Studies on Heating and Cooling of Synthetic Fibers, Yarns, and Fabrics. I. Properties of Nylon and Polyester Filament Yarns on Heat Setting in Silicone Oil

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Synopsis

Nylon 6, nylon 66, and polyester [poly(ethylene terephthalate)] filament yarns were heat set at different temperatures in oil under a variety of experimental conditions. The effect of time of heat setting, tension on the yarn during heat setting, as well as the effect of the initial tenacity and extension on subsequent changes in the mechanical properties of the heat-set yarns have been studied. The breaking strength, elongation at break, and work of rupture have been found to be different for samples heat set while slack and at constant length. The breaking strength remains more or less constant over a wide range of heat setting temperatures up to 240°C in the case of nylon 66 and polyester, and up to 200°C in the case of nylon 6, contrary to the observations of Dumbleton et al. When treated in the slack condition, the breaking extension increases by about 1–2.5 times the control value, while heat setting at constant length produces a decrease in the case of nylon 66 and a marginal increase in the case of nylon 6 and polyester. The initial modulus decreases irrespective of the conditions under which the filaments are heat set. From measurements of the shrinkage and the residual shrinkage in boiling water it appears that dimensional stability can be achieved by heat setting even at constant length. Heat setting produces significant improvement in the crease recovery and resiliency of the fibers. Heat setting has also been found to significantly increase the overall crystallinity of the fibers as determined by critical dissolution time and parallel and perpendicular refractive indices. The overall orientation of the polymer chains, as determined from sonic velocity measurements, decreases on heat setting in the slack condition. Heat setting at constant length produces a marginal improvement in the overall orientation only in the case of nylon 66 yarns. Shrinkage occurs instantaneously. Crystallinity, on the other hand, improves with increasing time of heat setting.

INTRODUCTION

It is well known that synthetic fibers have rather low glass transition temperatures (T_g) and that these temperatures are modified considerably by aqueous and nonaqueous solvents which are commonly employed for processing of textiles. When semicrystalline, oriented thermoplastic fibers such as nylon and polyester are exposed in air or in a fluid medium to temperatures in excess of their glass transition temperatures, shrinkage occurs because these drawn fibers are in a thermodynamically unfavorable state with built-in stresses and strains introduced during the spinning and drawing processes. When sufficient energy (thermal or chemical or both) is made available to the polymer system, the chain segments recrystallize into a structure with higher crystalline perfection, resulting in a partial or complete removal of the initial stresses and strains. Consequently, the dimensional stability and the mechanical, physical, as well as chemical properties are altered.

With the increasing production of synthetic fibers, such as nylon and polyester, the need for proper heat setting to impart proper dimensional stability to the treated fabric is of paramount importance. When finished synthetic fabrics are not subjected to proper heat setting, certain undesirable results are obtained. For instance, when these fabrics are washed at higher temperatures (above or even close to the glass transition temperature), the fabrics exhibit dimensional instability in the form of shrinkage as well as a certain amount of mussiness because of the wrinkles introduced during washing. These wrinkles or "crow's feet" as they are called do not disappear on drying, and the fabrics require ironing to improve their appearance. Consequently, the excellent smooth drying properties which synthetic fabrics ought to possess are not realized in practice merely because of improper heat setting.

Optimum heat setting involves proper control of four basic factors, namely, the initial high temperature to which the material has to be raised; the time of heat setting; the tension on the material, which determines the shrinkage; and the rate of cooling, which determines the extent of crystallization of the polymer structure. The importance of each one of these factors is not to be overlooked. Too low a heat setting temperature or too high a tension or too rapid a cooling process results in poor dimensional stability and a poor appearance rating after washing. On the other hand, too high a temperature or too long a duration of setting or too slow a cooling process would result in difficulties in process control and/or lower production rates. These fabrics also become harsh and possess poor drape. Apart from these factors, the medium in which heat setting is carried out has a great influence on the effectiveness of heat transfer into the material and hence on dimensional stability. Although several studies on individual properties have been reported,[1-8] no overall systematic study appears to have been carried out to examine all the factors that have a bearing on the heat setting of fibers. To examine these various aspects a program of basic research was initiated, and the results obtained so far will be discussed in a series of publication. In this communication, the changes in the mechanical and structural properties of commercial nylon 6, nylon 66, and polyester filament yarns on heat setting in silicone oil under different conditions are discussed.

EXPERIMENTAL

Materials

Commercially available medium- and high-tenacity nylon 6, nylon 66, and poly(ethylene terephthalate) (polyester) filament yarns were employed. The details regarding their origin, denier, tenacity, etc., are given in Table I.

Heat Treatment

The filament yarns were heat treated for different time intervals in a silicone oil bath whose temperature could be maintained at different levels within $\pm 1°C$. The samples were treated in the slack condition, in the stretched condition (at constant length), and also under a tension of 0.05 g/den. After treatment for a predetermined period (5 sec, 1 min, or 30 min), the sample was suddenly quenched in acetone at room temperature. This treatment cooled the sample rapidly and also removed the oil from the fiber surface.

