Based on the weight gain of the yarn, a maximum chlorine content of 0.54% was expected if all the chlorine was retained in the yarn. After the treatment with dilute caustic, the chlorine content was found to be 0.05%.

Treatment with either diisocyanate or diacid chloride lowers the zero strength temperature of the yarn appreciably and the melting point just perceptibly (Table III). The diisocyanates cause greater loss of zero strength temperature than do diacid chlorides.

TABLE III  
Effect of Chemical Treatment on the High Temperature Characteristics of Nylon 66 Yarn (Yarn A, Treated Relaxed)

Reagent	Gain in yarn weight, %	Zero strength temperature, °C.	Melting point, °C.
None (original yarn)	—	240	—
None (control, 2 hr. at 85°C. in xylene)	—	260	264
Tetramethylene diisocyanate	8.3	222	260
Hexamethylene diisocyanate	3.4	229	261
Sebacyl chloride	4.9	250	—
Dodecanedioyl chloride	7.4	242	259

The x-ray data indicate that diisocyanate treatment does not affect the perfection of the nylon 66 crystallites but does disorient them. Diacid chloride treatment actually makes the crystallites more regular and increases the apparent orientation compared to controls (Table IV).

The boiling water shrinkage of treated yarn A is lessened by relaxed treatment and increased by constant-length treatment (Table V).



The moisture regain is reduced by diisocyanate treatment but the reduction is very small (e.g., treated-control values are 3.02–3.08%; 2.96–3.04%; 2.90–3.14%; 3.04–3.06%). This reduction in regain is of the order of magnitude calculated for altering one site for holding a molecule of water for each functional group of crosslinking agent which reacts.

TABLE IV  
X-Ray Data on Yarn B Treated Relaxed

Reagent	Conditions of treatment			Wt. gain, %	Crystal-lite perfection <sup>a</sup>	$\beta$
	Time, hr.	Temp., °C.	Solvent			
Adipyl chloride	2.5	110	Toluene	1.4	+	14
Control	2.5	110	Toluene	0		18
Adipyl chloride	24	110	Toluene	11.2	+	16
Control	24	110	Toluene	0		19
Hexamethylenediamine	24	110	Toluene	3.3	±	16
Control	24	110	Toluene	0		10
Hexamethylenediamine	24	125	None	6.5	±	23
Control	24	125	None	0		14

<sup>a</sup> From observation of the x-ray film: + indicates improvement over the control; ± means same as the control.

TABLE V  
Boiling Water Shrinkage of Yarn A Treated with Diisocyanate

	Shrinkage, %	
	Treated at constant length	Treated relaxed
Original yarn	8.2	8.2
Control	3.5	1.3
Treated sample	5.0 <sup>a</sup>	0.67 <sup>b</sup>

<sup>a</sup> Treated 24 hr. in xylene, 125°C., weight gain of 9.2%, tolylene diisocyanate.

<sup>b</sup> Treated 4 hr. in xylene, 110°C., weight gain of 2.9%, tolylene diisocyanate.

There is no measurable change in the static build-up or static dissipation of the fiber as a result of the treatment with diacid chlorides and diisocyanates. Static was generated against 304 stainless steel at speeds of from 1 to 30 cm./sec.

## DISCUSSION

The yarn treatment as described herein involves many processes which occur simultaneously: crystallization, relaxation, shrinkage, crosslinking, chain scission, endgroup reaction, and plasticization. Physical changes appear to be more rapid than the chemical changes. Further, the evidence from physical measurements supports the previous conclusion that the chem-

ical reaction occurs in the less-ordered regions of the yarn<sup>1</sup> and suggests that reaction with diisocyanates increases the disorder in the solid state: (1) physical properties are affected more, the less ordered the yarn which is treated; (2) treatment at constant length results in greater property changes than treatment under relaxed conditions; (3) shrinkage is greater than the control yarn for constant-length treatment (i.e., the crosslinking reaction disrupts the order which thermal treatment at constant-length improves); (4) x-ray evidence shows an increase in crystallite perfection after treatment with diacid chlorides (which degrade the amorphous regions of the yarn) and disruption of the crystallites after treatment with diisocyanates (which react without causing degradation of the polymer chains); (5) the similar response to crosslinking as for amorphous rubber, i.e., an increase in modulus and frequent observation of maxima in the ultimate tenacity-crosslinking density curves; and (6) the decrease in the zero strength temperature as a result of chemical treatment (see below).

The maximum in the ultimate tenacity-crosslinking density curves was found to occur at a much higher crosslinking density for partially crystalline nylon 66 than for amorphous rubbers (at about  $1.4 \times 10^4$  versus  $0.2 \times 10^4$  effective network chains/cc.).<sup>2</sup>

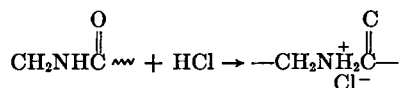
As anticipated, yarn A treated with reagent at constant-length shows the greatest change in properties compared with the control yarn. The untreated constant-length control exhibits a greater change in properties than the untreated relaxed control when compared with the original yarn (although both become more ordered in structure during the thermal treatment). The physical changes occur rapidly and for treated yarns subsequent crosslinking reactions disrupt the order and bring the properties closer to those of the original yarn.

While a general trend in change of properties as a function of the chain length of the crosslinking reagent cannot be deduced, the importance of chain length is obvious from the data. However, for any selected length chain, the properties can be regulated by regulating the crosslinking density so that it appears possible to obtain a preselected set of properties independent of the length of the crosslinking chain.

