Crystalline "Hard" Elastic Materials

II. Mechanical Properties

I. K. Park and *H. D. Noether (Summit, New Jersey/USA)*

With 21 figures and 5 tables

In the past, among high polymer solids, only
elastomers have been established as materials
that exhibit high "elasticity" (i.e., the ability
to retract rapidly from a large extension). On
the molecular scale, the deformation of
elastomers is controlled by a network of cross-
linked flexible polymer chains, where the
crosslinking results from either primary chem-
ical bonds or secondary bonding between the
chains. Thermodynamically, the elasticity has
its basis in an entropy effect involving the
return of polymer chains to their most prob-
ably configuration (unoriented state).

In the class of crystalline or semi-crystalline
polymers, some with a low degree of crys-
tallinity (e.g., less than perhaps 15%) can
manifest rubber-like elasticity, the crystallites
acting as the crosslinks. However, unoriented
polymers with an intermediate or high degree
of crystallinity usually undergo "necking"
at large extensions. Then rearrangement and/or
disruption of both crystallites and disordered
regions occur. The resulting macroscopic
deformation of the material is largely irre-
versible due to permanent changes in the
structure.

This paper described a new class of elastic
polymeric solids of high crystallinity which are
capable of undergoing large elastic deforma-
tions. These materials were prepared in the
form of extruded films and fibers under
specific conditions of crystallization from the
melt. They are termed "hard" elastic fibers
and films.

Polymers that can be used for formation of
such elastic materials have been found to
include such crystalline polymers as *Celcon®*,
polypropylene, poly-3-methylbutene-1 and po-
lyethylene sulfide. The essential morphological

feature of the elastic materials as revealed by
X-ray diffraction and electron microscopy (13)
is the presence of stacked crystalline lamellae.
Their lamellar surfaces are aligned normal to
the fiber or film extrusion direction. The
mechanism of elasticity is based on a splaying-
apart of these lamellae, involving their revers-
ible bending and torsional deformation during
macroscopic deformation of the material.
Thus, in contrast to rubber elasticity, where the
kinetic units are flexible chain segments, the
kinetic units for the elasticity of a "hard"
elastic material are the lamellar crystals. Due
to the orientation of the lamellae normal to
the fiber and film extrusion direction, the
elasticity is exhibited almost exclusively in
that direction.

Inasmuch as the elasticity of an elastic
"hard" material is based on the particular
morphology of the crystalline polymer, it is
expected that such material could be formed
with any polymer, regardless of chemical
structure, provided it can be crystallized in this
characteristic morphology. Here a study of
mechanical and other macroscopic properties
has been made with fibers and films of elastic
Celcon and elastic polypropylene.

Materials and experimental procedures

Materials

Elastic "hard" and non-elastic, cold-drawable
fibers and films of various polymers were prepared
by variation of appropriate spinning and extrusion
conditions including extrusion temperature, quench
rate and the amount of draw-down. The polymers
used for production of "hard" elastic materials were
such highly crystalline polymers as *Celcon®* (1) (acetal
copolymer), polypropylene, and poly-3-methylbutene-
1. A commercial grade acetal copolymer (*Celcon* M-90)

and an extrusion grade Profax (*Hercules*) were used respectively for *Celcon®* and polypropylene fibers and films. Elastic poly-3-methylbutene-1 fibers were prepared from polymer produced in this laboratory (9). The polyethylene sulfide used was made by *Thiokol* Chemical Corporation.

In order to improve their elasticity, the "as-produced" *Celcon®* and polypropylene fibers and films were annealed at temperatures between 80° and 160 °C for 45 to 60 min. Annealing at temperatures above 140 °C was carried out in nitrogen.

Du Pont Spandex monofil (*Lycra* Type 125; 140 dpf) was used for comparison of its sonic modulus behavior with that of elastic *Celcon®* and polypropylene.

For comparison of low temperature tensile properties, *Celanese Fortrel®* polyester fibers (3.5 dpf; 4.6 g/d tenacity; 42% elongation) were used.

For a comparative evaluation of creep properties, a melt spun high tenacity polypropylene fiber (Profax; 3.25 dpf; 5.7 g/d tenacity) was used.

Tensile testing

Tensile testing was conducted with an Instron tester. Elastic recovery, as defined below, was determined with fiber and film specimens along their extrusion direction by first subjecting them to a cycle of loading and unloading at a constant rate, and then to another loading cycle after a 2-min. pause. A hypothetical stress-strain curve that can be obtained in the test is illustrated in Fig. 1. Elastic recovery is defined here as the ratio of the sample length recovery BA to the applied extension OB. The abbreviation ER is used for the elastic recovery and its numeral sub-

Fig. 1. Hypothetical tensile curve used for tensile and work recovery measurements.