TABLE I
Fiber Characteristics

Type	Source	Denier	Bright/dull	Cross section	Tenacity
Nylon 66	Monsanto	210/34	bright	circular	high
Nylon 66	Monsanto	140/26	bright	trilobal	normal
Nylon 66	Monsanto	100/24	dull	circular	normal
Nylon 6	Garware	210/26	bright	circular	normal
Nylon 66	Garware	40/10	dull	circular	normal
Polyester	J. K. Synthetics	76/24	dull	circular	normal

Shrinkage

Yarn samples of 8-cm length were allowed to shrink freely for 1 min at different temperatures and quenched in acetone, and the percent shrinkage S was determined according to the formula

$$S = \frac{\text{initial length} - \text{final length}}{\text{initial length}} \times 100$$

Residual Shrinkage

The percent shrinkage of untreated yarns and also the residual shrinkage of different heat-set yarns were determined after allowing these yarns to shrink freely in boiling distilled water for 5 min. Some of the heat-set yarns were also given a sanforizing wash for 30 min at 70°C. The sanforizing bath consisted of sodium bicarbonate (2 g/l) and nonionic soap flakes (10 g/l.).

Test Methods

Tensile Strength and Extension at Break. Single filaments of 1-cm test length were broken on an Instron tester using an appropriate load cell. The rate of extension was suitably adjusted to have an average breaking time of about 30 sec; 25 filaments were tested in each case. From the load–extension curves the average breaking strength (g/den) and percent extension at break were determined. The area under the stress–strain curve for a filament whose load and extension were close to the average load and extension for the entire sample was measured using a planimeter, and the work of rupture was thus calculated.

Bundle Crease Recovery. The yarns were parallelized to form a thin fiber bundle, and the crease recovery angle of this pad was measured after conditioning at 65% R.H. and 27°C, according to the procedure described by Venkatesh and Dweltz.[9] Six pads were prepared and tested in each case and the average values calculated.

Birefringence. The parallel and perpendicular components of the refractive index n were determined by the Becke line method. For determining $n_{\parallel}$ and $n_{\perp}$ of nylon 6 and nylon 66 and n_1 of polyester, mixtures of spectroscopic quality α-bromonaphthalene and paraffin oil of known refractive indices were used, while for determining $n_{\parallel}$ of polyester filaments, mixtures of α-bromonaphthalene and methylene iodide were employed. Measurements were made at 30° ± 1°C.

Critical Dissolution Time. The critical dissolution time of polyester yarn in phenol or phenol/tetrachloroethane mixtures has been shown to be an ex-

tremely sensitive technique for measuring the crystallinity of treated and untreated yarns.[10] The critical dissolution time is the time taken to dissolve a filament in a given solvent. To determine these times the method suggested by Galil[10] was employed, and 100% phenol at 60°C or a mixture of phenol and tetrachloroethane in suitable proportions was employed depending upon the fiber material as well as upon the temperature of heat setting.

Sonic Modulus. The elastic constants before and after heat setting were determined using a Dynamic Modulus Tester PPM-5R (H. M. Morgan Co.). The sonic velocity was computed from the time taken by the pulse to travel through the filament between the transmitter and the receiver. The sonic modulus E (in grams per denier) was calculated from the equation $E = 11.3 \times C^2$, where $C = d/T$, d is the distance between the transmitter and the receiver (in kilometers), and T is the time (in seconds) taken by the pulse to traverse this distance.

Torsional Rigidity Modulus. The torsional properties of fibers have considerable influence on the performance characteristics of fabrics. Many different techniques[11] (torsion pendulum type and torsion balance type) have been employed to determine these properties. The torsion pendulum method[11] involving simple and double pendulums is convenient. In the present case, the time of oscillation of a simple pendulum was determined by the method described by Pierce.[11] The torsional rigidity modulus, which is a measure of the inherent resistance of the fibrous material to shear deformation, is given by

$$\eta = \frac{8\pi I}{r^4} \frac{L}{T^2}$$

where I is the moment of inertia of the pendulum bar, L is the specimen length, T is the time of oscillation, and r is the radius of the fibrous filament.

RESULTS AND DISCUSSION

The present study highlights the changes in morphology and in the structural and mechanical properties of nylon 6, nylon 66, and polyester filament yarns heat set in silicone oil under a variety of experimental conditions. The yarns develop crimp on heat setting in oil in the slack condition, and the magnitude of the crimp increases with increasing temperature of heat setting.

Effect of Time of Heat Setting

The mechanical properties of nylon 66 yarns heat set in silicone oil for 5 sec, 1 min, and 30 min in the slack state as well as without allowing them to shrink are given in Table II. Within about 5 sec, the fibers attain the temperature of the oil and undergo changes in their structure and morphology. The yarns treated in the slack condition show higher breaking extension. On the other hand, the extensibility of the yarns heated at constant length remains more or less unchanged or even decreases with increasing heat-setting temperature. Further heating does not produce any significant change in their mechanical properties. However, when heated in oil for extended periods, adverse effects such as loss in breaking strength and extension are produced simultaneously (Table II). The yarns heat set for 30 min either in the slack condition or at constant length were brownish yellow. The effects of heating nylon 6 and

