

Some Observations on the Melting Behavior of Textile Fibers. Part I. Core Melting During Hot-Stretching of Nylon

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Synopsis

It has been found that under certain conditions of heating, filaments of nylon melt from the center outwards. It has been established that this is associated with the presence of moisture in the filaments and that moisture lowers the melting point of the material. Well-defined core effects and internal cavitation resulting in delustering of the filament may occur under conditions of shock heating. The melting point of nylon is raised by the presence of stress.

INTRODUCTION

The phenomena to be described were encountered in the course of work on the hot-stretching of yarns. In this process yarn is passed fairly rapidly through a heated zone, commonly over an electrically heated hot-plate. It was found by W. Benson of these laboratories that when nylon or Terylene yarn with known and constant strain was run over a hot-plate, the temperature of which was gradually raised, the critical temperature—that at which the yarn broke or melted—was dependent on the strain, being, for example, about 5°C. higher when the yarn was strained 20% than when it was run without strain.

It was thought that failure of the yarn was perhaps a rather arbitrary indication of the critical temperature and that if birefringence measurements (providing a measurement of molecular orientation) could be made on the running thread it would probably be found that as melting was approached birefringence would fall to zero and that this would provide a more precisely defined endpoint. In order to make such measurements nylon monofilament was used. However, birefringence changes could not be followed to the critical temperature. At about 30°C. below this temperature a phenomenon that we feel justified in describing as core melting was observed. A substantial part of this paper is devoted to the examination and elucidation of this phenomenon.

EXPERIMENTAL

Materials

These were mostly regular commercial products of recent delivery and they were used without any special preparation. Multifilament yarns were of low (producer's) twist. Undrawn yarn was kindly supplied by British Nylon Spinners. Except in the instance where a nylon 6 monofilament was used, the nylon was of the 66 type.

Hot-Stretching and Treatment on Bulking Machine

For hot-stretching a machine built at the Institute was used. This machine, shown diagrammatically in Figure 1, embodies a hot-plate (A), 12 in. long, heated by embedded electrical elements with a Simmerstat for

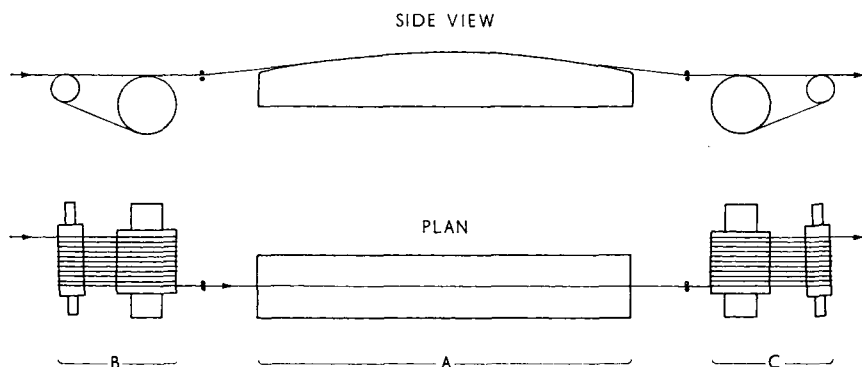


Fig. 1. Laboratory hot-stretching machine.

control of temperature. The plate is slightly convex to ensure good contact of the yarn as it passes over it. Yarn-advancing rollers (B and C) at each end of the plate can be run with a speed differential to provide the desired stretch. The yarn speed at the delivery end was 15 ft./min. The surface temperature of the plate was measured with a contact thermocouple.

For processing on a bulking machine, laboratory equipment built up of parts from a standard Scraggs CS9 bulking machine was used. Processing was normal except that no twist was inserted. Monofilament or yarn fed to either machine was in equilibrium with the laboratory atmosphere, controlled at 65% R.H.

Frame Experiments

These consisted of attaching a length of yarn or filament in an adjustable brass frame so that it could be held with any desired strain throughout a heat treatment. The top clamp of the frame was made so that an adjustment of the extension screw did not rotate this clamp; the lower clamp was

fixed. The frame with sample attached was heated by total immersion in the silicone oil bath described below.

Measurement of Birefringence

The birefringence, Δn , of the filament was obtained from the relation $\Delta n = r/t$, where r is the retardation (of the slow ray with respect to the fast ray) measured with a polarizing microscope with compensator, and t the specimen thickness (in the present work the diameter of the filament). For samples already modified, the diameter was measured directly under the microscope. For running monofilament this was not possible, because of the slight lateral movement of the filament, and the diameter was derived from a (linear) relation with strain that has been established by Davis.¹

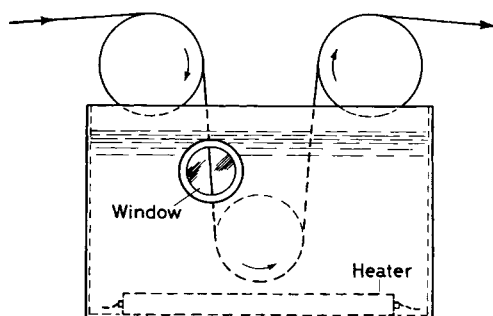


Fig. 2. Cell for liquid heating and observation of running monofilament. Used as an alternative to the heating plate (A) in Fig. 1.

For the measurements of retardation on the running monofilament the filament was passed over a system of pulleys to carry it through liquid paraffin or silicone oil contained in a small brass cell (Fig. 2) that replaced the hotplate unit A in Figure 1. This liquid medium reduced refraction effects and also provided a convenient heating medium. Windows (micro cover glasses cemented to the cell walls) on opposite faces of the cell afforded the optical path for a polarizing microscope fitted with a Babinet compensator, which was suitably positioned to observe the running thread. There was a small immersed heating coil at the bottom of the cell. Convection and rotation of the lower pulley gave adequate agitation.

Microscopy

Fibers to be sectioned were embedded in methacrylate resin (H.T. cement, Hopkin and Williams) which was then polymerized in an oven at 75°C. for 4 hr. Sections were cut on a rotary microtome and secured to microscope slides with Mayers albumen adhesive; where necessary, the resin was removed from the cut sections with boiling methylene chloride. Prior to mounting, sections and whole fibers to be examined with the interference microscope were conditioned overnight at 66% R.H.

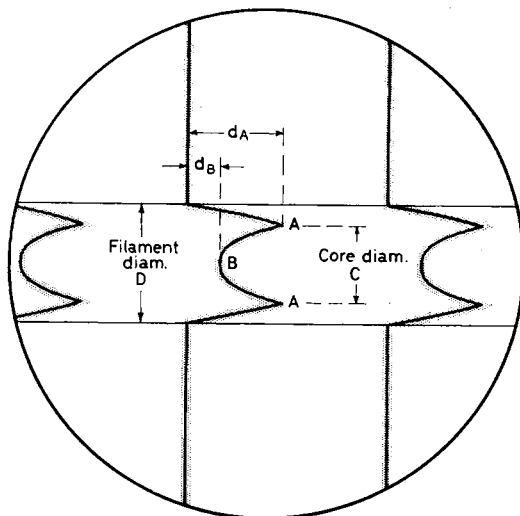


Fig. 3. The appearance of a cored filament as seen with a banded field in the interference microscope.

The refractive indices of fibers were measured with a Dyson-type interference microscope and plane-polarized mercury yellow light; the fibers were mounted in appropriate mixtures of butyl stearate and tricresyl phosphate. Figure 3 illustrates the appearance of a cored filament as seen with a banded field in the interference microscope. The refractive index of the skin region, n_s , was obtained from $(d_A/t_A) + n_m$, where d_A is the average fringe displacement measured at points A and t_A the average chord length through points A; n_m is the refractive index of the mounting liquid. The refractive index of the core was obtained from

$$n = [d_B - (d_A/t_A)(D - C)](1/C)$$

where d_B is the fringe displacement measured at B, and C and D are the core and filament diameters, respectively. The procedure was followed through with the light polarized parallel to, and normal to, the fiber length and the refractive indices n_{\parallel} and n_{\perp} obtained for both skin and core regions.

The optical property n_{iso} is a weighted mean given by

$$n_{iso} = 1/3(n_{\parallel} + 2n_{\perp})$$

For nylon this property has been related to the density of the fiber,² an increased density being accompanied by an increased value for n_{iso} .

