

Effect of Heat Treatment on Nylon-6 Tire Cords

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Synopsis

The behavior of nylon-6 tire cords at elevated temperature has been evaluated. The heat treatment of cords at 200°C for 16 h was found to reduce their tensile properties considerably. This has been attributed to the decrease in average molecular weight and change in molecular weight distribution as ascertained by fractionation studies. Heat setting of cords in the temperature range of 180–210°C without any applied tension showed some decrease in tensile properties. This has been ascribed to the higher degree of shrinkage of the cords and hence increased chain folding in the molecular structure. However, irrespective of time and temperature of heat treatment, shrinkage was reduced with increasing tension on the cord. Effect of heat setting on density and crystallinity was also evaluated.

INTRODUCTION

Tire is a composite material consisting of cords embedded in the rubber matrix. The overall strength, and ability to bear load by the tire depend strongly upon the nature of cord. Nylon-6 tire cords are being increasingly used for making heavy duty tires because of their higher strength characteristics. However, the overall performance of the tire gets affected following its continuous operation. During the actual running, the temperature of the tire increases due to frictional forces and hysteresis losses and may reach a temperature as high as 200°C. Hence, there exists a considerable possibility of tire cord undergoing chemical and structural changes under these conditions. This may even cause the failure of the tire.

Present investigation thus attempts at evaluating nylon-6 cords for their thermal behavior at elevated temperature.

EXPERIMENTAL

Materials

Four nylon-6 tire cords, used in the present investigation, were obtained from different manufacturers. *m*-Cresol (BDH grade) was distilled under vacuum and the middle fraction with specific gravity of 0.976 (20°C) and a boiling point of 202°C was collected. Cyclohexane (BDH grade) was also distilled before use.

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Fractionation

Fractionation studies of cords were carried out using *m*-cresol-cyclohexane system¹. Cord Samples were dissolved in *m*-cresol, and the polymer solution was transferred to a three-necked flask kept at a constant temperature of $29 \pm 1^\circ\text{C}$. The nonsolvent cyclohexane was added dropwise to the flask along with continuous stirring till turbidity appeared. The temperature of the solution was raised by 5°C and again cooled to 29°C , leaving it as such for 24 h. Precipitated phase was separated by filtration through a sintered G-4 crucible and dried in vacuum at 85°C . The process was repeated several times till no more turbidity appeared upon further addition of cyclohexane.

Molecular Weight

Viscosity average molecular weight for each fraction of cord sample was obtained from intrinsic viscosity measurement at $25 \pm 0.1^\circ\text{C}$ using a Ubbelohde viscometer. The polymer solution was prepared by dissolving the sample in concentrated sulfuric acid (36 normal).¹

Density Measurements

Density measurements of cords were carried out at $26 \pm 1^\circ\text{C}$, using a density gradient column (Davenport, London). The column was prepared using xylene (density 0.866) and carbon tetrachloride (density 1.595).²

Birefringence Measurements

Birefringence of cords was measured using a Berek Compensator equipped with a polarizing microscope.

Denier and Twist Measurements

Ply twist was measured by detwist and retwist method, using test length of 25 cm. An average of five tests has been reported for each sample. For denier measurement, an average of 10 tests has been reported.

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) of cord samples was evaluated, using a TG-750 Stanton Redcroft thermal analyzer. The sample was heated under nitrogen atmosphere at a uniform heating rate of $10^\circ\text{C}/\text{min}$ starting from room temperature to 800°C . Primary thermograms were obtained by plotting residual weight against temperature. The thermal stability of cords was evaluated in terms of initial decomposition temperature (IDT) and integral procedural decomposition temperature (IPDT), as calculated according to the method given by Doyle.³

Tensile Properties

Tensile studies of the cord samples were carried out using an Instron Tensile Tester 1122, under the following conditions: gauge length = 15 cm; full scale load = 50 kg; Chart speed = 200 mm/min; crosshead speed =

200 mm/min; pressure on pneumatic jaws = 4 kg/cm²; temperature = 20°C; relative humidity = 65%.