TABLE II
Mechanical Properties of Oil-Annealed Nylon 66 and Nylon 6 Filaments

Temperature, °C	Time of treatment	Treated in slack condition				Treated at constant length			
		Tensile strength, g/den	Breaking extension, %	Work of rupture, g·wt·cm	Sonic modulus, g/den	Tensile strength, g/den	Breaking extension, %	Work of rupture, g·wt·cm	Sonic modulus, g/den
				Nylon 66 (210/34)					
Blank		9.8	38	12.4	79				
200	5 sec	7.7	45	13.0	74	7.6	39	11.0	77
200	1 min	7.7	50	14.8	74	7.6	34	9.6	77
200	30 min	4.4	26	3.8	77	4.2	22	3.5	77
215	1 min	7.9	51	14.3	75	7.2	30	7.5	89
230	5 sec	7.4	46	13.3	72	7.5	39	12.4	—
230	1 min	7.3	49	13.2	74	6.5	25	5.4	99
230	30 min	2.9	20	1.9	79	2.5	11	0.9	—
240	5 sec	7.3	51	12.7	74	6.8	26	5.0	87
240	1 min	7.2	47	11.3	78	6.2	23	4.2	94
240	30 min	2.2	18	1.3	78	2.0	10	0.6	89
				Nylon 6 (210/24)					
Blank		7.5	42	17.2	55				
160	5 se	7.4	57	21.9	54	7.6	48	20.2	56
160	1 min	7.4	54	20.8	53	7.6	46	18.1	57
160	30 min	7.3	56	21.0	60	7.2	42	14.7	60
175	1 min	7.4	57	21.5	55	7.5	48	20.9	57
190	5 sec	7.3	78	24.6	42	7.4	55	21.0	63
190	1 min	7.2	76	25.3	46	7.5	52	19.9	64
190	30 min	3.9	36	5.4	55	4.1	19	3.4	75
200	5 sec	5.4	106	37.6	37	7.2	57	21.6	63
200	1 min	5.9	122	39.4	36	6.2	42	13.8	64
200	30 min	4.2	41	8.4	49	3.6	15	2.1	79

polyester yarn in oil for short time intervals have been found to be similar to those observed for nylon 66, except that nylon 6 and polyester yarns show slightly improved extensibility even when heat set at constant length (Tables II and III).

Heat treatment for extended time intervals at temperatures up to 190°C for nylon 6 and 230°C for polyester does not produce any adverse effect on breaking strength and extension at break. However, prolonged heat treatment at higher temperatures either in the slack condition or at constant length results in significant reduction in the breaking strength and extension of nylon 6 and polyester filament yarns compared to the samples heat set for 1 min. Extension values of nylon 6 and polyester samples slack treated for 30 min are higher than those of their respective controls. In contrast, the extensions of nylon 66 yarns heat set for 30 min in the slack condition are significantly lower than that of the control. However, the work of rupture is considerably reduced for nylon 6, nylon 66, and polyester yarns heat set in the slack condition for 30 min.

Effect of Initial Tenacity

The mechanical properties of high-, medium-, and normal-tenacity nylon filament yarn after heat setting are given in Tables II and IV. It can be seen that all three types of nylon 66 yarn behave similarly. Those heat set in the slack state show higher breaking extension than their respective controls, while samples not allowed to undergo shrinkage during heat setting show decreased extension at break. High- and medium-tenacity nylon 6 filament yarn exhibit somewhat similar behavior except that samples heat set under constant length conditions (not allowed to shrink) also exhibit slightly higher extension to rupture.

Effect of Tension During Heat Setting

From Table III, in which the mechanical properties of polyester yarn heat set in oil under a tension of 0.05 g/den are given, it is clear that a tension of about 0.05 g/den was found to be sufficient to prevent shrinkage in polyester filaments during heat setting. Nylon yarns also behave similarly.

Stress–Strain Curves

Typical Instron load–extension curves are shown in Figures 1–3 for nylon 6, nylon 66, and polyester filaments before and after heat setting in oil in the slack condition as well as at constant length without allowing them to shrink. The elastic moduli decreased for all the three samples irrespective of the conditions under which they were heat set, the decrease being maximum for the samples heat set in the slack condition. The initial moduli have been found to decrease with increasing temperatures of heat setting.

The mechanical properties of nylon 66 and polyester filament yarn almost remain constant over a wide range of temperature of heat setting, even though the shrinkage increases significantly with increasing temperature. On the other hand, the elongation at break of nylon 6 filaments increases significantly with increasing temperature of heat setting. The tenacity at break is not significantly affected by heat setting in oil for 1 min at any temperature up to about 25°C

TABLE III
Mechanical Properties of Polyester Filaments Heat Set in Oil

Temperature of treatment, °C	Time of treatment, min	Treated slack			Treated at constant length			Treated under load of 0.05 g/den	
		Breaking strength, g/den	Extension, %	Sonic modulus, g/den	Breaking strength, g/den	Extension, %	Sonic modulus, g/den	Breaking strength, g/den	Extension, %
Blank	—	5.1	45	161					
200	1	4.8	79	93	5.2	50	104	5.2	50
200	30	4.7	61	100	5.0	30	138	—	—
220	1	4.9	94	90	5.2	48	100	5.1	51
220	30	4.7	63	95	4.5	26	140	—	—
230	1	4.9	93	78	5.2	47	96	5.0	49
230	30	3.9	63	87	4.5	30	135	—	—
240	1	4.7	90	75	4.7	49	100	4.7	49
240	30	2.5	73	83	3.4	24	125	—	—

TABLE IV
Mechanical Properties of Nylon Filaments Heat Set in Oil

| Temp., °C | Nylon 66 (140/26) | | | | Nylon 66 (100/24) | | | | Temp., °C | Nylon 6 (40/10) | | | |
| | Treated slack breaking | | Treated stretched breaking | | Treated slack breaking | | Treated stretched breaking | | | Treated slack breaking | | Treated stretched breaking | |
	Strength, g/den	Extn., %	Strength, g/den	Extn., %	Strength, g/den	Extn., %	Strength, g/den	Extn., %		Strength, g/den	Extn., %	Strength, g/den	Extn., %
Blank	5.7	57			4.5	59			Blank	5.4	62		
200	5.7	71	5.6	39	4.5	65	4.0	28	160	5.4	75	5.7	56
215	5.6	71	5.0	32	4.3	65	4.3	21	175	5.1	72	5.5	57
230	5.5	77	4.6	28	4.4	65	3.5	18	190	4.8	75	5.4	50
240	4.7	51	4.1	23	4.3	60	2.7	17	200	4.7	92	5.0	44