¹) *Celcon®* and *Fortrel®*, Trademarks Celanese Corporation.

script designates the amount of extension used in the measurement. A standard strain rate of 100%/min was used in this work unless specified otherwise. Work recovery is similarly defined as the ratio of the areas CBD/OCB and CBD/ACB for later cycles.

Tensile measurements at elevated temperatures were carried out in a circulating air oven, where the temperature was controlled within ±1 °C. Measurements at liquid nitrogen temperatures were made in a test chamber, adapted for use with the Instron machine, the floor of which was flooded with liquid nitrogen. The test sample was located approximately 2 inches above the liquid surface, and the temperature was kept at −190 °C with a fluctuation of approximately 5 °C.

Stress relaxation and creep measurements

Measurements of stress relaxation were made at room temperature at 100% extension with the Instron tensile tester, where a strain rate of 100%/min was used. Single fibers of both elastic and non-elastic polypropylene fibers were investigated. The relaxation measurements were made over a period of up to 93 hours.

Creep measurements were also made at room temperature with both elastic and non-elastic polypropylene fibers using nominal initial stresses of 0.15, 0.38, 0.76 and 0.91 g/d, where these stresses were chosen to cover, respectively, stress levels below and above the apparent yield stress of the elastic fiber (0.65 g/d). Single fibers were vertically loaded with a dead weight, and their length increase was determined visually.

Elastic measurements as function of temperature

Using an Instron tensile tester, retractive force at a constant extension of 50% was measured for an elastic *Celcon* fiber (ER_{50} of 89%). The stress level recorded at each temperature was that value which remained constant over a period of 10 min. following the rapid initial stress relaxation. Temperature was controlled to ±1 °C.

Determination of sonic modulus

Sonic velocity measurements were made on single fibers with the Dynamic Modulus Tester PPM-5 (*H. M. Morgan Co.*). The tester consists of a pulse propagation meter incorporating circuits for pulse transmitting and receiving, and a timer. The specimen mounts and two transducers are assembled on the scanner unit, where one of the transducers can be cycled between two points along the fiber, providing the relationship between the pulse transit time and the path length.

Sonic velocity in the unextended state was determined under a nominal stress of 0.1 g/d. Continuous measurement of sonic velocity with elongation was made by extending the fiber sample clamped at the posts on which the transducers were mounted in the scanner unit. The increase in sample length was synchronized with the separation of the two transducers. The extension rate used was 80%/min.
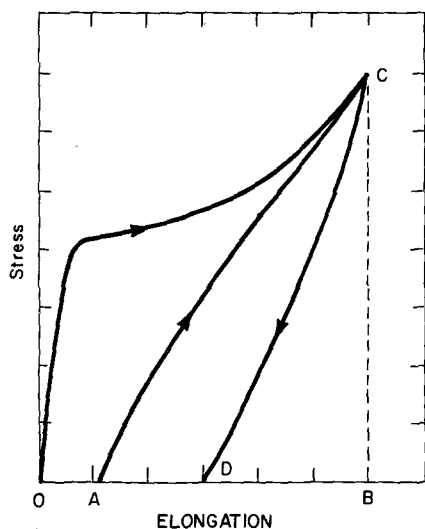
Birefringence

Optical birefringence of an elastic polypropylene fiber (ER_{100} of 97% after annealing at 145 °C) was measured with a *Berek* compensator as a function of extension in various media (air, water, a silicone fluid and a series of organic liquids ranging in refractive index from 1.00 to 1.72). The sample was extended manually and incrementally while the fiber diameter (t) and the retardation (r) were measured after each extension in order to calculate an "apparent" birefringence (r/t) and, also, a birefringence corrected for volume changes: $(r/t_0)(1 + \Delta L/L)^{1/2}$, where $\Delta L/L$ is the fractional length change in extension and t_0 is the diameter of the unextended fiber.

Results and discussion

Effects of crystallization and annealing conditions

Typical tensile extension and retraction curves obtained with the Instron tester for elastic "hard" fibers and films of polypropylene and *Celcon*® are shown in Figs. 2, 3 and 4. Elastic and other tensile properties of various other crystalline polymers are presented in Table 1. A characteristic feature of the tensile behavior of the elastic materials is that they undergo a large extension without occurrence of "necking" and plastic flow. A relatively high immediate elastic recovery as measured by the intercept of the retraction curve with the elongation scale indicates the

dominance of instantaneous elasticity in the elastic deformation of an elastic "hard" material, although a small additional recovery in length is observed after a 2-min. delay time.