RESULTS AND DISCUSSION

The nylon-6 tire cords containing similar groups of antioxidants were obtained from four different manufacturers. In practice, all the cord samples had similar behavior in regard to twist, denier, breaking strength, modulus, and elongation (Table I).

The fractionation data of cord samples have been presented in Table II. It can be seen from the results that on an average six fractions were obtained with a recovery of about 95%. Similar results have also been reported during earlier studies on nylon-6 fibers.¹ A loss of 5% may be because of the low molecular weight fractions which were not possible to recover and, partly, due to the loss during fractionation. The intrinsic viscosity of all the fractions for each cord sample show a decreasing trend with the increase in fraction number.

Figure 1 shows the differential molecular weight distribution curves of the samples. It can be seen from the figure that all the samples have unimodal distribution. However, the peaks in samples A and C occur at a higher molecular weight values than that in sample B and D. The relationship between molecular weight distribution and tensile properties has been explained in terms of the concept of shape factor.⁴ The values of shape factor for all the cords were calculated as suggested by Scheren and Rouse⁴ and have been presented in Table III. The results show that sample A has the highest value of molecular weight along with shape factor, and thus show the highest breaking load. The shape factor in sample C is quite close to that of A, but the molecular weight is much lower which is reflected in a lower breaking load in sample C. Molecular weight value in sample D is still lower than C, but the shape factor is also lowered, which indicates a narrower molecular weight distribution in D as compared to C. Hence, both these samples have similar breaking load. Effect of molecular weight in lowering the breaking load is evident from sample B where the shape factor is comparable to that of sample D, but molecular weight decreases resulting in a decrease in breaking load.

The TGA studies of cord samples have been presented in Table IV. The results show that IDT values for all the samples lie in the range of 356–366°C. However, IPDT values vary in the range of 420–435°C. These values are much higher than ordinary textile grade nylon-6 fiber.⁵ This may be attributed due to the presence of antioxidants and stabilizers, which seem

TABLE I
Physical Properties of Nylon-6 Cords

Cord	Twist ply (tpi)	Denier	Breaking load (kg)	Tenacity (gpd)	Elongation (%)	Modulus (gpd)
A	8.3	2881.88	21.69	7.53	31.20	26.5
B	8.3	2830.00	19.68	6.95	32.20	26.0
C	8.7	2900.57	20.97	7.23	31.96	27.0
D	8.0	2885.50	20.96	7.26	31.78	29.0

TABLE II
 Fractionation Data of Nylon-6 Cords

Cord	Fraction no.	Weight fraction (g)	Wt % of the fraction	Cumulative weight fraction W	$[\eta]$ (dL/g)	$\bar{M}_v \times 10^{-3}$
A	1	0.1553	15.53	0.9571	2.56	60.70
	2	0.2752	27.52	0.8018	2.08	44.15
	3	0.0873	8.37	0.5266	1.78	34.74
	4	0.2424	24.24	0.4393	1.22	19.42
	5	0.1212	12.12	0.1969	1.08	16.10
	6	0.0757	7.57	0.0757	0.60	6.52
B	1	0.2786	27.86	0.8823	2.80	69.75
	2	0.1928	19.28	0.6037	1.74	33.54
	3	0.2793	27.93	0.4109	1.38	23.48
	4	0.0196	9.16	0.1316	1.00	14.30
	5	0.1120	11.20	0.112	0.24	1.59
C	1	0.1357	13.57	0.9481	2.54	60.03
	2	0.2683	26.83	0.8124	2.12	45.46
	3	0.2374	23.74	0.5441	1.76	34.14
	4	0.1022	10.22	0.3067	1.64	30.62
	5	0.0821	8.21	0.2045	1.22	19.42
	6	0.0583	5.83	0.1224	1.08	16.10
	7	0.0641	6.41	0.0641	0.60	6.50
D	1	0.2187	21.87	0.9500	2.94	75.18
	2	0.2336	23.36	0.7317	1.99	39.64
	3	0.2681	26.81	0.4977	1.36	22.96
	4	0.0931	9.32	0.2296	1.09	16.33
	5	0.0752	7.52	0.1365	0.92	12.56
	6	0.0613	6.13	0.0613	0.60	6.52