Fig. 1. Load–elongation curves for nylon 6 before and after heat setting in oil at 190°C for 1 min: (—) untreated; (- · · · -) treated slack; (- - -) treated stretched.
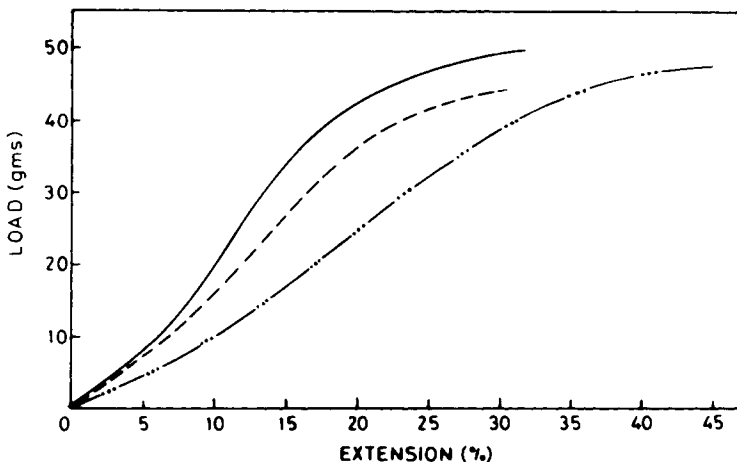

Fig. 2. Load–elongation curves for nylon 66 before and after heat setting in oil at 215°C for 1 min: (–) untreated; (- · · · -) treated slack; (- - -) treated stretched.

below the melting temperature of the material (Tables V and VI). These results are in contrast to those of Buchanan and Dumbleton.[12] The tenacity of polyester samples with a draw ratio of 5 have been found to decrease, from about 7 g/den to about 2 g/den, on heat setting in silicone oil at 225°C for 1 min in the slack condition. Dismore and Statton[13] have also observed a fall in the breaking tenacity of nylon 66 filaments on heat setting in oil in the slack condition. However, their data show that annealing at temperatures up to about 240°C does not result in any significant loss in tenacity. On the other hand, the samples heat set at higher temperatures (especially above 250°C) were found to exhibit a drastic reduction in their tenacity at break. The data on nylon 6, nylon 66, and polyester filaments, as well as fibers of different tenacities obtained from different
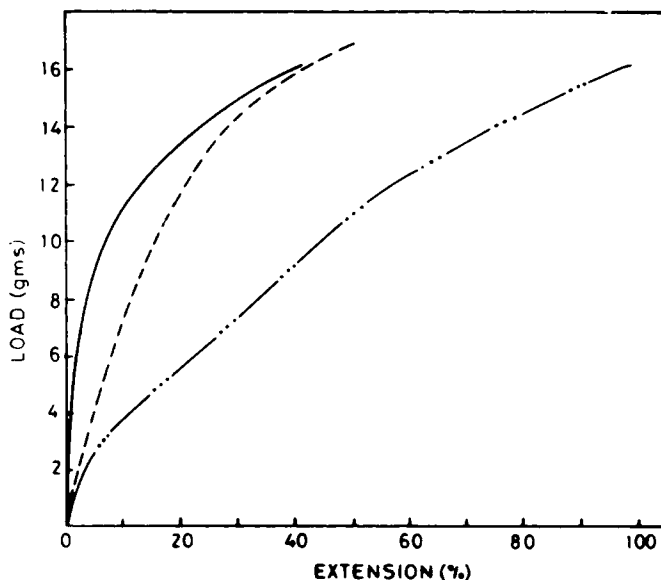
Fig. 3. Load–elongation curves for polyester before and after heat setting in oil at 215°C for 1 min: (—) untreated; (- · · · ·-) treated slack; (- - -) treated stretched.

sources, do not show any significant fall in breaking tenacity on heat setting in oil for 1 min at temperatures up to 200°C for nylon 6 and up to 240°C for nylon 66 and polyester (Tables II to VII). The present results for polyester are in agreement with those of Sibilia et al.[14]

The changes in the breaking extension are dependent on the type of fiber. The extensibility of nylon 6 and polyester yarn heat set without allowing any shrinkage remains more or less unchanged, while it decreases for high-tenacity tire cord (nylon 66), as shown in Tables V and VI. On the other hand, all three samples when allowed to undergo free shrinkage during heat setting exhibit higher breaking extension up to 2.5 times their respective controls. The work of rupture, which is a measure of toughness and wear life, is also significantly improved on slack treatment.

Free Shrinkage

The free shrinkage of nylon 66 and polyester yarn in oil is shown in Figure 4 as a function of heating temperature. The data for nylon 6 are graphically represented in Figure 5. Nylon 66 and polyester samplex exhibit two rates of shrinkage: a slow rate which becomes operative as the heating temperature exceeds the glass transition temperature of the sample, and a fast rate which commences at about 150°C. Above 150°C, for both nylon 66 and polyester yarns, the shrinkage is linearly related to the temperature of heat setting. The straight line extrapolated to the temperature axis intercepts it at 148°C for polyester and at 165°C for nylon 66.