However, due to the particular morphology of elastic "hard" materials, in which the crystalline lamellar surfaces are mainly oriented normal to the extrusion direction, the elastic polypropylene film suffers from a high degree
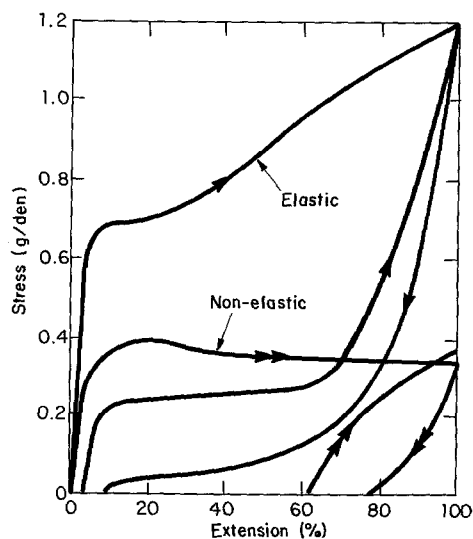

Fig. 2. Tensile curves of polypropylene fibers. Temp. 23 °C, elongation rate: 100%/min.

Table 1. Tensile properties of fiber and films at 23 °C (Elong. rate: 100%/min.)

Material	dpf	ER_{50} (%)	ER_{100} (%)	Tensile Modulus (g/d)	Elong. (%)	Tenacity (g/d)	Work[b] Recovery (%)
Celcon Fibers							
Elastic (As-spun)	5.2	88	74	19	250	1.1	16
Elastic (Annealed) [a]	5.2	97	90	26	244	1.2	22
Cold-drawable Non-elastic	102	47	32	11	601	1.2	7
Polypropylene Fibers							
Elastic (As-spun)	13.2		80	19	750	1.1	17
Elastic (Annealed)	13.2		96	22	382	2.4	22
Non-elastic	41		35	7	615	2.7	7
High Tenacity	3.25			58.9	29.6	5.7	
Elastic Polypropylene Film (Annealed at 140°C for 45 min)	1 mil. thick			3.1×10^5 (psi)	327	10,934 (psi)	
Elastic Poly-3-methylbutene-1 Fiber	6.9	86[c]		37	46	5.6	28.5
Elastic Polyethylene Sulfide Fiber	1.7		81	18	140	1.1	23
Fortrel Polyester Fiber	1.5			50	42	4.6	

[a] Annealed at 150 °C for 60 min. in nitrogen.   [b] Work Recovery from 100% extension.   [c] ER_{30}
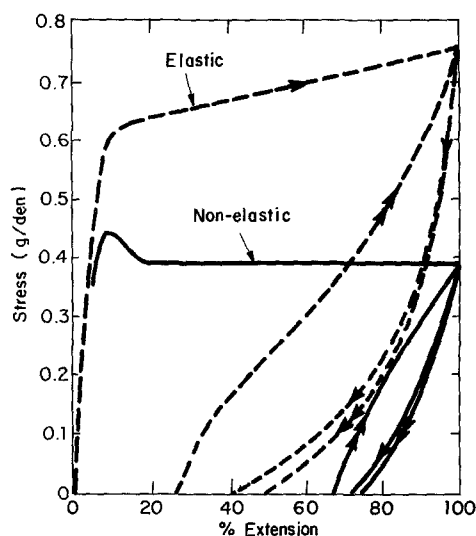
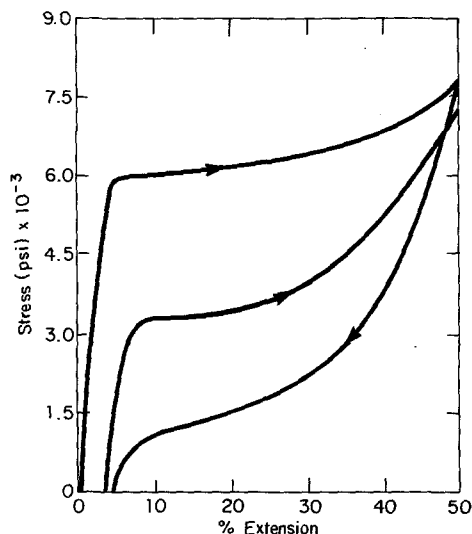Fig. 3. Tensile curves of *Celcon* fibers. Temp.: 23 °C, elongation rate: 100%/min.

Fig. 4. Tensile curve of elastic polypropylene film. Temp.: 23 °C, elongation rate: 100%/min.

of anisotropy in tensile behavior. The elastic film (ER$_{100}$ of 93%) has a breaking elongation of only 14% in the direction transverse to the extrusion direction, whereas the elongation parallel to the extrusion direction is 327%. On the other hand, a cold-drawable, non-elastic film of the same polymer (ER$_{100}$ of 40%) has a much better balance of properties in these directions (790% and 860% elongation, resp.).