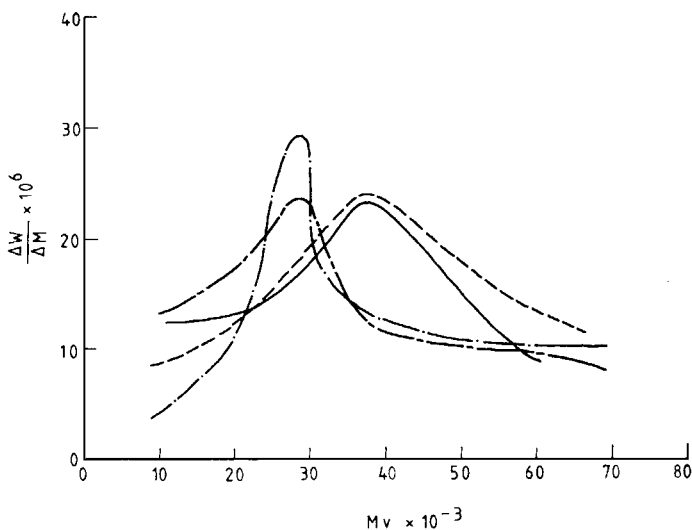


Fig. 1. Differential molecular weight distribution curves for different cords: (—) cord A; (---) cord B; (-·-) cord C; (— — —) cord D.

TABLE III
Average Intrinsic Viscosity and Molecular Weight of Nylon-6 Cords

Cord	Before heating			After heating at 200°C for 16 h		
	$[\eta]$ (dL/g)	\bar{M}_v	Shape factor SF $\times 10^{-3}$	$[\eta]$ (dL/g)	\bar{M}_v	Shape factor SF $\times 10^{-3}$
A	2.45	56,797	4.287	2.08	44,131	2.070
B	2.07	43,824	3.337	1.85	36,796	0.899
C	2.23	49,143	4.270	1.93	39,297	2.510
D	2.13	45,771	3.30	1.77	34,429	1.317

to be effective enough to prevent the thermal degradation of cords to a large extent.⁶ Since the stabilizers are from the same group, they may be expected to act in the similar manner. Therefore, the presence of stabilizers in cords cannot account for such a variation in IDT and IPDT values. The variation in thermal behavior may then be attributed to the molecular weight and molecular weight distribution in cords.

Dorten⁷ has also shown that the tensile properties strongly depend upon the molecular weight and its distribution. The authors found that the tensile properties show an improvement with the decrease in the breadth of molecular weight distribution. During the continuous running of the tire, a considerable amount of heat is generated, which may increase the temperature of the tire as high as to 200°C. Rubber being a bad conductor of heat, heat dissipation is poor in tire. This may produce a considerable change in the inherent properties of the tire as a whole. Keeping this in mind, a study on heat treatment of cord samples was carried out at an elevated temperature to understand the nature of changes occurring in the cords.

Intrinsic viscosity and molecular weight of nylon cords after heat treatment at 200°C for 16 h have been presented in Table III. It can be seen from the results that both intrinsic viscosity and average molecular weight decrease for all samples. This is a general phenomenon observed during the prolonged exposure of sample to heat at elevated temperature, probably due to the degradation of molecular chains. Kausch⁸ also has shown that both mechanical as well as thermal excitations cause degradation of polymer chains.