The silicone oil which was employed as the medium for heat setting is highly viscous at room temperature, and its viscosity decreases with increasing temperature. The mobility of the macromolecular segments in the fiber increases slowly up to, and rapidly above, 170°C. It appears that up to about 150°C heat

TABLE V

Mechanical Properties of Nylon 6 and Nylon 66 Heat Set in Oil

Temp. of treatment, °C	Treated in slack condition					Treated at constant length				
	Breaking strength, g/den	Extension, %	Work of rupture, g-wt-cm	Crease recovery angle, deg	C.D.T. 1:10 mixture, sec	Breaking strength, g/den	Extension, %	Work of rupture, g-wt-cm	Crease recovery angle, deg	C.D.T. 1:10 mixture, sec
Nylon 6 (210/24)										
Blank	7.5	42	17.2	—	—					
100	7.5	44	17.6	—	—	7.6	40	17.8	—	—
145	7.5	50	18.1	154	35	7.5	44	18.2	—	—
160	7.4	54	20.8	137	40	7.6	46	18.1	146	38
175	7.4	57	22.5	137	51	7.5	48	20.0	127	44
190	7.2	76	25.3	132	74	7.5	52	19.9	130	58
200	5.9	122	39.4			6.2	42	13.8	117	91
Nylon 66 (210/34)										
Blank	7.9	38	12.4	107	18[a]					
150	7.6	40	12.8	—	—	7.6	34	11.7	—	—
180	7.5	45	13.4	—	—	7.3	30	10.8	—	—
200	7.7	50	14.8	129	27	7.6	34	9.6	141	26
215	7.9	51	14.3	117	32	7.3	30	7.5	125	33
230	7.5	49	13.2	107	51	6.5	25	5.4	127	77
240	7.2	47	11.3	105	76	6.2	23	4.9	124	150

[a] C.D.T. determined in a 1:6 mixture of phenol and tetrachloroethane.

TABLE VI
Mechanical Properties of Heat-Set Polyester Filaments

Temp. of treatment, °C	Treated in slack condition					Treated at constant length				
	Breaking strength, g/den	Exten-sion, %	Work of rupture, g·wt·cm	Crease recovery angle, deg	C.D.T. 2:3 mixture	Breaking strength, g/den	Exten-sion, %	Work of rupture, g·wt·cm	Crease recovery angle, deg	C.D.T. 2:3 mixture
Blank	5.1	45	5.5	97	—					
150	4.9	50	6.4	—	—	5.2	42	5.6	—	—
180	4.9	58	7.0	—	—	5.2	44	5.8	—	—
200	4.8	79	7.9	140	799 sec	5.2	50	6.2	129	1679 sec
220	4.9	94	9.8	142	1414 sec	5.2	48	5.8	136	~2 hr
230	4.9	93	10.3	136	~4 hr	5.2	47	5.8	132	>8 hr
240	4.7	90	10.0	139	>8 hr	4.7	48	5.0	134	>8 hr

TABLE VII
Mechanical Properties of Polyester Filament Yarns and Fibers Heat Set in Oil in the Slack
Condition for 1 Minute

Temperature of treatment, °C	Breaking strength, g/den	Extension, %	Breaking strength, ġ/den	Extension, %
	Nirester (80/34)		Staple Fiber	
Control	4.5	18	3.2	23
200	4.8	42	3.3	32
230	4.7	37	3.0	42
240	4.1	43	2.8	40
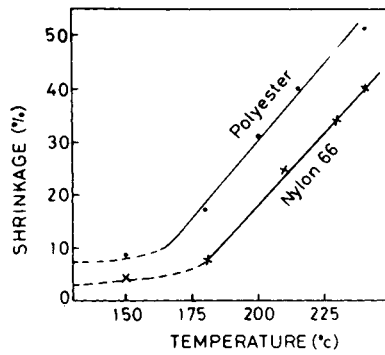
Fig. 4. Shrinkage as a function of temperature of heat setting for polyester and nylon 66.
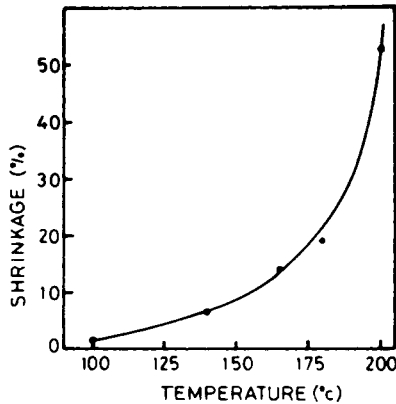
Fig. 5. Shrinkage of nylon 6 as a function of temperature of heat setting.

transfer from the oil to the fiber, which is diffusion controlled, is slow because of the high viscosity of the oil, and hence the shrinkage of the fiber is low as in the case of heat setting in air.[12,15] However, the viscosity of the oil decreases with increasing temperature. Because of better heat transfer from the oil to the

fiber and consequent greater mobility of the molecular segments in the fiber, a fast rate of shrinkage is observed above 150°C or so, in proportion to the rise in temperature.

The shrinkage temperature relationship in the case of nylon 6 is curvilinear. It is seen from Figure 5 that up to 150°C the fiber shows a slow rate of shrinkage as in the case of nylon 66 and polyester. On the other hand, above 150°C, and especially above 180°C, the shrinkage rate suddenly increases because of better heat transfer and also because of the nearness of the heat setting temperature to the melting point of the drawn fibers. It has been shown earlier[16] that a fast rate of shrinkage becomes operative in nylon 6 from about 148°C. This results in a curvilinear relationship.