Melting Point Determinations

A Koffler hot-stage and polarizing microscope were used for the microscopical determination of fiber melting points. The filaments to be evaluated were mounted in a silicone oil to prevent thermal oxidation effects and to facilitate the observation of detail; the presence of the oil

did not affect the melting point of nylon fibers. This procedure gave the melting point of dry fibers, and the values obtained were in agreement with published figures.

To determine the melting point of fibers in a known atmosphere, they were sealed into glass capillary tubes. These were 8–10 cm. long, internal bore 0.8 mm. and external diameter 1.0 mm. Prior to sealing, distilled water was introduced for the wet melting points; dry values were obtained by placing the tubes containing the fibers in an oven at 100°C. for 2 hr. prior to sealing. The sealed tubes were heated by completely immersing them in a silicone oil bath for 4 min. and during this period generally two heating-cooling cycles of the bath occurred, the variation within a cycle not exceeding 1°C. from the mean value. The silicone oil bath was maintained at a given temperature by a mercury-type control and an electrical heater. The thermometers employed for the work were calibrated against a N.P.L. standard thermometer. Pressures developed within the sealed capillary tubes were more than 100 psi upwards and the work was done with a safety screen between operator and oil bath; about 5% of the tubes blew out during heating. A sealed tube was immersed only once, i.e., a fresh specimen was used for each temperature employed. Although this technique involved the preparation of a large number of sealed tubes, it was thought more desirable than one involving a single preparation that had been raised through a range of temperatures and might thereby have become modified, e.g., thermally degraded, by the time the melting point was attained. The technique of shock heating was also more directly comparable with many textile processes in which the yarn or fabric enters rapidly into a high temperature zone.

BIREFRINGENCE OF A RUNNING MONOFILAMENT AT DIFFERENT STRAINS AND OVER A RANGE OF TEMPERATURES

Retardation, as defined in the Experimental Section, from which birefringence was calculated, was measured on the running monofilament as it passed through a liquid-paraffin bath. As a preliminary to experiments at elevated temperatures, observations were made at room temperature, over a range of strain. Figure 4*a* shows the results obtained and Figure 4*b* shows the same results added to a curve of birefringence versus draw ratio that is typical of that found when measurements are made on monofilament drawn to different extents.³ The variation of birefringence with temperature for the same monofilament running with 2% and with 12% strain is shown in Figure 5. Each curve is drawn through a large number of points (not shown), all lying on the curves. The curves show a steady but small decrease in molecular orientation from room temperature to about 200°C. and a rapid fall as the temperature is raised above 200°C. It was not possible to make birefringence measurements at temperatures above about 220°C. At, or a few degrees above, this temperature, the apices of the fringes observed in the compensator flattened, then inverted, and there-

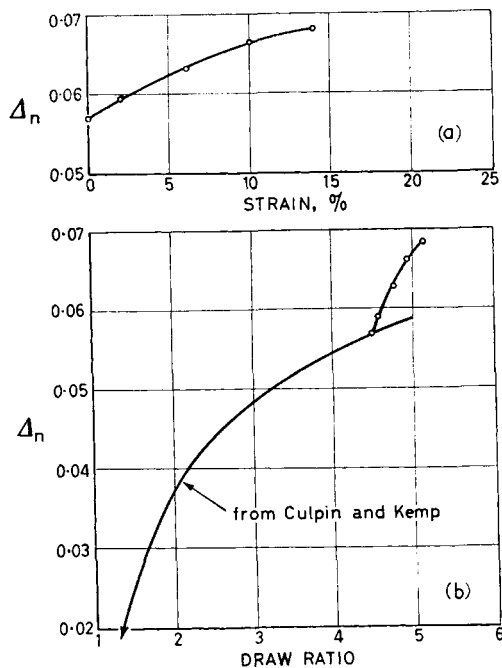


Fig. 4. (a) Birefringence Δn of 15-den. nylon monofilament running at different strains at 20°C.; (b) results shown in (a) added to a curve showing the relation between birefringence and draw ratio commonly found during the drawing of nylon monofilament.

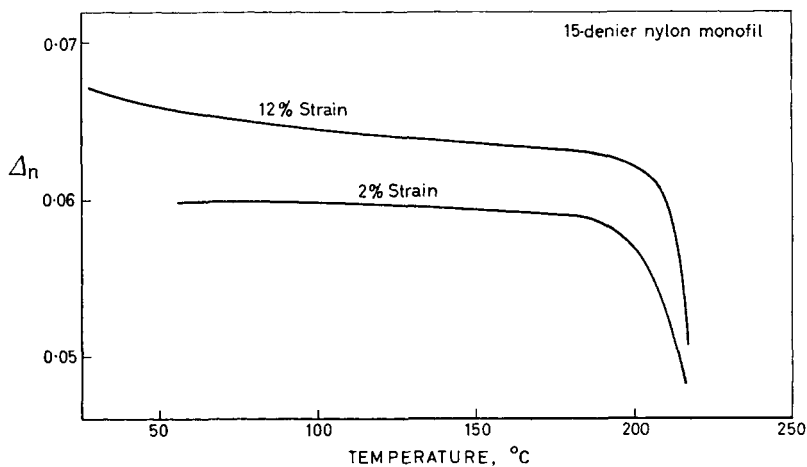


Fig. 5. Birefringence of monofilament during passage through heated liquid paraffin.

after the filament appeared opaque in the field. It is to be noted that the level of birefringence, though falling rapidly, is still high (about 0.05) at 220°C. and that birefringence could not be used, as hoped, to define the critical temperature, which was in the region of the normal melting point of the material, 250°C.

EXAMINATION OF MONOFILAMENT AND YARN PASSED THROUGH THE LABORATORY STRETCHING MACHINE AT DIFFERENT STRAINS AND WITH VARIOUS HEATING MEDIA

The appearance of 15-den. monofilament after being passed through liquid paraffin at 2% strain and at different temperature is illustrated by Figure 6. It can be seen that with increasing temperature, discontinuities or cavities appear in the filament. At the higher temperatures

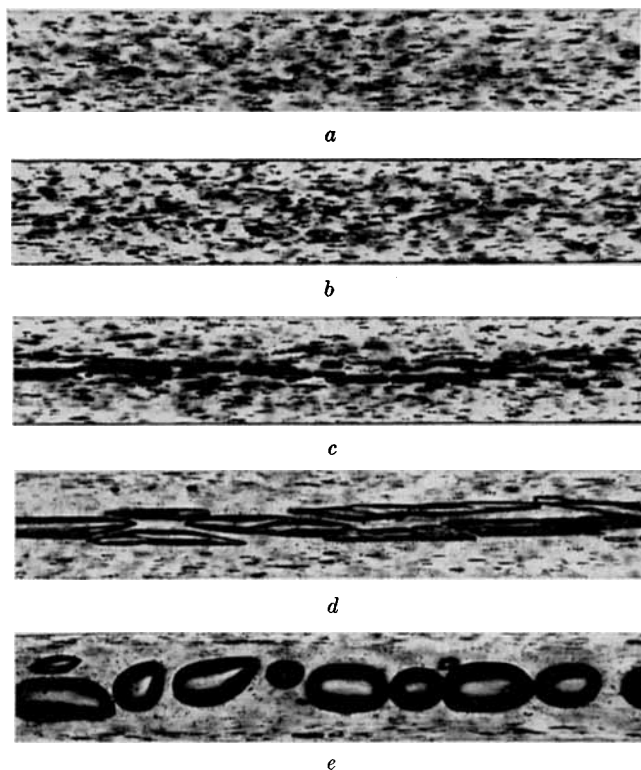


Fig. 6. Nylon monofilaments, hot-stretched through liquid paraffin at 2% strain: (a) 210°C.; (b) 215°C.; (c) 220°C.; (d) 228°C.; (e) 235°C. 320 \times .

the cavities are appreciably larger but less numerous and also tend to approach a spherical form. There was no evidence to suggest that liquid paraffin was present within the cavities. Samples treated at 235°C. and higher temperatures showed evidence of a redistribution of the delustrant particles. Transverse sections of the 235°C. sample were cut, and Figure 7 illustrates a typical appearance. It can be seen that within the filament there is in addition to the cavities, an optical discontinuity. The nature of monofilament nylon before treatment is illustrated by interference microscopy in Figure 8, and it can be seen that, within the limits of sensitivity of the interference microscope, the ordinary refractive index of nylon remains

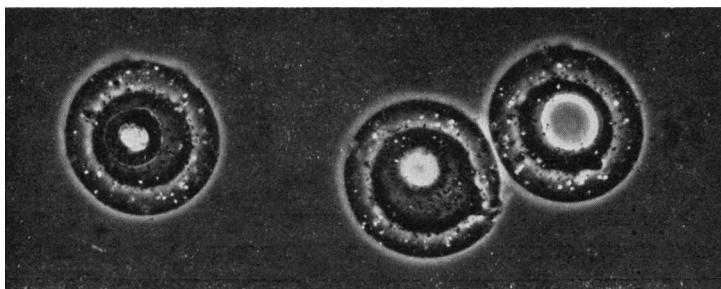


Fig. 7. Sections, $8\ \mu$ thick, of monofilament hot-stretched through liquid paraffin at 235°C . and 2% strain. Phase contrast microscope. $450\times$.