Heating of the nylon cords at 200°C for 16 h results in a considerable decrease in strength characteristics, such as breaking load, tenacity, and elongation (Table V). This behavior may be attributed to the possible deg-

TABLE IV
Thermogravimetric Analysis of Nylon-6 Cords

Cord	Decomposition temperature (°C)									IDT	IPDT
	10	20	30	40	50	60	70	80	90		
A	402	425	432	440	445	450	455	458	461	356	432
B	410	422	434	445	450	455	458	462	465	357	414
C	406	417	425	435	440	440	445	449	459	361	430
D	401	425	430	438	448	450	452	455	458	366	420

TABLE V
Strength Retention of Nylon-6 Cords after Heat Treatment at 200°C for 16 h

Cord	Breaking load (kg)	Elongation at break (%)	Tenacity (gpd)	Loss in breaking load (%)
A	16.06	42.3	5.57	25.96
B	16.10	43.7	5.69	18.19
C	10.00	42.7	3.45	52.31
D	15.21	40.6	5.27	27.43

radation of cords at higher temperature.^{9,10} Similar observations for strength loss in polycapromide fiber at an elevated temperature have been made by Agsler.¹¹

The degradation of polymeric chains is noticed from the fractionation studies on all the heat treated cords. The results have been presented in Table VI. The number of fractions obtained were more or less similar to those obtained before heat treatment. The differential distribution curves have been shown in Figure 2. It may be seen from the figure that molecular weight distribution has undergone a remarkable change after the heat treatment. All the peaks have shifted to much lower values than those in

TABLE VI
Fractionation Data of Nylon-6 Cords after Heat Treatment at 200°C for 16 h

Cord	Fraction no.	Weight fraction (g)	Wt % of the fraction	Cumulative weight fraction W	[η] (dL/g)	$\bar{M}_v \times 10^{-3}$
A	1	0.0926	9.26	0.957	1.28	20.92
	2	0.2897	28.97	0.865	1.02	14.75
	3	0.1340	13.40	0.575	0.98	13.87
	4	0.1820	18.20	0.441	0.76	9.38
	5	0.0867	8.73	0.259	0.52	5.23
	6	0.0904	9.04	0.172	0.32	2.48
	7	0.0820	8.20	0.082	0.08	0.29
B	1	0.1221	12.21	0.964	1.60	29.48
	2	0.2140	21.40	0.842	1.28	20.91
	3	0.1388	13.88	0.628	0.54	5.55
	4	0.2648	26.48	0.489	0.46	4.33
	5	0.1415	14.15	0.224	0.26	1.80
	6	0.0825	8.25	0.083	0.10	0.41
C	1	0.2607	26.07	0.948	1.40	24.01
	2	0.2673	26.73	0.687	1.29	21.17
	3	0.2082	20.82	0.419	1.00	14.30
	4	0.0750	7.50	0.211	0.98	13.87
	5	0.0748	7.48	0.136	0.80	10.15
	6	0.0615	6.15	0.062	0.39	3.36
D	1	0.1547	15.47	0.954	1.16	17.97
	2	0.2083	20.83	0.799	0.88	11.75
	3	0.2219	22.19	0.591	0.78	9.76
	4	0.0826	8.26	0.369	0.72	8.63
	5	0.1948	19.48	0.287	0.64	7.20
	6	0.0915	9.15	0.092	0.46	4.33

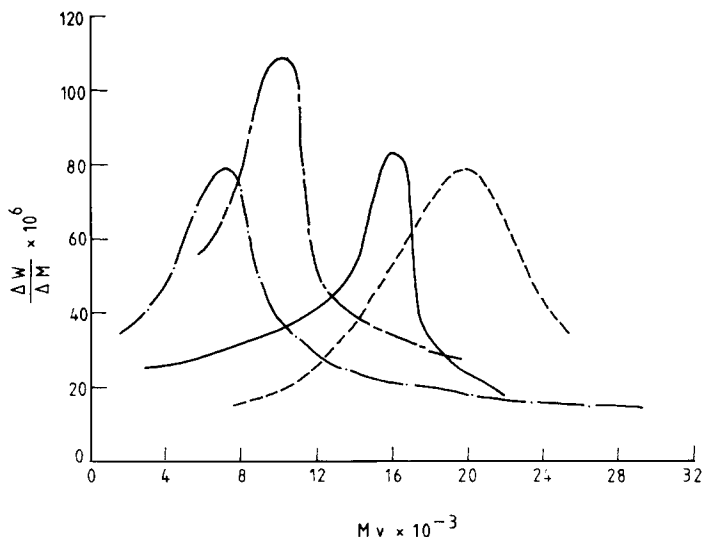


Fig. 2. Differential molecular weight distribution curves for different cords after heat treatment at 200°C for 16 h: (· · ·) cord A; (- · -) cord B; (- - -) cord C; (—) cord D.