Although subsequent annealing in general increases the elastic recovery of the elastic materials, the conditions of the initial crystallization process are critically important with respect to the route by which a high degree of elastic recovery is achieved. As shown in Table 2 and Fig. 5, inappropriate extrusion and

spinning conditions may lead to fibers and films which exhibit not only a relatively low level of elastic recovery, but also require comparatively more stringent annealing conditions to reach the same degree of elastic recovery. Good "as-produced" fibers and films of both polypropylene and *Celcon*® require only a mild degree of annealing (e.g., at 120 °C for 60 min.) to effect the maximum value of elastic recovery (ER$_{50}$ ranging from 90 to 97%) that can be attained with given "as-produced" fibers or films.

As shown in Table 2, a good "as-extruded" elastic polypropylene film has a relatively high degree of orientation of the lamellar crystals as revealed by both X-ray diffraction and

Table 2. Physical properties of polypropylene fibers of varying elastic recovery

Sample		ER$_{50}$ (%)	Density[a] (g/cc)	X-ray small-angle Spacing (Å)	Bire-fringence[b]	Orientation by X-ray[c]
A	As-extruded	24.5	0.8864	110	0.0026	None
	Annealed	42.0	0.9086	200	0.0055	
B	As-extruded	34.5	0.9004	130	0.0072	Fair
	Annealed	84.7	0.9074	180	0.0103	
C	As-extruded	40.6	0.8996	140	0.0185	Highly Oriented
	Annealed	93.2	0.9086	180	0.0176	

All samples annealed at 140 °C for 45 min. in air

[a] Determined with a density-gradient tube containing isopropanol-water mixture
[b] Measured in silicone oil (Dow Corning-550)
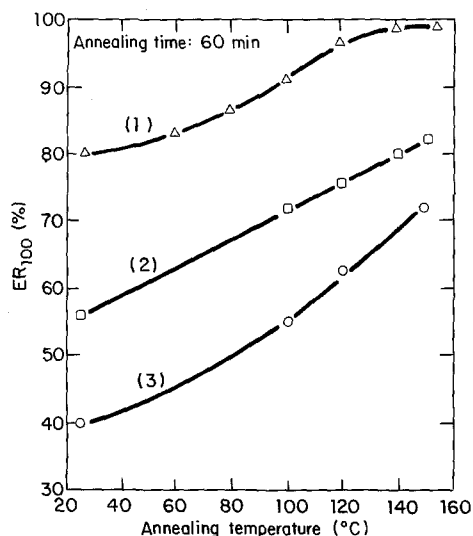[c] By wide-angle X-ray diffraction

Fig. 5. Dependence of elastic recovery on annealing temperature of polypropylene fibers spun under various conditions. Nominal spin temperature (1) 230 °C; (2) 260 °C; (3) 280 °C. Annealing time: 60 min.

Fig. 6. Tensile curves of *Celcon*, polypropylene, polyester, spandex fibers at −190 °C. Elongation rate: 100%/min.

birefringence measurements. The overall effect of annealing, as observed by X-ray small-angle scattering indicates increased superstructural perfection and order (13).

Tensile properties at low temperature

The tensile curves at −190 °C for the various fibers studied are shown in Fig. 6. Their tensile properties at room temperature and at −190 °C are compared in Table 3. As can be noted in this Fig., the tensile curves of both elastic *Celcon®* and polypropylene fibers essentially retain their shapes on going from room temperature to −190 °C, including the absence of necking behavior. On the other
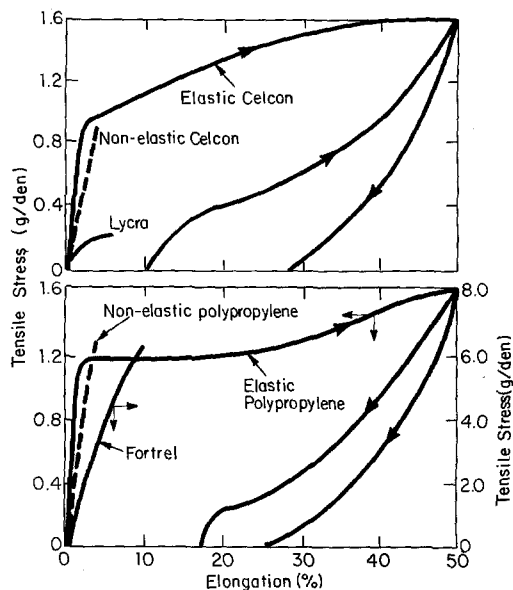
hand, the corresponding nonelastic fibers become brittle at the low temperature, reflecting the glassy state of the polymer. The observed superiority of the elastic fibers over the spandex and polyester fibers at the low temperature is indeed remarkable.