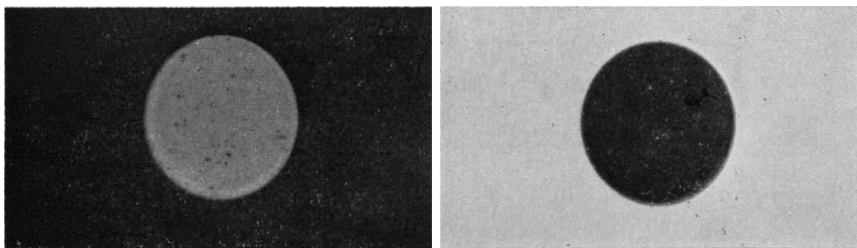


Fig. 8. Sections, $8\ \mu$ thick, of untreated nylon monofilament as seen in the interference microscope at two different phase settings. $450\times$.

constant over the cross section. Sections of the 235°C . samples examined in a polarizing microscope also showed the optical discontinuity, and at high magnification and with a strong light source a fine and granular texture was observed in the core but not in the skin. This type of appearance is often obtained in laboratory experiments when nylon is cooling from the melt; it is not a feature of drawn commercial nylon monofilament. Transverse sections of the 235°C . sample were examined with the interference microscope. It was seen that within a given region, core or skin, the ordinary refractive index, n_{\perp} , was uniform in value. This latter observation, in some ways a surprising result, plus the fact that core and skin were well defined, made possible a full evaluation of the optical properties of skin and core, and these are shown in Table I. The values obtained show that

TABLE I
Optical Properties of Skin and Core^a

Sample treatment	n_{\parallel}	n_{\perp}	Δn	n_{180}
Untreated	1.574	1.518	0.056	1.537
Paraffin at 235°C ., 2% strain				
Skin	1.587	1.522	0.065	1.544
Core	1.549	1.546	0.003	1.547

^a Measured values for $\lambda = 578\ \text{m}\mu$.

hot stretching has produced a rise in n_{iso} (a property related to true density) of about 0.01 in both skin and core; this is a similar rise to that produced by annealing treatments lasting many hours.² The rise in birefringence of the skin region of the hot-stretched monofilament may be explained on the basis of the combined effects of increased density and strain.

Although no penetration of paraffin into the treated monofilaments had been observed, it was thought advisable to examine the behavior of the nylon with other heating media, and for some experiments the paraffin bath was replaced by a bath of silicone oil and for others by the electrically heated plate. The appearance of the monofilament obtained from these experiments was generally similar to that obtained previously, in that an obvious skin and core were produced at temperatures above about 225°C. In the monofilament that had passed over the heated plate, the core and the associated cavities were noticeably smaller for corresponding birefringence values than in the samples heated by liquid media. Table II shows the relation between the birefringence of the skin and the core and the diameter of the core.

TABLE II
Monofilament at 2% Strain Treated at Temperatures in the Range 230–245°C.

Heating medium	Skin Δn	Core Δn	Core fraction
Silicone oil	0.056	0.020	0.63
	0.056	0.014	0.75
	0.058	0.006	0.76
Liquid paraffin	0.059	0.017	0.64
	0.058	0.010	0.67
	0.062	0.004	0.78
Electrically heated plate	0.057	0.024	0.30
	0.055	0.018	0.33
	0.054	0.012	0.41
	0.055	0.014	0.44

It can be seen that whereas the birefringence of the skin remains reasonably constant, that of the core decreases as core size increases; also, that for similar levels of core birefringence, the core in the monofilament heated by passage through the liquids is appreciably larger than in the monofilament heated by passage over the plate. In the samples heated by passage through the liquids, the skin-core boundary was observed to be sharp irrespective of the level of birefringence in the core; the boundary was less sharp in the material heated by passage over the plate, but even so was contained within 2 or 3 μ . Figure 9 shows the appearances obtained for sections of monofilament with two different phase settings of the interference microscope; the monofilament had been heated by passage over the plate. It can be seen that a core region is present, but that its periphery is not so sharply defined as in the liquid-treated monofilament.

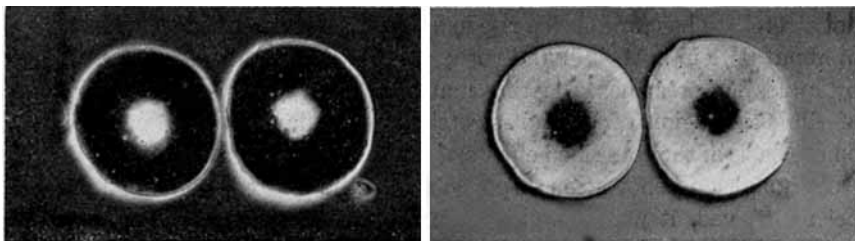


Fig. 9. Sections, $8\ \mu$ thick, of monofilament hot-stretched by passage over an electrically heated hot-plate at 245°C . and 2% strain. Interference microscope, two different phase settings. $450\times$.

The untreated material was examined by various means, including a technique used by Andrews⁴ that will be referred to in a later publication, but no evidence was obtained that the central region of a monofilament is any different from the exterior region.

Commercial-type nylon of 30 den. and 10 filaments was passed through heated liquid paraffin at 2% strain and at different temperatures. The results were variable, in that some filaments in yarns treated between 240 and 250°C . contained core effects, while others did not.

Undrawn nylon yarn of 118 den. and 13 filaments was passed through heated liquid paraffin at two different strains, 60 and 200%. The resulting yarns contained well-defined skin-core effects and cavities when treated between 230 and 250°C .

High tenacity nylon yarn of 840 den. and 140 filaments was passed through heated liquid paraffin at 2% strain; the yarn broke at a temperature of 262°C . Microscopical examination of the yarn did not disclose any evidence indicative of the presence of a skin-and-core effect, e.g., no inversion of Babinet fringes, no cavities or bubble effects. Yarn treated at temperatures between 250°C . and the breaking temperature showed evidence of fusion between filaments, this being an expected and normal occurrence for yarn heated at this high temperature.

The results of all the work so far described showed that with processing temperatures approaching, yet below, the normal melting point of nylon it was possible to produce a well-defined core effect in monofilament and in some but not all multifilament yarns. No explanation for this unexpected core effect was available, and in order to provide a more flexible and precise means of investigation it was decided to subject short lengths of nylon to various treatments and then examine them microscopically.