parent samples. It appears that this reduction in molecular weight and its distribution are responsible for the loss in the strength characteristics of the cords.

A correlation between the loss in tensile properties and molecular weight distribution may be made in terms of shape factor. The shape factor value is lowest in sample B (Table III), which indicates that the molecular weight distribution is narrower in the cord. Bhattacharya¹² has shown that lower the distribution of molecular weight in nylon-6, the better is the retention in mechanical properties. This is also visible from the lowest percent loss in breaking load for sample B. Although sample A has the highest molecular weight, the shape factor also increases considerably, suggesting a broadening in the molecular weight distribution of the cord, and thus undergoes higher loss in strength in comparison to sample B. Sample C has the highest shape factor value, indicating the maximum spread in molecular weight distribution in the cord. On the other hand, molecular weight also decreases sharply. Hence, these two structural changes in the cord provide a composite factor which may be responsible for a remarkable loss in the strength to 52% of the parent sample. Sample D has a higher shape factor but a lower molecular weight value than that in sample B, which is visible from higher percent loss in breaking load in comparison to sample B.

Shrinkage behavior of cords has been presented in Table VII and was found in the order of 13–15%. The maximum shrinkage was observed in sample C. As the strength of a material is affected, largely, due to disorientation imparted as a result of shrinkage, this effect becomes visible from higher percent loss in breaking load (sample C). A rapid increase in shrinkage accompanied by the loss in strength above 190°C has been reported by Dismore and Statton.¹³

A marked decrease in the birefringence values has been observed after heat treatment of cords (Table VII). The birefringence studies further sug-

TABLE VII
Shrinkage and Birefringence of Nylon-6 Cords after Heat Treatment at 200°C for 16 h

Cord	Shrinkage (%)	Birefringence		Loss (%)
		Before treatment	After treatment	
A	12.9	0.0590	0.0492	16.60
B	13.5	0.0550	0.4820	12.36
C	15.7	0.0602	0.0480	20.26
D	14.2	0.0595	0.0413	18.82

gest that the heat treatment results in a high degree of disorientation in the cords. As the disorientation imparts irregularity in the polymeric chains, the strength of material also decreases. These results thus indicate that, irrespective of the nature of the sample, degradation is the prominent reaction, taking place during the course of heat treatment, which is also visible from the lowering of molecular weight and molecular weight distribution values of cords. Tensile properties being dependent not only on molecular weight, but also on its distribution,¹⁴ thus show a considerable decrease in the heat-set samples.

Effect of Heat Setting on Cords

In an industrial practice, nylon-6 cords are dipped in resorcinol-formaldehyde-latex adhesive (RFL) solution, followed by drying and heat-setting so as to develop good adhesion characteristics. However, the ultimate strength of cord-rubber composite depends largely upon the various conditions used during the RFL treatment. In order to study the effect of such parameters with a view to ascertain the optimum conditions in the dipping process, the heat setting of nylon cords was studied at three temperatures, viz., 180, 200, and 210°C with threefold variation in the time period under different tensions. The variation in shrinkage with the temperature for different timings has been presented in Table VIII.