The elastic recovery of the elastic *Celcon®* fiber is still high at −190 °C (84% at 50% extension) while that for the elastic polypropylene fiber is 68%.

Thus the tensile properties, primarily elongation and elastic recovery of "hard" elastic fibers and films of polypropylene and *Celcon®* undergo a relatively small change over the

Table 3. Tensile properties of elastic and non-elastic *Celcon* and polypropylene fibers, and polyester and spandex fibers at room and liquid nitrogen temperatures (Elongation rate: 100%/min.)

	Tensile Modulus g/d		Elastic Recovery at 50% Extension, %		Break Elong., %		Tenacity, g/d	
	23 °C	−190 °C	23 °C	−190 °C	23 °C	−190 °C	23 °C	−190 °C
Polypropylene								
Elastic	22	77	98	68	382	96	2.4	2.0
Nonelastic	7	61	35	—	615	4	2.7	1.9
Celcon								
Elastic	27	48	97	84	244	94	1.2	2.0
Nonelastic	11	49	47	—	601	5	1.2	1.0
Fortrel	50	95	—	—	42	10	4.6	6.5
Lycra	0.08	14	99	—	959	7	0.5	0.24

temperature range to −190 °C compared with "non-elastic" polypropylene, *Celcon®*, spandex, and polyester fibers. The tensile properties of the "hard" elastic materials are quite free from the embrittling effect normally observed in amorphous and semi-crystalline polymers below the glass transition temperature. This behavior indicates that the tensile deformation mechanism (the reversible bending deformation of lamellar crystals (13)) of these elastic materials is different from the one normally assumed for "non-elastic" and rubber-elastic materials.

Elastic properties as function of annealing temperature

The variations in elastic recovery of an elastic polypropylene fiber (from 100% extension) at room temperature with annealing temperature was shown in Fig. 5. The elastic recovery increases rapidly with annealing temperature between 80° and 120 °C levelling off at a value of approximately 95%. Annealing at 120 °C for 60 min. introduces a sufficient degree of structural perfection for the maximum attainable value of elastic recovery (Curve 1).

Although comparable at room temperature, the values for elastic recovery of samples annealed at 120 °C or at higher temperatures are expected to be different at elevated temperatures. In Fig. 7a, the elastic recovery at elevated temperatures is shown for three samples, unannealed, annealed at 120 °C and
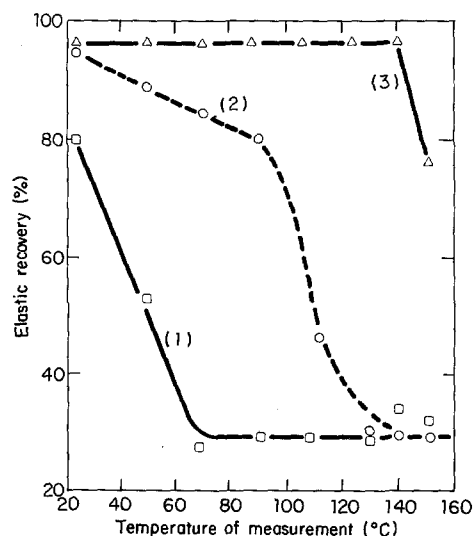

Fig. 7a. Temperature dependence of elastic recovery of elastic polypropylene fibers (1) "as spun", (2) annealed at 120 °C, (3) annealed at 150 °C. Testing conditions: Temp.: 23 °C, extension 100%, elongation rate: 100%/min.

at 150 °C, respectively, for one hour. The elastic recovery of the unannealed sample starts to decrease immediately with an increase in temperature of measurement reaching a constant value of about 30% at 70 °C. With the 120 °C annealed sample, due to its relatively more perfect structure, the elastic recovery decreases only slightly over the temperature region up to 100 °C, and drops rapidly in the neighborhood of the annealing temperature. The elastic recovery of the sample annealed at
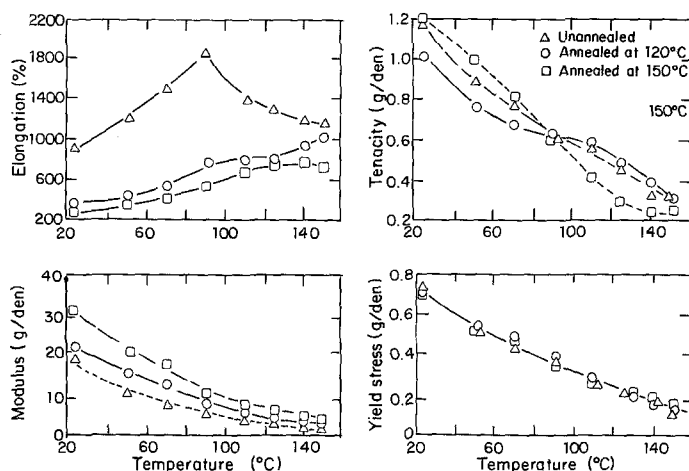

Fig. 7b. Temperature dependence of tensile properties of elastic polypropylene fibers. △ unannealed; ○ annealed at 120°C; □ annealed at 150°C. Elongation rate: 100%/min.