SUPPLEMENTARY EXPERIMENTS ON SHORT LENGTHS OF MONOFILAMENT AND YARN

Short lengths of monofilament and yarn held in stretching frames at known strain and with different pretreatments, were rapidly immersed for a brief time in a heated silicone oil bath and later examined microscopically. The effects of temperature, strain, moisture, filament, and yarn

TABLE III
Effect of Temperature of Shock-Heating in 15-den. Nylon Monofilament (Zero Applied Strain and 2 sec. Immersion in Silicone Oil)

Immersion temp., °C.	Observations
215	No visible change
230	Babinet fringes abnormal, TiO ₂ cavities enlarged
235	Skin-and-core structure present, additional cavities (elongated) in core, apices of Babinet fringes inverted
240	Similar, but more pronounced, effects to above
245	Monofilament partially melted

TABLE IV
Effect of Strain during Shock-Heating in 15-den. Nylon Monofilament (2 sec. Immersion in Silicone Oil)

Applied strain, %	Immersion temp., °C.	Observations
-30	218	Babinet fringes abnormal, TiO ₂ cavities enlarged
-30	220	Skin-and-core structure present, pronounced cavity effects; Babinet fringes partially obscured and abnormal
-20	225	Babinet fringes abnormal, TiO ₂ cavities enlarged
-20	227	Skin-and-core structure present, additional cavities in core, apices of Babinet fringes inverted
0	^a	
+10	231	Babinet fringes abnormal, TiO ₂ cavities enlarged
+10	235	Skin-and-core structure present, additional cavities in core, apices of Babinet fringes inverted
+20	235	Babinet fringes abnormal, small additional cavities
+20	236	Skin-and-core structure present, additional cavities in core, apices of Babinet fringes inverted

^a See Table III.

denier were examined in this way, and Tables III-VII summarize the results obtained.

In addition to the experiments summarized in Table V a monofilament held at 10% strain was immersed in silicone oil at 170°C. and the temperature of the oil raised to 250°C. It was observed that the treatment produced no visible change in the nylon. From this experiment and the results shown in Table V, a direct connection between the presence of moisture and the production of a skin-and-core structure is evident, and

TABLE V
Effect of Moisture during Shock-Heating in 15-den. Nylon Monofilament (10% Applied Strain and 2 sec. Immersion in Silicone Oil)

Pretreatment	Immersion temp., °C.	Observations
10 min. in silicone oil at 150°C., cooled in the oil, then rapidly transferred to the high temperature bath	240	No visible change
10 min. in silicone oil at 150°C., removed, washed in petroleum ether, conditioned at 65% R.H.	240	Skin-and-core structure present, additional cavities, in core, apices of Babinet fringes inverted
Heated in oven for 1 hr. at 105°C., transferred to immersion bath in the dry state	240	No visible change
Heated as above, then conditioned at 65% R.H.	240	Skin-and-core structure present, additional cavities in core, apices of Babinet fringes inverted
Dried over P ₂ O ₅ for 72 hr., transferred to immersion bath in dry state	240	No visible change
Dried as above then conditioned at 65% R.H.	235	Skin-and-core structure present; numerous additional cavities, Babinet fringes very abnormal

TABLE VI
Effect of Filament Denier and Number of Filaments during the Shock-Heating of Nylon Except where Stated Otherwise (2 sec. Immersion in Silicone Oil)

Sample	Applied strain, %	Immersion temp., °C.	Observations
6-den. monofilament	+10	240	Skin-and-core structure present, additional cavities, apices of Babinet fringes inverted
9-den. monofilament	"	"	As above
15-den. monofilament	"	"	"
59-den. monofilament	"	"	"
840/140 high tenacity yarn	"	"	No visible change.
"	"	241	(30 sec. immersion) No visible change.
Single filament from 840/140 high tenacity yarn	"	235	Filament broke in bath
As above	0	236	Skin-and-core structure present, apices of Babinet fringes inverted
Single filament from 30/10 yarn	"	242	As above

TABLE VII

Effect on 15-den. Nylon of Immersion in Hydroxylic Liquids Other than Water (10% Applied Strain, 2 sec. Immersion)

Immersion liquid	Immersion temp., °C.	Observations
Glycerol	190	Surface partially dissolved
"	200	Dissolved
Ethanediol	150	Surface partially dissolved
"	158	Dissolved

it is concluded from the experiments that the presence of moisture within the nylon at the time of heating is essential for core formation.

The combined effect of heat and water on nylon prompted the use of other liquids of a hydroxylic nature. Table VII shows that they have a pronounced effect on nylon. However, the appearance of the treated material suggests that dissolution rather than fusion is occurring, as with increasing temperature the first sign of a change in the nylon is a dissolution of the outer surface, rather than transformation to a fused mass. Some of the partially dissolved monofilaments showed rather unusual etched patterns; Figure 10 illustrates one of the types observed.

Figure 11 shows the relation found between strain and the temperature of onset of the inversion of the apices of the Babinet fringes, an indication of the presence of a core region of reduced orientation.

A 9-den. monofilament was immersed in silicone oil at 241°C. and permitted to cool slowly to 130°C. It was found that a core region containing large (negatively birefringent) spherulites was present in the treated monofilament. It is reasonable to assume that such growths formed from a molecular state wherein the nylon molecules had sufficient freedom to permit such a drastic rearrangement—in fact from a melt.

The different behavior of 840/140 high tenacity yarn and of single filaments from this yarn is important, and is considered later alongside the results of other experiments.

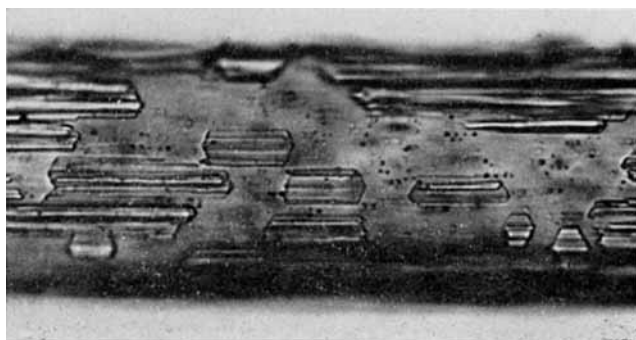


Fig. 10. Etch pattern in the surface of nylon monofilament after immersion in ethanediol at 148°C. for 2 sec. and at constant length. 750×.

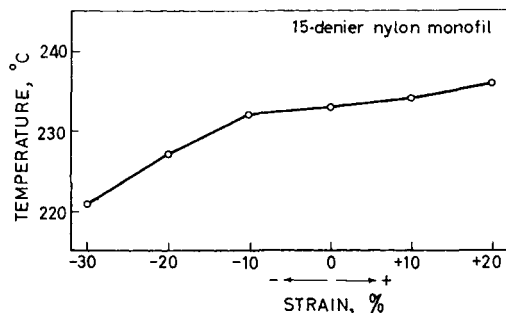


Fig. 11. The temperature of onset of inversion of the Babinet fringes in monofilament strained on a frame at room conditions and heated by rapid immersion in silicon oil for 2 sec.

Other experiments were done to ascertain the effect of the presence or absence in the nylon of spinning finish. No effect related to spinning finish was found. Nylon 6 was observed to behave in a similar manner to nylon 66, in that shock-heating at temperatures below its recognized melting point produced a core and other associated effects: 15-den. nylon 6 monofil at 10% applied strain, when immersed in silicone oil for 2 sec. at a temperature of 203°C. developed a skin-core structure and additional large cavities and gave Babinet fringes with inverted apices.

EXAMINATION OF MONOFILAMENT AND YARN HEATED IN COMMERCIAL-TYPE MACHINERY AT HIGH SPEED

Monofilament of 15 den. was processed on a bulking machine with 2% overfeed and without insertion of twist. This machine provided a convenient means of passing monofilament over an electrically heated plate at high speed. Speeds of 750 and 300 ft./min. were employed, giving heater contact times of 0.16 and 0.4 sec., respectively. For the higher speed, Figures 12 and 13 illustrate the microscopical appearance observed at different temperatures, and Figure 14 shows the variation of birefringence with temperature for the whole filament (integrated value) and values for skin and core regions. Monofilament processed at the lower speed showed very similar effects.