The results show that all the cords undergo shrinkage under various loads in the range of 0.0–0.80 kg. Irrespective of the time and temperature of treatment, shrinkage decreases with the increase in tension. However, when the load was increased to 1.70 kg, absolutely no shrinkage was observed. Hence, an increase in tension beyond 1.70 kg may be expected to result in some extension in the cord during heat treatment. Shrinkage is essentially a function of disorientation of the molecular chains in the amorphous region. The macromolecular chains undergo coiling during the relaxation of stress, resulting in the folding process. Under the relaxed conditions, molecular chains are free to undergo folding and the result is reflected in a high degree of shrinkage.¹⁵

On the other hand, an increase in temperature has been found to increase the percent shrinkage in cords. Since the thermal shrinkage in polymers is a structural transformation, the molecular rotation around the single bond is restricted by an energy barrier. With the increase in temperature, potential energy increases, which allows the segments to move and assume new conformations. This in turn facilitates the phase transformation to

TABLE VIII
Percent Shrinkage of Nylon-6 Cords after Heat Setting at Various Conditions

Cord	Tension (kg)	210°C			200°C			180°C		
		90 s	60 s	30 s	90 s	60 s	30 s	90 s	60 s	30 s
		A	—	—	—	—	—	—	—	—
	1.7	1.40	1.33	1.27	1.32	1.22	1.15	1.20	1.18	1.01
	0.8	3.21	3.01	2.54	2.49	2.33	2.13	2.29	2.01	1.89
	0.5	13.99	13.48	12.27	13.13	12.08	11.03	11.18	10.09	10.40
B	0.0	—	—	—	—	—	—	—	—	—
	1.7	1.63	1.52	1.37	1.33	1.24	1.18	1.22	1.19	1.01
	0.8	3.99	3.86	2.90	3.70	3.42	2.0	2.92	2.93	1.98
	0.5	16.10	15.90	13.98	13.33	12.68	11.00	13.17	12.97	12.30
C	0.0	—	—	—	—	—	—	—	—	—
	1.7	1.52	1.48	1.30	1.38	1.32	1.21	1.29	1.22	1.01
	0.8	3.89	3.70	2.67	3.55	3.28	2.10	3.12	3.00	1.94
	0.5	13.56	13.41	12.39	12.42	12.08	11.01	11.98	11.49	10.08
D	0.0	—	—	—	—	—	—	—	—	—
	1.7	1.69	1.52	1.32	1.63	1.43	1.20	1.93	1.13	1.50
	0.8	3.89	3.69	2.70	2.99	2.48	2.18	2.23	2.13	1.81
	0.5	13.69	13.50	12.38	12.28	12.21	11.03	11.13	10.18	10.91

folded chain conformation.¹⁶ Hence, it is the chain folding during heat treatment which appears to be the major contributor to the increased shrinkage in cords at higher temperatures.

The variation in tenacity and elongation with the increase in temperature and time have been shown in Figures 3 and 4. It was observed that, for any tension, the increase in temperature results in a decrease in the strength of cord samples. Tsuruta and Koshimo¹⁷ carried out investigation on heat setting of nylon-6 fiber in the temperature range of 140–180°C. Tensile strength of the fiber showed slight improvement, initially up to 160°C, but beyond that a sharp decrease in strength characteristics was observed. The present studies in the temperature range of 180–210°C also follow similar behavior.

However, the heat treatment of cords under tension is followed by an improvement in the tensile properties (Fig. 5). The results are in good agreement with the concept that refolding is greater under the relaxed condition.¹⁵ As the tension to the cord increases, the orientation of the molecular chains could be kept more or less to a level of the parent sample due to the restriction in mobility imposed by the application of tension.¹⁸ Simultaneously, shrinkage is also minimised to a higher extent. The overall result is then reflected in an increase in the strength characteristics of the cords.