Residual Shrinkage

In practice, washing, drying, and often dyeing processes are carried out after the material is heat set. Hence, the residual shrinkage in boiling water is a useful parameter for assessing dimensional stability. The lower the residual shrinkage, the better will be the dimensional stability of the heat-set fabric. Residual shrinkage data for samples heat set in the slack condition, as well as at constant length, are given in Table VIII. The samples heat set at constant length (i.e., not allowed to undergo any shrinkage during heat setting) show higher residual shrinkage below a heat-setting temperature of 200°C for nylon 66 and polyester and below 180°C for nylon 6. Above these temperatures, not only does the difference in the residual shrinkage for samples heat set with and without free shrinkage become negligible but also the shrinkage is almost independent of the temperature of heat setting. Polyester filament yarn heat set at 210°C at constant length has been found to show less than 2% shrinkage when heat set at 210°C in the slack condition. Nylon 6 exhibits comparatively higher residual shrinkages in the temperature range of 150°–180°C than those shown by nylon 66 and polyester in the temperature range of 180°–230°C. The higher residual shrinkage of nylon 6 probably arises from improper heat setting because of inefficient heat transfer from the viscous oil to the fiber at the lower temperatures. The residual shrinkage values obtained at sanforizing wash temperatures are comparatively lower than those obtained in boiling distilled water, but they generally substantiate the conclusions already drawn.

It is very interesting to note that heat setting in oil for 1 min at or above 200°C for nylon 66 and polyester and at or above 180°C for nylon 6 produces minimum shrinkage, irrespective of whether the fibers are allowed to shrink freely or not during heat setting. This suggests that the heat-set fabrics will be dimensionally stable, despite small variations in tension and temperature during the heat setting operation. This is an important observation from the industrial point of view as less critical controls will be sufficient.

To discover the effect of time of treatment on the dimensional stability, the residual shrinkage of the samples heat treated for 5 sec was determined. The results that heat treatment in oil, either in the slack condition or at constant length, for about 5 sec is quite sufficient to confer adequate dimensional stability (Table VIII) at the appropriate temperatures for the different materials.

TABLE VIII
Shrinkage in Oil and Residual Shrinkage of Heat-Set Filaments in Boiling Water

Temp., °C	Shrinkage in oil, %	Residual shrinkage in boiling water, %			
		Treated slack		Treated at constant length	
		5 sec	1 min	5 sec	1 min
Nylon 6					
Blank			12.3		
100	1.3		6.9		11.3
140	6.5		2.2		8.8
160	14.0	4.0	2.8	6.3	5.7
175	19.0	3.5	2.2	4.8	3.8
190	29.9	2.4	1.8	3.5	2.7
200	52.8	1.5	0.2	2.1	0.5
Nylon 66					
Blank			11.6		
150	5.0		1.8		7.5
180	7.3		1.0		5.4
200	18.4	1.5	0.8	3.3	1.5
215	25.0	1.1	1.0	2.3	1.9
230	34.2	0.4	0.3	1.4	1.8
240	40.3	0.3	0.3	1.0	0.8
Polyester					
Blank			6.6		
150	9.1		1.1		2.4
180	15.5		0.9		1.9
200	33.3	2.1	1.6	2.6	2.1
215	40.1	1.4	1.2	2.3	2.1
230	47.9	0.3	0.5	1.8	1.7
240	51.1	0.3	0.4	0.7	0.9

Bundle Crease Recovery

An increase in the bundle crease recovery is an indication of the improvement in wrinkle resistance and resiliency of the material after heat treatment. The samples heat set in oil exhibit improved Monsanto crease recovery angles (Tables V and VI). In the case of nylon 6 and polyester, the samples heat set in the slack condition exhibit slightly higher crease recovery than samples heat set at constant length. In the case of polyester, the crease recovery angle almost remains constant over a wide range of temperature, while setting temperatures above 160°C for nylon 6 and above 200°C for nylon 66 appear to produce less improvements in the bundle crease recovery angle.

Crystallinity

Heat setting in general above a particular temperature increases the average crystallinity and lateral order in the heat-set material. In order to study and characterize these changes in molecular order the critical dissolution time (CDT), birefringence, sonic modulus, and torsional modulus were determined.

Critical Dissolution Time

The critical dissolution time (CDT) has been shown to clearly bring out small changes in the crystallinity of polyester samples due to heat treatment. The increase in this time is a measure of the increase in the overall crystallinity and fibrillar perfection (molecular order) of the sample. In the present investigation, the blank, or nonheat-set, polyester yarn was found to dissolve in about 7 sec in a 1:3 mixture of phenol and tetrachloroethane at room temperature (30°C). The CDT increases substantially with increasing temperature of heat setting above 100°C, suggesting changes in the crystalline structure of the fibers. Above 180°C the CDT increases rapidly to values in excess of 8 hr. These increases in CDT suggest the onset of a major structural change in the polyester fiber which corresponds to improvement in crystalline perfection. It is significant that CDT and percent shrinkage show sudden increases in approximately the same temperature range.

Yarn heat set in the slack condition at 200°C took about 25 min to dissolve, while the sample heat set without being allowed to shrink dissolved in only 2 hr. On the other hand, the samples heat set at 220°C in the slack condition and at constant length required about 1.5 and 3.5 hr, respectively, while the samples heat set at 230° and 240°C in either of the conditions took considerably longer times (ranging from 8 to 24 hr) to dissolve in the same mixture. When the CDT were determined in a 2:3 mixture, the times for the slack-treated samples at 200° and 220°C were respectively 13 and 23 min (Table VI). The samples heat set at 230° and 240°C took much longer. Even 100% phenol at 60°C could not dissolve the samples heat treated at 240°C in less than 8 hr. These results, at different temperatures, are in general agreement with the results of Weigmann et al.[17] In the present case, however, the CDT values for the samples heat set at constant length are higher than those for the slack treated samples, though the opposite results have been observed by Weigmann et al.[17]

In the case of nylon 6, the CDT measured in a 1:3 or 1:6 mixture for the samples heat set at different temperatures with and without being allowed to shrink are not significantly different. The CDT measured in a 1:10 mixture are given in Table V. The time taken to dissolve the heat-set yarn increases with increasing heating temperature, and the sample treated at constant length takes a longer time to dissolve than the sample treated in the slack condition at any heat-setting temperature. The CDT for nylon 66 yarns heat set in the slack condition and at constant length are significantly different (Table V) from that of nylon 6.