150 °C is essentially constant at a high value of 95% at temperatures up to 140 °C.

Thus, a highly elastic polypropylene prepared by annealing at 150 °C maintains a high degree of elasticity over the entire temperature region between 140° and −190 °C.

The temperature dependence of the tensile characteristics, break elongation, tenacity, initial modulus and yield stress, for the same three fibers are shown in Fig. 7b. Modulus, tenacity and yield stress behave as normally expected; the maximum in elongation at 90 °C is an effect of measurement conditions, at and above this temperature some crystallization occurs while the sample reaches temperature equilibrium for the tensile test and therefore the break elongation approaches the values of annealed fibers. The "yield" stress seems to be independent of annealing conditions; as will be shown below, it correlates with the onset of void formation and the transition to a different super-molecular deformation mechanism.

Thermoelastic measurements

In order to determine the nature of elasticity of elastic "hard" materials, elastic measurements were carried out with a *Celcon*® fiber over the temperature region between −120 °C and 22 °C. The variation of the retractive force at a constant elongation of 50% was determined, and the results are presented in Fig. 8.
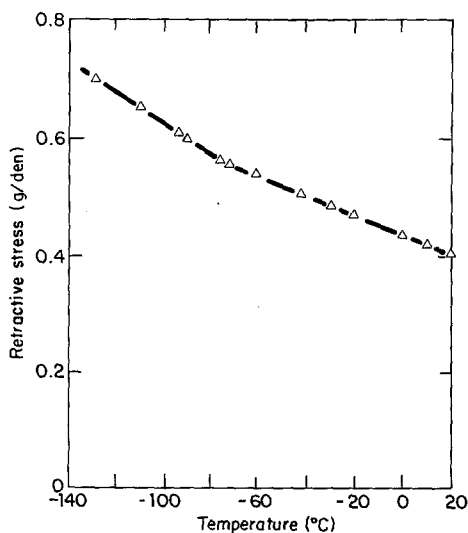
The thermodynamics of elastic deformation dictates that the retractive force be the sum of the entropy and the internal energy effects. Rubber elasticity is characterized by the dominance of the entropy effects, which appear as a positive temperature coefficient of the retractive force. The present study shows a negative slope in the retractive force-temperature curve, and therefore the elasticity of the elastic fiber is primarily *not* rubber-like, but rather controlled by the energy effect. The change in the slope of the curve at about −70 °C is believed to be due to the γ-transition of the polymer, where a large change in elastic modulus occurs (1). The change in the slope of the curve is in the direction predicted by the change in modulus.

Effects of elongation, elongation rate and cyclic loading

The variations of elastic recovery of an elastic *Celcon*® fiber with amount of extension at different rates of extension are shown in Fig. 9. At a given rate of extension, an increase in elongation decreases the elastic recovery due to damage done to the superstructure by extension. Over the observed range of strain rate, elastic recovery generally increases with an increase in extension rate.
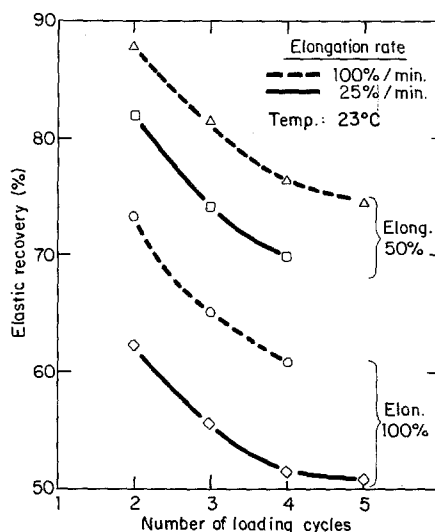

Fig. 8. Temperature dependence of retractive force of elastic *Celcon* fiber at 50% extension

Fig. 9. Effect of repeated loading and loading rate on elastic recovery of *Celcon* fibers. Temp.: 23 °C; elongation rate: ----- 100%/min. — — 25%/min. △, □ 50% elongation; ○, ◇ 100% elongation