In a usual process, after dipping in RFL solution, the cords are dried for a short period so as to remove water, and, subsequently, heat setting is done at elevated temperatures. To understand the nature of changes occurring in the cords, all the samples were dipped in water for 8 s and dried at 110°C for 2 min, followed by heat setting at 210°C for 30 sec. The results have been presented in Figure 6. It may be seen from the results that the trend in shrinkage behavior in water-treated cords is similar to dry heat-

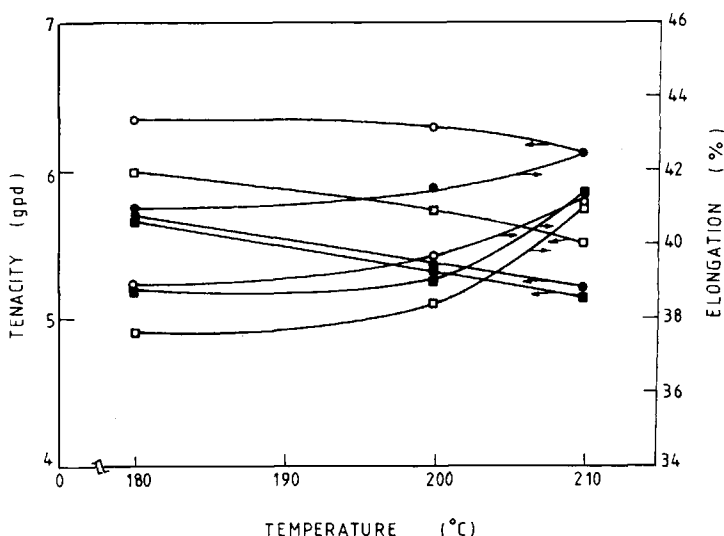


Fig. 3. Variation in tenacity and elongation with temperature of heat treatment at zero tension, time 30 s: (○) cord A; (●) cord B; (■) cord C; (□) cord D.

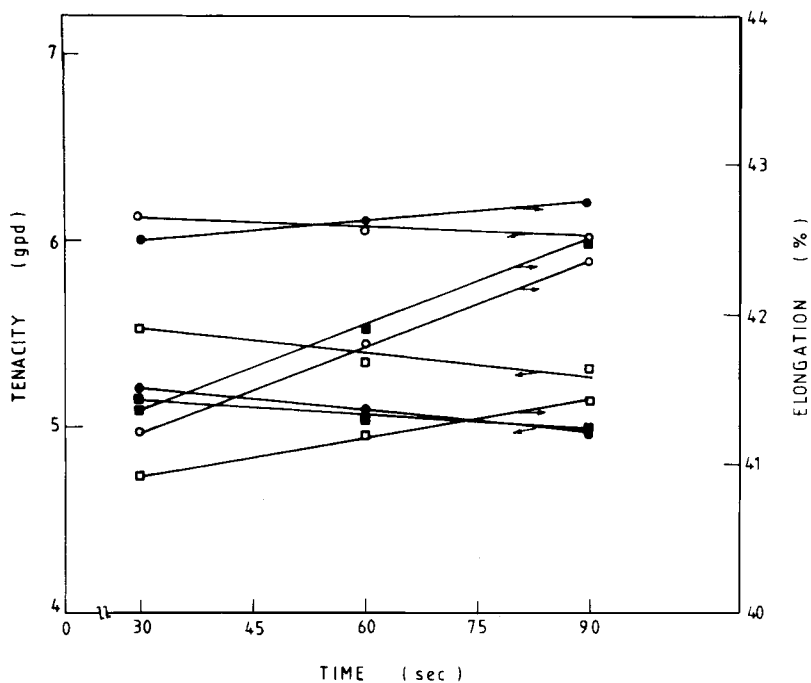


Fig. 4. Variation in tenacity and elongation with time of heat treatment at zero tension, temperature 210°C: (○) cord A; (●) cord B; (■) cord C; (□) cord D.