Birefringence

The data on the optical properties of the heat-set nylon and polyester yarns are given in Table IX. Nylon 6 filaments exhibit a decrease in birefringence on heat setting in oil either in the slack condition or at constant length. The decrease in the birefringence is caused by an increase in the value of $n_\perp$. The parallel refractive index only increases marginally. This suggests that the decrease in birefringence should not be attributed to the disorientation of the molecular chains in the crystalline region alone. Nylon 66 exhibits similar changes. However, these changes are smaller. In the case of polyester, both the parallel and perpendicular refractive indices increase on heating in oil when the sample is not allowed to shrink while heating. As a consequence, the bire-

TABLE IX
Refractive Indices of Filaments Heat Treated in Oil

Temperature of treatment, °C	Heat-treated slack			Treated at constant length		
	Refractive index			Refractive index		
	$n_\parallel$	$n_\perp$	Δn	$n_\parallel$	$n_\perp$	Δn
Nylon 6						
Blank	1.580	1.522	0.058	1.578	1.522	0.056
100	1.578	1.523	0.055	1.578	1.522	0.056
140	1.578	1.523	0.055	1.581	1.531	0.050
160	1.582	1.528	0.054	1.581	1.531	0.050
175	1.581	1.531	0.050	1.581	1.531	0.050
190	1.582	1.530	0.052	1.581	1.531	0.050
200	1.581	1.531	0.050	1.582	1.531	0.051
Nylon 66						
Blank	1.582	1.523	0.059	1.582	1.523	0.059
150	1.578	1.523	0.055	1.582	1.523	0.059
180	1.581	1.525	0.056	1.581	1.530	0.051
200	1.581	1.531	0.050	1.583	1.531	0.052
215	1.583	1.531	0.052	1.583	1.532	0.051
230	1.581	1.531	0.050	1.583	1.533	0.050
240	1.583	1.533	0.050			
Polyester						
Blank	1.716	1.541	0.175	1.718	1.543	0.175
150	1.716	1.545	0.171	1.720	1.546	0.174
180	1.715	1.545	0.170	1.722	1.545	0.177
200	1.716	1.545	0.171	1.722	1.545	0.177
215	1.716	1.545	0.171	1.724	1.547	0.177
230	1.716	1.548	0.168	1.722	1.549	0.173
240	1.716	1.547	0.169			

fringence values are unaffected. On the other hand, the samples that have undergone free shrinkage during oil heating register a fall in their birefringence caused mainly by an increase in the value of $n_\perp$.

Normally, only the birefringence of the heat-set samples is measured using a Berek compensator, and the decrease in Δn as a result of heat setting is interpreted to be a fall in orientation. The present results indicate that both $n_\parallel$ and $n_\perp$ can vary independently and hence should be measured separately.

Heat setting probably results in a decrease in the orientation of the molecular chains in the amorphous region of the fibrous material. This is, however, accompanied by a significant increase in the total crystallinity of the sample. The decrease in the orientation depends upon the tension on the material during heat treatment. If disorientation alone occurs, without a significant change in crystallinity, then $n_\parallel$ should decrease and $n_\perp$ increase with a net decrease in Δn. When the heat-setting results in an increase in crystallization alone, $n_\parallel$ and $n_\perp$ will both increase, with a small net increase in Δn. Changes in orientation will affect $n_\parallel$ much more than $n_\perp$. The net effect of heat setting a drawn fiber may be a decrease or an increase in $n_\parallel$ and $n_\perp$, and hence in Δn, depending upon the fibrous material and also on the experimental conditions. The present results indicate that the heat-setting process results in an appreciable improvement in the overall crystallinity of the fibrous material, irrespective of the conditions under which it was heat set.

Dynamic Young's Modulus

The dynamic Young's moduli of heat-set nylon and polyester yarns determined by using a pulse propagation meter are given in Tables II and III. An increase in the elastic constant is a measure of the increase in overall (crystalline and amorphous) orientation of the material. For nylon 66 heat set at different temperatures in the slack condition, the elastic constants are more or less equal and also equal to that of the untreated control. On the other hand, nylon 66 filaments heat set at constant length show appreciable improvements in their moduli. The Young's modulus increases with increasing setting temperature. In the case of nylon 6, the Young's modulus in fact decreases on heat setting in the slack condition, while heat setting at constant length leads to a slight improvement. On the other hand, polyester filaments behave very differently. Heat setting in the slack conditions causes a reduction in the sonic modulus to an extent of 60%, while on heat setting at constant length the reduction is of the order of 30%. The results suggest a drastic reduction in the overall orientation of the polyester filaments on heat setting even when not being allowed to shrink. This is particularly true of the orientation in the amorphous region.

Dismore and Statton[13] as well as Dumbleton and Buchanan[15] have observed a drastic reduction in the dynamic modulus of nylon 66 filaments heat set in the slack condition. The sonic modulus determined under a tension of 0.05 g/den decreased from a value of 33 g/den for the untreated control to 1–2 g/den for the sample heat set at 240°C in the slack condition.[15] As pointed out by Dumbleton and Buchanan,[15] the experimentally determined values are significantly altered by the applied tension. If the applied tension is not sufficiently high to remove the crimp developed on heat setting at high temperatures, especially in oil, the sound velocity will be low, and hence the sonic modulus will be lower. In the

present case the applied tension was about 0.1 g/den and was sufficient to keep the yarn taut. Under these experimental conditions, no drastic reduction in the sonic modulus was observed both for nylon 6 and 66 filament yarns.