The effect of repeated loading cycles on elastic recoveries of an "as-spun" elastic polypropylene fiber (ER_{100} of 80%) and its annealed counterpart (ER_{100} of 96%) is shown in Fig. 10. After an initial decrease,
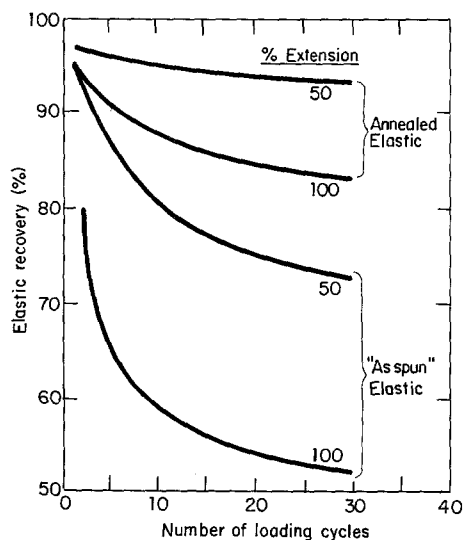

Fig. 10. Effect of repeated loading cycles on elastic properties of elastic polypropylene fibers. Elongation rate: 100%/min. 50 and 100% extension for "as spun" and annealed fibers
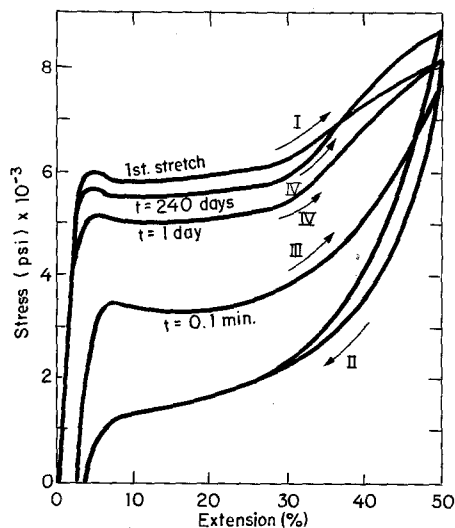

Fig. 11. Stress-strain recovery behavior of elastic polypropylene film as function of time interval between first and second extension cycle. I. First extension curve; II. Recovery curve from 50% extension. Second extension curve: III. After 0.1 min.; IV. After 1 day; V. After 240 days

recoveries of the annealed fiber tend to level off at large numbers of loading cycles, whereas elastic recovery of the unannealed sample seems to continue to decrease over the observed range of loading cycles. This indicates that the structure of the annealed elastic material is more stable under repeated loading and unloading, and its fatigue resistance is less strain-sensitive.

The time dependence of the recovery of the initial stress level and thus of the original stress-strain curve of an elastic "hard" material was studied with an elastic polypropylene. Five strips of highly elastic polypropylene film (ER_{50} of 93%) were cycled between 0% and 50% extension, allowed to recover in or out of the machine for varying amounts of time, ranging from ~0.1 minute to 240 days, and retested. Representative curves are shown in Fig. 11.

The unloading curve (II) is representative of all samples regardless of history. The load-ing curves subsequent to the first (III and IV) show a dimensional recovery which appears to be essentially complete within one day.

Work recovery

While the elastic recovery (ER_{50} and ER_{100}) is of the order of 95% on the first cycle and gradually reaches a constant level of about 85–95% depending on extension (50–100%), the work recovery in the initial cycle is relatively low at 30–40% (Fig. 1 and 11). This is due to large amounts of energy required to overcome the *van der Waals* forces in the intercrystalline regions during the first 5–10% extension.

On immediate and repeated cycling (Fig. 12), the "yield" point is considerably lowered and the work recovery increases to about 60% within a few cycles (Fig. 13a). Eventually, both elastic and work recoveries reach practically constant values, the paths of extension and retraction becoming constant. The major change in stress-strain curves occurs in the initial stage of extension (up to 25%) between the first and second cycle. The stress level at the extension limit (50%, 100%), however, is not greatly affected. Equally, the change in the shape and position of the retraction curve is
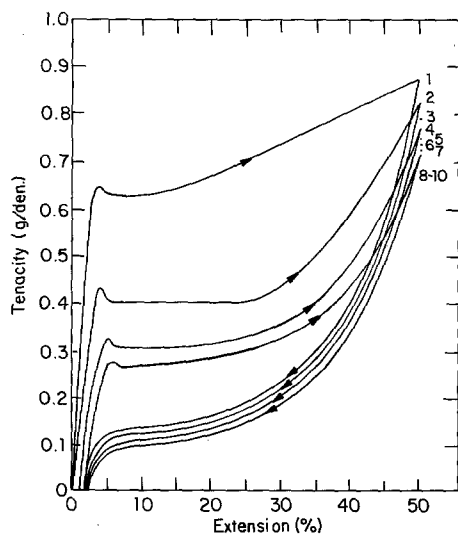
Fig. 12. Annealed elastic polypropylene stress-strain behavior on cycling to 50% extension (10 cycles). Extension rate: 100%/min.
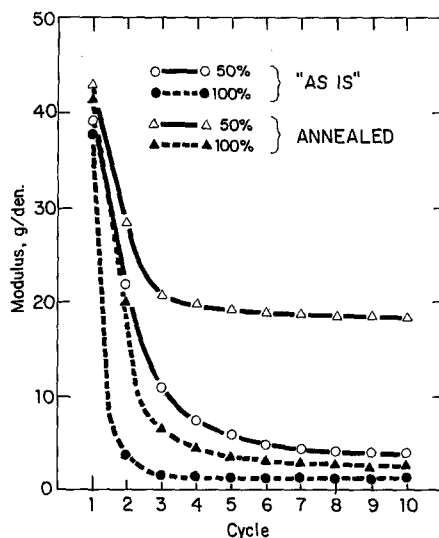