The results are in general agreement with the work done on the hot-stretching machine, in that skin-and-core effects are present. However for similar effects (large additional cavities, core of corresponding diameter, etc.) to occur, the temperature of the hot-plate in the bulking machine has to be set about 20°C. higher than with the liquid heating medium; as liquid heating provides the more efficient means of heat transfer, this is understandable. The marked difference in property between skin and core is clearly shown in Figure 14, where at a heater temperature of 260°C. the birefringence and therefore the molecular alignment of the outer regions of the monofilament are relatively unchanged, whereas the core is virtually

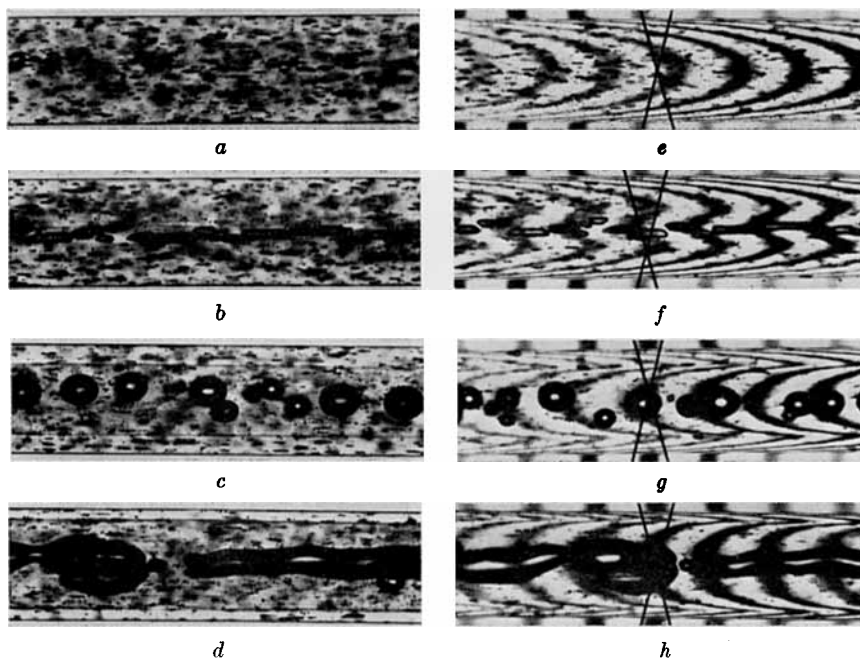


Fig. 12. Longitudinal views of monofilament processed on a bulking machine with a heater contact time of 0.16 sec. at 750 ft./min. and 2% overfeed: (a, e) 230°C.; (b, f) 240°C.; (c, g) 250°C.; (d, h) 260°C. Views (e)–(h) with polarizing microscope and Babinet compensator. 320 \times .

isotropic. The progressive nature of the effects with increasing temperature is evident, and it can be seen that the point of onset of deterioration in molecular alignment is difficult to define or recognize; the first indication from microscopy of a change in structure is provided by measurements of birefringence.

Two multifilament yarns, a 30-den. 10-filaments, medium tenacity yarn and a 840-den. 140 filaments, high tenacity yarn, were processed on the bulking machine with heater-contact times of 0.4 and 0.5 sec., respectively, and with 2% and zero overfeed, respectively. The 30/10 yarn showed no change detectable by microscopy up to a heater temperature of 250°C., but on approaching 255°C. it was noticed that some of the filaments showed skin-core effects and gave Babinet fringes whose apices were inverted; others showed no obvious effects, while the remainder gave irregular shaped Babinet fringes. The yarn broke at a temperature a little above 255°C. Figure 15 illustrates the fringes obtained with two filaments from a portion of yarn treated at 255°C.; the filaments shown have integrated birefringence values of 0.054 and 0.023, the later value being that of the filament having an irregular fringe shape. The 840/140 yarn showed no obvious change in property up to a heater temperature of 270°C. Above this value and up to the break, at 286°C., an increasing amount of filament

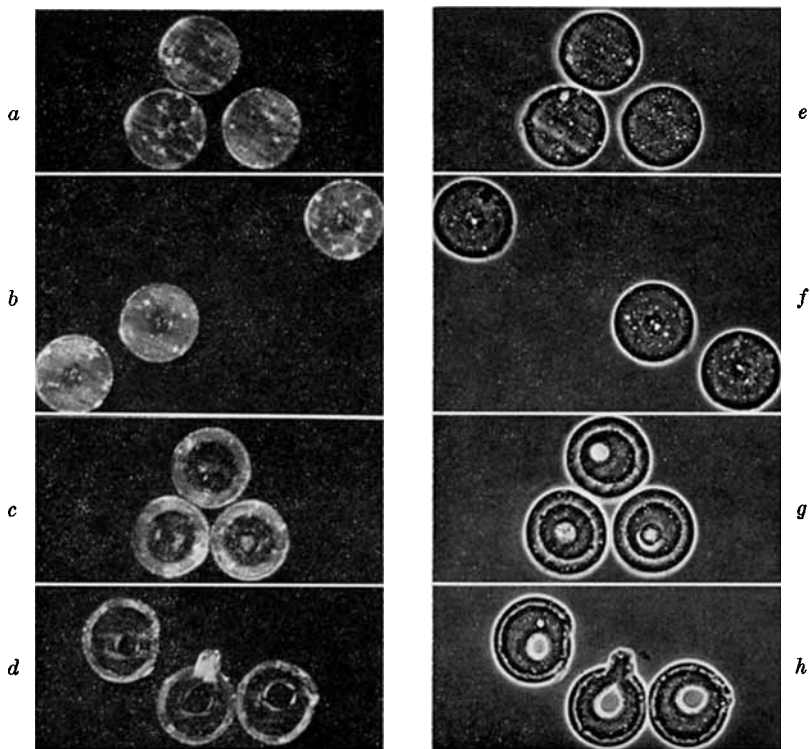


Fig. 13. Sections, $8\ \mu$ thick, of monofilament processed as in Fig. 12: (a, e) 230°C .; (b, f) 240°C .; (c, g) 250°C .; (d, h) 260°C . Views (a)–(d) with polarizing microscope; views (e)–(h) with phase contrast.

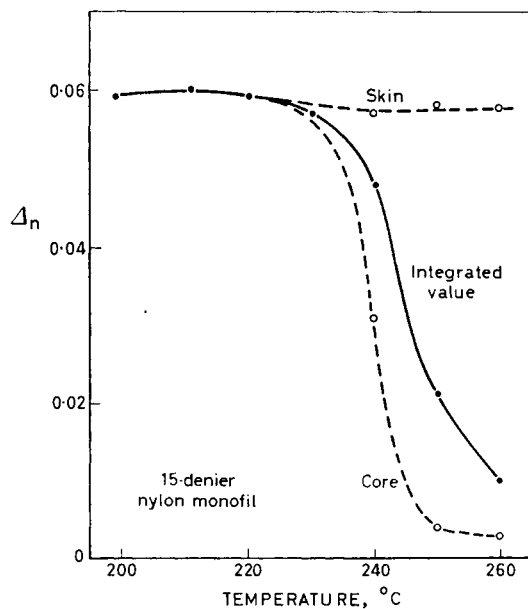


Fig. 14. Birefringence of nylon monofilament processed on bulking machine with a heater contact time of 0.16 sec. at 750 ft./min. and with 2% overfeed.

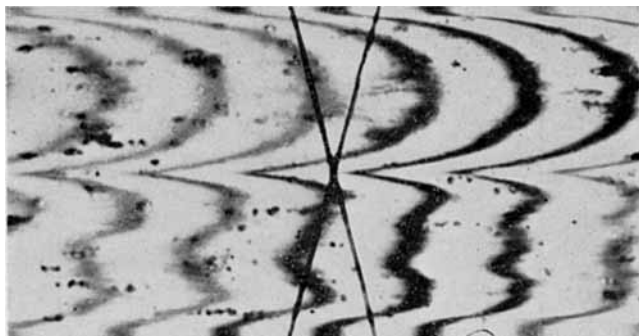


Fig. 15. Babinet compensator fringe in two filaments from a 30/10 nylon yarn processed on a bulking machine with a heater contact time of 0.4 sec. $1500\times$.

damage was present; filaments on the outside of the yarn showed signs of having undergone surface melting, and from 280°C . upwards many broken filaments with fused ends were present. No recognizable core effects were seen, and such distorted Babinet fringes as were observed appeared to be associated with deformity in shape and not internal effects. These results for the heavy denier yarn are consistent with processing at such high temperatures and reveal no unusual behavior.