The decrease in the zero strength temperature as a result of chemical treatment may be explained in either of two ways. If the amorphous regions are involved in the crosslinking and if these amorphous chains have little orientation, the theory of Flory anticipates a decrease in the zero strength temperature.<sup>3</sup> Direct experimental support for Flory's theory is meager,<sup>4</sup> but the zero strength temperature and x-ray data reported here may lend some support to it. Since the methods which are used for measuring the melting point depend only on the presence of a small quantity of residual ordered material in the sample, a limited crosslinking treatment would not be expected to affect this type of melting point greatly. The other possibility which can rationalize the observed decrease in zero strength temperature as a result of the chemical treatment

is the thermal instability of the urethane linkage at temperatures above 200°C.<sup>5,6</sup> and the similar instability of the substituted imide group for aliphatic materials at temperatures near 250°C.<sup>7</sup> If a crosslink is broken, the aliphatic unit becomes a branch of the nylon 66 chain and would be expected to cause the polymer to flow more easily.

The lowering of the strength properties as a result of treatment with diacid chlorides is due not only to degradation of the molecular chains but also to disruption of the interchain forces:



Breaking of hydrogen bond forces by HCl molecules appears to be reversible because a caustic wash restores some but not all of the loss in properties. In general, treatment with diacid chlorides lowers the tenacity, elongation, and energy while leaving the modulus unchanged.

Improvement in the physical properties of nylon 66 by crosslinking with diisocyanates is interesting in view of the degradation of properties brought about by crosslinking treatments reported previously: radiation<sup>8</sup>, formaldehyde.<sup>10,11</sup>

It is worth noting that comparison of the properties of treated yarns with those of the original yarns instead of with the controls leads to the same general conclusions about the effect of the treatment, but the degree of change in the physical properties of the yarns is not as striking.

## CONCLUSIONS

Treatment of nylon 66 yarn with diisocyanates leads to an improvement in the mechanical properties at ambient conditions.

Crosslinking does not improve the following properties: strength at high temperatures, static, and moisture regain.

Property improvement is a function of the chain length of the crosslinking unit and of the crosslinking density.

Samples treated at constant length show a greater change in properties compared to controls than do samples treated relaxed.

Crosslinking occurs in the less ordered regions of the yarn. The less ordered the yarn, the greater the change in properties for a given set of treating conditions.

Treatment of nylon 66 yarn with diacid chlorides leads to a lowering of the mechanical properties.

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### Résumé

Les propriétés physiques du fil de nylon-66 traité aux  $\alpha$ ,  $\omega$ -diisocyanates (tétraméthylène, hexaméthylène, décaméthylène et éicosane) et aux chlorures de diacides (succinyle, adipyle, pimeloyle, sébacyle, dodécane et docosane) ont été comparées aux propriétés d'un échantillon contrôlé exposé aux mêmes conditions de réaction mais en absence du réactif en question. Deux types de fil ont été étudiés: (1) un fil fortement ordonné, à en juger par la densité et le spectre de rayons-X, fait au départ d'un polymère de poids moléculaire moyen en nombre voisin de 21.000 et (2) un fil peu ordonné fait au départ d'un polymère de poids moléculaire de 14.800. Le traitement a été effectué sur un fil placé dans des conditions de longueur constante et à l'état relâché. Les propriétés sont le plus fortement modifiées par le traitement à longueur constante et en utilisant le fil le moins ordonné. Le traitement aux diisocyanates entraîne une augmentation simultanée de la tenacité et du module. Les propriétés de résistance passent souvent par un maximum en fonction du degré d'avancement de la réaction. Le traitement aux chlorures de diacide détériore les propriétés physiques à la suite d'une scission de la chaîne polymérique et de l'affaiblissement des forces intercaténaïres. Le traitement avec n'importe lequel de ces réactifs diminue la température de résistance nulle, mais n'a qu'un faible effet sur la récupération d'humidité et la propriété de la fibre à dissiper l'électricité statique.

### Zusammenfassung

Die physikalischen Eigenschaften von Nylon-66-Garn nach Behandlung mit  $\alpha,\omega$ -Diisocyanaten (Tetramethylen, Hexamethylen, Dekamethylen und Eikosan) und mit Dicarbonsäurechloriden (Succinyl, Adipyl, Pimeloyl, Sebacyl, Dodekan und Dokosan) wurden mit den Eigenschaften einer den gleichen Reaktionsbedingungen, aber ohne Anwesenheit des Reagens, unterworfenen Kontrollprobe verglichen. Zwei Garntypen wurden verwendet: (1) hochgradig geordnet, wie Dichte und Röntgen zeigen, aus Polymerem mit einem Zahlenmittelmolekulargewicht von 21000 und (2) weniger geordnet, aus Polymerem mit einem Molekulargewicht von 14800. Die Behandlung wurde an Garn bei konstanter Länge und unter Relaxationsbedingungen durchgeführt. Die Eigenschaften wurden am stärksten durch Behandlung bei konstanter Länge und bei Verwendung des weniger geordneten Garnes verändert. Behandlung mit Diisocyanaten führte zu einer gleichzeitigen Zunahme von Zähfestigkeit und Modul. Die Festigkeitseigenschaften gingen als Funktion des Reaktionsgrades oft

durch ein Maximum. Behandlung mit Dicarbonsäurechloriden verschlechterte die physikalischen Eigenschaften als Ergebnis einer Kettenspaltung des Polymeren und einer Schwächung der Kräfte zwischen den Ketten. Die Behandlung mit jedem der beiden Reagentypen erniedrigte die Nullfestigkeits-Temperatur, hatte aber wenig Einfluss auf Feuchtigkeitsaufnahme oder auf die Fähigkeit des Garns zur Dissipierung statischer Elektrizität.

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