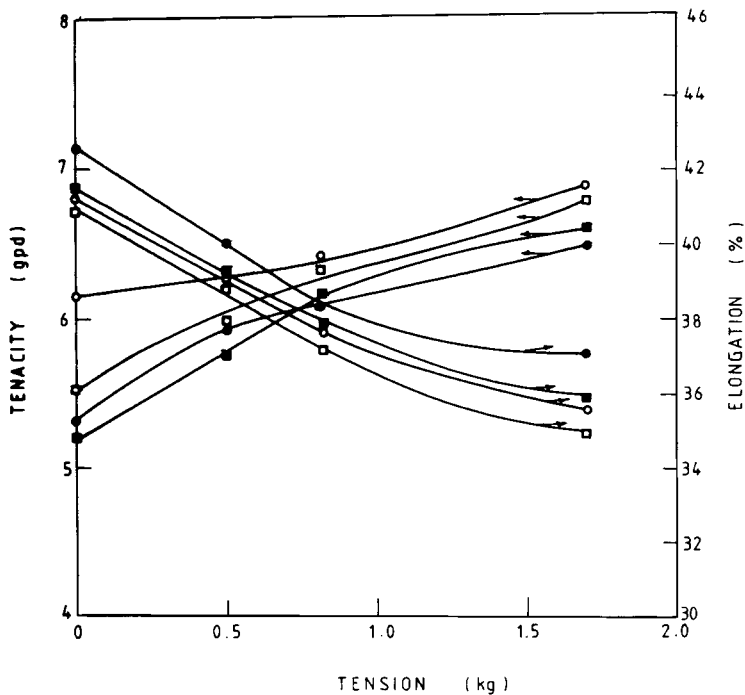


Fig. 5. Variation in tenacity and elongation with tension load, temperature, 210°C, time, 30 s: (○) cord A; (●) cord B; (■) cord C; (□) cord D.

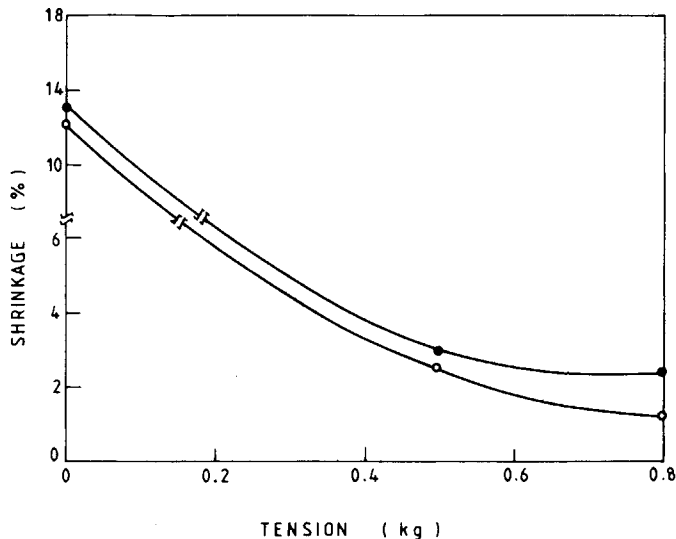


Fig. 6. Variation in shrinkage with tension load, temperature 210°C, time, 30 s: (○) dry cord; (●) water-treated cord.

set ones. However, percent shrinkage is higher in water-treated samples. This may be because of the fact that water acts as a medium in which relaxation of cords can take place, thus contributing more to the shrinkage of the cords.

The effect of temperature and tension on density and crystallinity of cords has been shown in Table IX. Density shows an increase at 210°C even for a shorter treatment period of 30 s. This may be attributed to the decrease in amorphous region followed by an increase in crystallinity. Investigations of Tsuruta and Koshimo¹⁹ based on X-ray diffraction technique also show that the heat treatment of nylon-6 fiber results in an increase in crystallinity.

When tension to the cord was increased, the change in density was lower than at zero tension. This should obviously be due to the resistive action of the mechanical force which prevents the free movement of molecular chains in the amorphous region.

TABLE IX
Density and Crystallinity of Nylon-6 Cord at 210°C for 30 s

Cord sample	Tension (kg)	Density	Crystallinity (%)
Parent sample	—	1.1425	49.33
Heat-set sample	0.0	1.1480	53.67
	0.5	1.1445	50.91
	1.7	1.1436	50.20
H ₂ O-pretreated sample	0.0	1.0489	54.38
	0.5	1.1474	53.19
	1.7	1.1448	51.14

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