MECHANICAL PROPERTIES OF TREATED MATERIALS

Stress-Extension Characteristics

Curves are given for material treated at various temperatures from 200°C . upwards as follows: in Figure 16 for a 15-den. nylon monofilament passed through a heated paraffin bath with 14% stretch; in Figure 17 for 15-den. nylon monofilament processed on a bulking machine with a heater contact time of 0.16 sec. and 2% overfeed; in Figure 18 for 840/140 (tire cord) nylon processed on a bulking machine with a heater contact time of 0.5 sec. and zero overfeed. In Figure 19 tenacity is plotted against temperature for the first two of these sets of results and for another run of the monofilament through the bulking machine but with contact time of 0.4 sec.

It will be seen that for the monofilament there is a progressive lowering of the stress-strain curve (as plotted with load as the ordinate); the breaking stress (tenacity) falls, but breaking extension remains constant with increasing temperature of treatment. Tenacity is thus a fairly satisfactory property to use for showing the effect of temperature of treatment. It will be noticed that the monofilament processed on the bulking machine with a contact time of 0.4 sec., but not that with a contact time of 0.16 sec., shows a slight increase in tenacity up to 230°C . From other work this is known to occur, but it is not clear why the experiments with shorter time of contact should not show the same effect. It is clear that with the onset of core melting the strength of the monofilament falls.

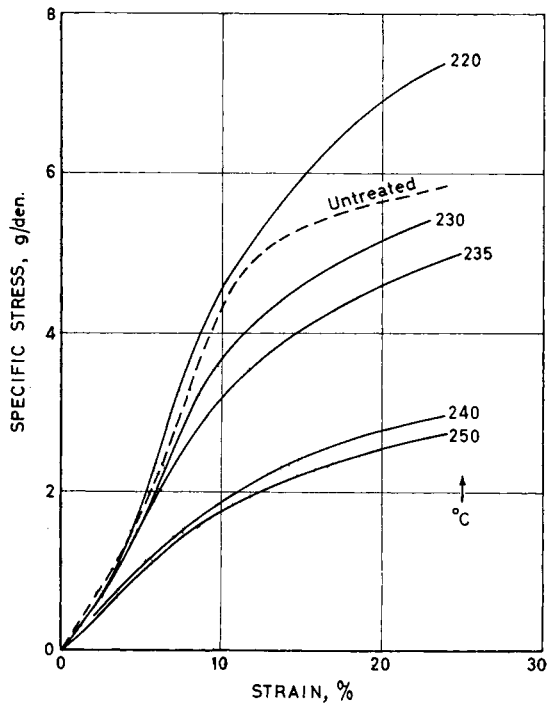


Fig. 16. Nylon monofilament passed through heated liquid paraffin at 14% strain.

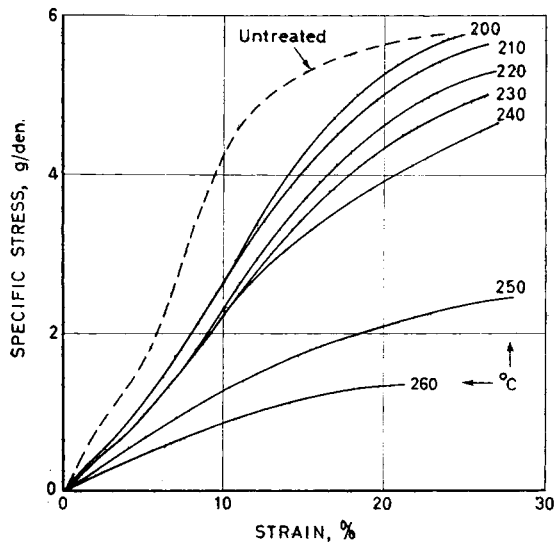


Fig. 17. Nylon monofilament processed on a bulking machine with a heater contact time of 0.16 sec. at 750 ft./min. and with 2% overfeed.

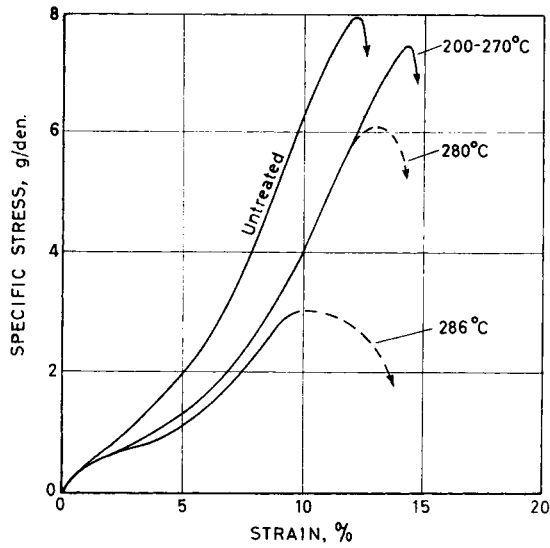


Fig. 18. Nylon yarn, 840/140 high tenacity, processed on a bulking machine with a heater contact time of 0.5 sec. and zero overfeed.

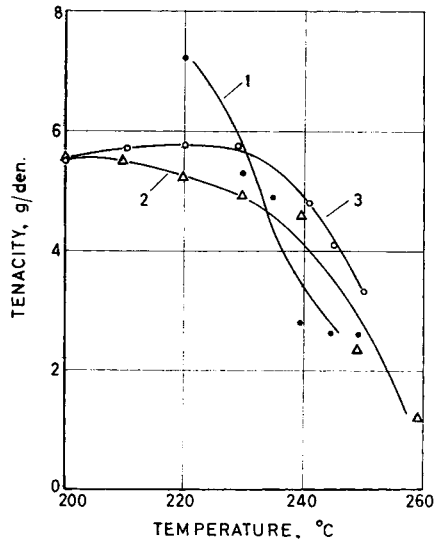


Fig. 19. Nylon monofilament: (1) heated in liquid paraffin at 14% strain; (2) processed on bulking machine, heater contact time 0.16 sec.; (3) processed on bulking machine, heater contact time 0.4 sec.

The picture presented by the heavy multifilament (Fig. 18) is rather different. There is no shift of the stress-extension curve in the temperature range 200–270°C., and break becomes less sharp (the strength of the individual filaments is more variable) and occurs at lower stress the higher the

temperature. This is in conformity with nonuniform treatment through the mass of filaments. The higher temperature at which weakening of the yarn occurs (as compared with the monofilament) presumably arises from a greater temperature difference between a significant portion of the yarn and the heater than is present between the monofilament and the heater.

Comparison of Tensile Modulus and Bending Modulus

The results of measurement of tensile modulus and bending modulus (measured with a scaled-down version of Searle's double pendulum apparatus) on the untreated 15-den. monofilament and on the same monofilament after passage with 14% stretch through paraffin at 240°C. are given in Table VIII.

TABLE VIII

	Initial tensile modulus, dyne/cm. ² × 10 ⁻¹⁰	Bending modulus, dyne/cm. ² × 10 ⁻¹⁰
Untreated	3.79	4.20
Treated	2.86	4.84

For the untreated material the bending modulus is 10% greater than the tensile modulus, indicating that the modulus of the surface zone, which largely determines the bending modulus figure, is greater than that of the core. For the treated sample the bending modulus is 70% higher than the tensile modulus, indicating that the surface zone is much more highly oriented than the core.

MELTING POINT OF NYLON DETERMINED UNDER DIFFERENT CONDITIONS

Work described above demonstrated that the presence of moisture affects the behavior of nylon when it is subjected to heat, and the following experiments were done to ascertain the influence of water on the melting point of nylon.

Autoclave Experiments

The apparatus used was a large autoclave of 1 liter capacity, fitted with pressure- and temperature-recording instruments. Nylon, in chip form, and sufficient distilled water to saturate the atmosphere at high temperature, were placed in separate beakers in the autoclave, which was then sealed and heated to a known temperature. The experiment was repeated with different temperatures, with fresh material on each occasion. It was found that as a result of the treatment the nylon chip became discolored, and at temperatures above 180°C. the chip was fused and strongly dis-

colored. The experiments demonstrated that nylon could be fused in moist atmospheres at temperatures appreciably below its recognized melting point but were open to the serious objection that the duration of each experiment, about 5 hr., produced appreciable thermal degradation in the nylon. The melting point of fresh chip and of fused and discolored chip from an autoclave experiment were determined by means of a microscope hot-stage method; the results were 258 and 255°C. respectively, the difference being of the same order as the experimental error of the method. The relatively unchanged dry melting point of thermally degraded nylon suggests that the autoclave experiments, though producing a modified product, do provide a reasonable guide to the behavior of nylon on heating in a water-saturated atmosphere.