Torsional Rigidity Modulus

The torsional rigidity moduli of heat-set nylon 66 filaments determined by the simple torsion pendulum method are given in Table X. These rigidity moduli are lower for the samples heat set at constant length than for the slack-treated samples. This difference may be partly due to the slight increase in diameter when slack treated. A uniform shrinkage was observed in the case of slack treatment. Both sets of values are, however, lower than that for the untreated control. Nylon 6 filament yarn also shows similar behavior. However, the changes in the rigidity modulus for nylon 6 as a consequence of heat setting, either in the slack condition or at constant length, are much smaller than in the case of nylon 66. On the other hand, heat treatment in the slack condition or at constant length does not cause any significant change in the torsional rigidity of polyester yarn.

Equilibrium Dye Uptake

Polyester yarn, untreated as well as heat set, was dyed with a disperse dye, Dispersol Red B-2B (C.I. 60756) by the carrier method at 95°C for 45 min. The dye uptake of the heat-set samples was found to be less than that of the untreated control. In addition, the samples heat set at constant length were found to pick up less dye than those heat set in the slack condition. These dyeing properties are quite consistent with current theories of structure. In terms of the two-phase theory of structure involving a crystalline and a so-called amorphous region, two opposing factors play a part. An increase in the overall crystallinity (i.e., growth of crystallites) results in a reduction of the rate as well as the equilibrium dye uptake, while the disorientation of the amorphous regions leads to increased dye uptake. Both these processes increase with increasing heat-setting temperature. Because the changes in the overall crystallinity are considerable, the net effect is a decrease in the dye uptake. When the disorientation is prevented to some extent by the application of tension during heat setting, the dye uptake is further reduced. This structure theory fails to account for the variations in the rate of dye uptake when dyed in the absence of a carrier in the dye bath, either with the temperature of heat setting or as a result of the application of tension during

TABLE X
Torsional Rigidity Modulus of Nylon 66 Heat Set in Oil

| Treatment Temp., °C | Modulus $\eta \times 10^{-9}$, dynes/cm^2 | | | | | |
| | Treated slack | | | Treated at constant length | | |
	5 sec	1 min	30 min	5 sec	1 min	30 min
Blank	16.2					
200	9.1	9.4	10.0	8.6	8.1	9.3
215	—	9.9	—	—	8.6	—
230	9.4	9.9	9.7	8.0	8.3	8.5
240	9.9	10.3	11.3	8.4	8.3	8.9

dyeing. Marvin[18] and others[19,20] have shown that the dye uptake initially decreased as the temperature of heat setting was raised. However, at higher temperatures the rate of dye uptake increased with increasing temperature and could be greater than that for the untreated control. Warwicker[20] has shown that the dye uptake rate could be further improved by the application of tension during dyeing. The dye uptake rate as suggested by Wariwcker[20] is governed by the void structure and its variation, either due to heat setting or due to the application of tension during dyeing. However, the work on the kinetics of dyeing of heat-set fibers was not planned from practical considerations. In practice, fibers and fabrics are dyed by the carrier method or by the HT-HP method, and the equilibrium dye pickups thus obtained could always be explained in terms of structure.

Effect of Prolonged Heat Setting

As the heat treatment time increases, the critical dissolution time increases (Table XI), suggesting that the crystallinity increases with increasing time of heat setting. The sonic moduli for nylon 66 and polyester samples heat set for 1 and 30 min in the slack condition, and also at constant length, are given in Tables II and III. The sonic moduli for the samples heat set for 30 min in either of the conditions are higher than those for the samples heat set for 1 min. The improvement in the sonic modulus of the heat-set samples should be attributed to the improved overall crystallinity.[21] As a result of prolonged heat setting, there is a significant improvement in the size and crystallite perfection of the fibrillar lamellae. Secondly, the heat setting is accompanied by significant disorientation of the amorphous region, specially when heat set in the slack condition. Thirdly, there is a possibility of molecular degradation when the sample is heat set in oil for extended periods of time. These three factors are responsible for the reductions in strength and extension observed for the samples heat set for 30 min. Molecular degradation appears to be maximum for nylon 66.

The present results indicate that dimensional stability can be achieved even when the fibers are held at constant length during heat setting i.e., even when not allowed to recrystallize in the folded-chain configuration.[12,13] However, it may be argued that even when the filaments are heat set at constant length, the thermal energy supplied to the system might result in local melting of lower energy bonds. Thereafter the molecular segments are free to refold. If this is true, the breaking extension of the fibers heat set at constant length should approach that of the sample heat set in the slack condition. This is not borne out

TABLE XI
Critical Dissolution Time of Heat-Set Nylon 66

| Treatment temp., °C | Critical dissolution time | | | | | |
| | Treated slack | | | Treated at constant length | | |
	5 sec	1 min	30 min	5 sec	1 min	30 min
200	23	26	96	21	26	35
215	30	32	199	31	33	365
230	37	51	256	73	77	1046
240	43	76	366	83	150	1449

by the data on breaking extension. The improvement in the crystallite perfection of the lamellae that accompanies chain refolding should result in fiber embrittlement, as there are only a few tie molecules after heat setting to share the applied load. Again the experimental results do not support this hypothesis. Further, heat setting in the slack condition always results in a decrease in the overall orientation of the fibrous material. Even the samples that are heat set at constant length exhibit a decrease in the overall orientation, though to a lesser extent. The changes in fiber morphology are almost instantaneous, while the changes in crystallite growth continue to occur with increasing time of heat setting.[21]

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