Shock Heating of Nylon in Dry and in Water-Saturated Atmospheres

To overcome the practical difficulties and theoretical objections to the use of an autoclave a simple technique that required only short times of heating and that was therefore more comparable to conditions likely to be encountered by textile material, was employed; this technique is described in the Experimental Section. For the nylon filaments used, the endpoint of these determinations was well defined and reproducible. Nylon that had passed through a molten stage during heating was often present in the tubes as a spherulitic film. Apart from the determinations in the sealed tubes, the melting point of nylon was also determined on a microscope hot-stage. The results from this work showed no significant differences between the different types of nylon 66, and they can conveniently be summarized as shown in Table IX.

TABLE IX

Method of determination	Melting point, °C.
Koffler hot-stage	251
Sealed tube, dry	251
Sealed tube, wet	172

The experimental errors involved are not thought to exceed $\pm 1.5^\circ\text{C}$.

EFFECT OF STRAIN ON CRITICAL TEMPERATURE

A note is added on the results of a few further measurements in connection with the observations from which the work described in this paper arose.

The first results, showing that the temperature to which yarn passing through the hot-stretching machine could be raised was dependent on the imposed strain, are recorded in Figure 20. In all these experiments the yarns were passed over the hot-plate and it will be seen that, with one possible exception, (the 60/20 nylon yarn) the critical temperature rises steadily when the applied strain is increased.

Subsequent observations were made with a 15-den. and a 59-den. nylon monofilament and a 210/34 high tenacity nylon yarn, and they were supplemented by measurements of tension on the running thread as it passed through the system. It was found that at a given temperature, tension is greater the higher the strain and falls with rising temperature at about the same relative rate for various strain values. At low values of strain the tension fell with rising temperature to about 1 g. (about the lower limit

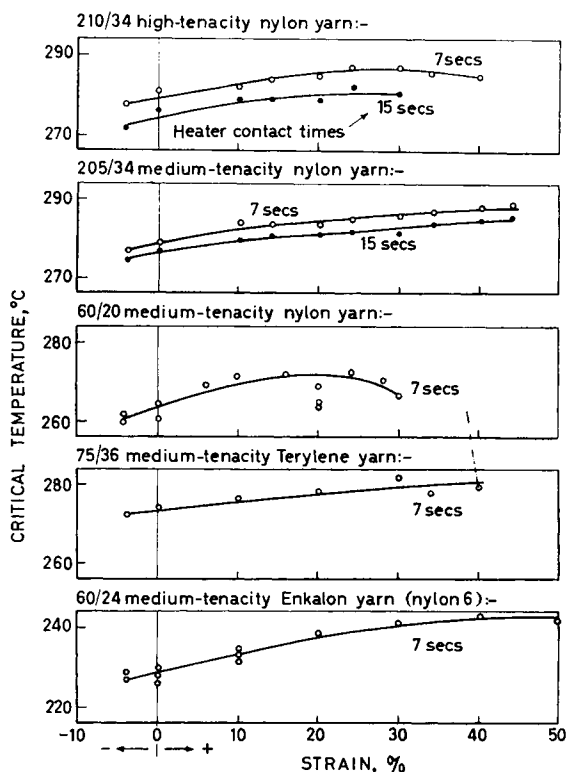


Fig. 20. Effect of strain on critical temperature (breaking temperature) for different yarns.

measurable with the apparatus used) at break. At high values of strain, the filament or yarn broke when the tension was still high, and the greater the strain the higher was this tension. It would seem that the filaments melt at low strain but snap at high strain.

When the hot-plate was used for the heating, the relation between critical temperature and strain found for these three materials was similar to that given by the first measurements. When the monofilaments or the yarn were passed through a heated paraffin bath it was found that, after rising with increasing strain to about 24% strain, the critical temperature then fell sharply by about 20°C. over the strain range from 24-40%. The re-

sults of the tension measurements were on the same pattern as with hot-plate heating.

DISCUSSION

The primary purpose of the work at its outset was to examine further the effect found by Benson, i.e., the rise in critical temperature with increasing strain occurring during the hot-stretching of various yarns. Benson's findings have now been confirmed by experiments similar to his, and a comparable behavior has been obtained with strained nylon filaments heated on frames. The rise in critical temperature is therefore considered to be real and not a feature of experimental technique. With nylon, an applied strain is also accompanied by a considerable rise in birefringence. This increase is clearly (Fig. 4) not a direct continuation of the drawing process (and that it is not is understandable, as drawing involves localized heating and marked structural changes that are quite different from the effects occurring during the straining of a well-drawn product). Possibly the explanation for this increase lies in changes that occur in the quantity and degree of molecular order in the nylon; such changes may be reversible and temperature-dependent. From this work there is no evidence to indicate the precise mechanism. However, moderate improvements in molecular order (as between monofilament and high tenacity yarn) produce no detectable difference in melting point in samples free from restraint, and from the evidence available it is concluded that the presence of a stress is the vital feature and that stress raises the melting point of those man-made fibres whose critical temperature increases with increasing strain. The possibility that stress restricts thermal agitation and thereby retards the onset of melting, appears to be most likely.

The dynamic system under examination in these experiments is a complex one. That yarn can be passed through the machine at high applied strain at a temperature higher than that at which it would break down if at a lower applied strain implies that somewhere in its path it must be partially strained at a temperature below the maximum temperature it attains. This presumably is in the approach to the heating zone. It is possible that the results obtained can be accounted for on the following basis. In Figure 21 the line *A* represents a possible critical temperature curve is drawn on the assumption that the dependence of this on stretch follows the trend of the initial observations. The line *B* indicates the relation between breaking extension and temperature. It is obvious that a filament can remain intact only under conditions represented by the area *C*. If in passing through the machine the filament is, at some element of its length, in a state of strain and temperature falling outside *C* it will break down. It is unfortunate that experimentation on simpler lines (as on stretching frames, for example) cannot be carried to the high strain values that can be reached with running filaments. Over the smaller range of strain available there is, however, some supporting evidence from the examination of filaments treated on frames.

The presence of a skin-and-core structure, as a possible consequence of hot-stretching, is shown by the optical measurements and the photomicrographs made with treated materials; the abnormal or unexpected effect is the presence of a core.

From all the evidence obtained concerning the core region it is clear that during the brief passage through the heating zone a well-defined central region within the filament, whose size depends upon the heating conditions and which is in no way preformed, has suffered large-scale structural changes. The evidence concerning the replacement of the original spherulitic structures with a different type of spherulitic formation, and the growth of large spherulites in the frame experiments, the occasional eruption of core material through the skin, the presence of large gaseous cavities, and a

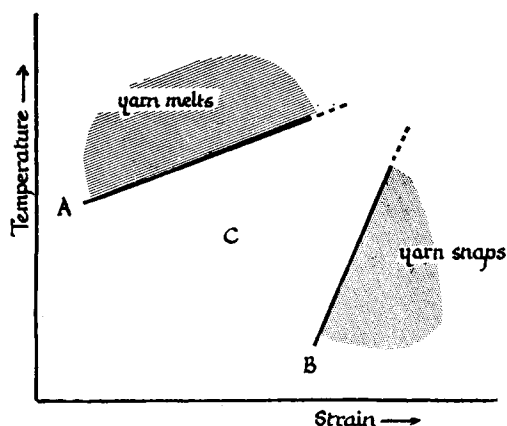


Fig. 21. Suggested relation between strain and temperature during hot-stretching: (A) represents a critical temperature curve, (B) the relation between breaking extension and temperature, and (C) the conditions wherein a yarn will remain intact during hot-stretching.

modified distribution of pigment, all show clearly that a large degree of molecular freedom has been present within the central region, and it is concluded that this region has been molten during passage through the heating zone. However, birefringence measurements made on the core region of treated filaments suggest that complete molecular freedom was not present. For example, with a core diameter of 0.63 of the total diameter the core birefringence was 0.020. Such a value cannot be accounted for by molecular realignment from the melt during an applied strain of only 2%, and it follows that the original birefringence has not been entirely destroyed during the heating. This implies that the core substance, though molten, has not been free from restraint, but in view of the brief duration of heating and the forces imposed by the strained skin region this is understandable. It can be seen that as core size increases, retained birefringence decreases—a result indicating the temperature dependence of the restraint.

Determinations of the melting point of nylon in the presence and in the

absence of water show the profound effect brought about by water and agree well with those frame experiments showing the direct relation that exists between moisture and core formation. This knowledge of the combined effect of heat and water leads to a picture of the mechanism of core melting. A monofilament entering a high temperature zone, initially will develop a radial temperature gradient, the temperature decreasing from outside to the center of the filament, and this will be accompanied by a corresponding gradient of vapor pressure. Under the influence of this behavior, moisture will be trapped within the fiber and concentrated in the central region. If the temperature is adequate, the mixture nylon plus water will then melt; if it is inadequate, moisture will escape from the filament when temperature equilibrium has been attained. The essence of this mechanism is that the heating must be uniform and rapid if moisture is not to be lost. The question of whether there is adequate moisture within the nylon to account for the large core regions at times obtained, is also pertinent, and leads to a consideration of the moisture relations of nylon. Regain values for nylon in standard and saturated atmospheres at room temperature are approximately 4.5 and 8.5%, respectively, these being mean values obtained from the literature.⁵⁻⁹ By calculation it can be shown that the amount of moisture within nylon at standard regain is sufficient to saturate a region (at the 8.5% level) whose diameter is approximately 0.73 of the total filament diameter. This value is based on a simple inverse relation of concentration to volume; other calculations may be employed but all are approximations in that precise knowledge of the properties of nylon and nylon plus water at high temperatures are not available. It is considered that such changes in volume and density as do occur are secondary in importance to the system being investigated, and that a figure of maximum core diameter of 0.73 for a saturation level of 8.5% is reasonable. This value falls short of the maximum size of core observed. Figure 13*d* shows core regions with a diameter of 0.8. The origin of the discrepancy may lie in one or more of a variety of effects; the most probable major effect is that at the higher temperatures less water is required for saturation. Jeffries¹⁰ has shown the sorption value of nylon to decrease with increase in temperature at all values of relative humidity, including saturation, and from his work a reasonable extrapolation (from 150 to 170°C.) would appear to give 6.5% as a value for saturation at the "wet" melting point of nylon. Application of the calculation used previously leads to a maximum core diameter fraction of approximately 0.83, a value that adequately covers the observed effect. The foregoing quantitative explanation is somewhat rigid; it makes assumption, for example, that the water content of the core is increased by water from the skin, and that a molten core implies a previously saturated core. These assumptions may be incorrect—a reduced melting point for nylon may be obtained at water contents below the saturation level. The explanation does demonstrate that nylon conditioned at 65% R.H. at room temperature contains sufficient water to saturate at high temperature a large part of its volume.

The figures in Table II obtained with the laboratory hot-stretching machine show that for similar levels of core birefringence the size of the core for monofilament treated on the hot-plate was appreciably less than with liquid heating media. Following the reasoning applied earlier, similar levels of core birefringence are interpreted as the results of similar core temperatures being operative during heating, while the smaller cores obtained with hot-plate heating is thought to be the result of a loss of moisture during the initial heating. The results obtained therefore demonstrate the relative inefficiency (with respect to trapping the moisture within the filament) of the hot-plate heating employed in the laboratory machine. A full quantitative analysis has not been applied to the products obtained with high-speed commercial machinery, but qualitatively it was obvious (from core birefringence and size) that this was a relatively more efficient system.

It has been shown, with respect to core formation, that the filaments from a heavy-denier, high tenacity nylon yarn are not significantly different from monofilament, the yarn results however are quite different. The different behavior of monofilament and of multifilament yarns is undoubtedly a reflection of the different efficiencies of heating in the two materials. The work of Arthur and Jones¹¹ indicates that a time of 4 sec. is fully adequate to ensure that the entire yarn has attained the temperature of the heating medium. However, the variable results obtained between filaments in a 30/10 yarn show that the heating conditions were not similar at all places within the yarn and that for some filaments the thermal and vapor pressure gradients have been such as to permit moisture to escape from the filaments before equilibrium with the bath temperature was attained. The work of Arthur and Jones also showed that the difference between surface and axis temperature within yarns in the region of the setting temperature (230–240°C.) is negligible and that at the setting temperature it is the molecular process, rather than the heating process, that limits the rate of heat setting. The alternative condition considered by these authors as leading to poor heat setting of nylon, was that an incomplete conduction of heat within the yarn could occur. In the present work the observed differences between filaments in a multifilament yarn does not directly conflict with the final conclusion of Arthur and Jones, but does demonstrate that a heat process involving adequate time for the establishment of temperature equilibrium and molecular rearrangement does not necessarily lead to a uniformly modified product.

The experimental work has revealed a number of interesting and unexpected features concerning the behavior of nylon during heat treatment of various kinds, but it is not practicable to discuss these fully; in some instances, for example, the effect of glycerol and similar "waterlike" liquids on nylon at high temperature, further work is required; in others, for example, the stress-strain properties, the interpretation is direct and as indicated in the description of the results. The most significant aspect of the work is the picture that emerges of the profound effect of water on

the melting behavior of nylon. The fact that such a relation of heat to nylon plus water exists is implicit in many processes—for example, the recommended safe ironing temperature of 180°C.,¹² the lower setting temperatures generally applied to nylon fabrics as compared with Terylene (dry melting values of these two materials are similar, wet values are quite dissimilar), and the knowledge that at curing temperatures well below the dry melting points of both nylon 6 and nylon 66 during the manufacture of a rubber tire, nylon 6 will fuse whereas nylon 6.6 will not. These and other examples show the importance of melting behavior, yet from the literature it does not appear that the importance of moisture effects during processes involving heat have been fully recognized. Certainly the lack of melting point values for fibers in the presence of water is surprising, as heat and moisture are encountered in many textile processes.

That the melting point in polyamides is lowered by the presence of water was recognized by Brill¹³ in 1943, and while the values he found for nylon 6 (221°C. dry, 193°C. in nitrogen saturated with water) do not agree with those shown in Part III of this work,¹⁴ the general nature of his observations agrees with the present work. The effect of waterlike liquids, e.g., glycerol, on nylon at high temperatures agrees with the effect produced by water, but also raises the question whether the process is more correctly termed one of solvation rather than of melting. A consideration of this aspect and of the precise nature of the reaction between nylon and water is, however, beyond the purpose of this examination, although Part III of this work will demonstrate a systematic behavior over a range of polyamide material.

This work was done under the direction of the late Dr. S. G. Smith whose interest and stimulating discussions were of considerable assistance to the authors. The authors are also grateful to Mr. W. Benson for providing access to his earlier work, to Miss B. Lomas who made the supplementary experiments on short lengths of monofilament and yarn, to Dr. J. D. Owen for the comparison of tensile and bending modulus, and to Mr. W. J. Morris for processing monofilament and yarn on a commercial-type bulking machine.

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Résumé

On a trouvé que, dans des conditions déterminées de chauffage, la fusion des filaments de nylon se propage du centre vers l'extérieur. On a établi que ce phénomène est associé à la présence d'humidité dans le filament et que l'humidité abaisse le point de fusion de la substance. Des effets bien définis originaires au centre, et la formation de cavités internes provoquant le délustrage du filament, peuvent se produire sous l'action d'un chauffage brutal. L'existence d'une tension cause une élévation du point de fusion du nylon.

Zusammenfassung

Unter gewissen Erhitzungsbedingungen schmelzen Nylonfäden von Innen nach aussen. Es wurde gezeigt, dass dies mit der Anwesenheit von Feuchtigkeit in den Fäden zusammenhängt und dass Feuchtigkeit den Schmelzpunkt des Materials herabsetzt. Gut definierte Kerneffekte und innere Kavitation, die den Glanz der Fäden herabsetzen, können bei Stosserhitzen eintreten. Der Schmelzpunkt von Nylon wird durch Spannung erhöht.

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