Fig. 13b. Modulus of elastic polypropylene fibers as function of cycle for 50% and 100% extension. "As is" fibers: ○ 50% extension, ● 100% extension; annealed fibers: △ 50% extension, ▲ 100% extension
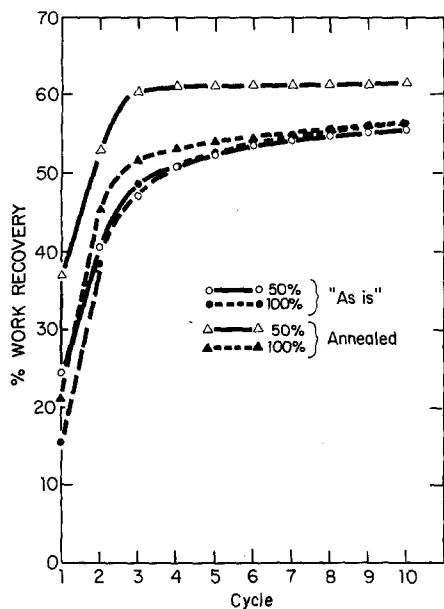

Fig. 13a. Work recovery of elastic polypropylene for cycling to 50% and 100% extension. "as spun" fibers: ○ 50% extension; ● 100% extension; annealed fibers: △ 50% extension, ▲ 100% extension

relatively minor. As seen from Fig. 13b, initial moduli of "as is" and annealed fibers show a complimentary behavior, also reaching a constant level after a few cycles.

Considering the highly elastic behavior of the "hard" elastic fibers in the whole range of extensions of Fig. 11 and 12 and the vast difference in the time of recovery on both sides of the "yield" point, it becomes apparent that we are dealing here with two types of elastic mechanisms; (a) a relatively slow process restoring the original stress level of the "yield" point after relaxation to a low or zero load level (relaxation time of hours), and (b) a very fast practically instantaneous recovery mechanism beyond this point.

It seems appropriate here to shortly review the general interpretation of the shape of stress-strain curves and the nature of the deformation mechanisms. In the initial steep and linear increase of stress with strain (the *Hookian* region), extensions are fully recoverable (15). Usually, when the curve deflects from linearity or shows a pronounced decrease in slope, mechanisms of delayed elastic recovery and irreversible deformations are invoked. This is the case with many natural and synthetic fibers, where the completely reversible elongation does not extend beyond 5–10%. Certainly, elastic recoveries of the order observed with the "hard" elastic materials have not been noted for other fibers beyond the yield point. Thus, to define the area of

strong change in slope of the "hard" elastic materials as "yield" point is not appropriate since it would imply that the highly elastic behavior in range (b) besides being unexpected, is unexplainable.

However, considering the molecular or morphological model of the structure as established by wide and small angle X-ray diffraction and electron microscopy for the unextended as well as the extended fibers and films (13), the elastic mechanisms of ranges (a) and (b) become clear.

In range (a), the steep slope of the stress-strain curve is due to the resistance to deformation of *van der Waals* forces between adjacent polymer chains in the intercrystalline regions. The same kind of behavior (modulus, etc.) is usually observed for spherulitic materials in a cold drawing process prior to the yield point. Beyond the yield point, unravelling of folded polymer chains and their complete reorientation takes place (16).

SAXR diffraction studies of the "hard" elastic materials have shown (13) that during the initial extension (5–25%), interlamellar regions are extended and ruptured and lateral voids begin to form between the lamellar surfaces. Beyond this range, the small angle spacing increases proportional to the extension. Here the elastic behavior is based on the bending deformation of the lamellae. In the annealed materials which have an extremely uniform superstructure nearly all the lamellae after interlamellar opening contribute to the deformation. In the unannealed sample, a broad distribution of lamellar dimensions (lateral size and thickness) exist due to the temperature range of their formation; thus, also a wide range of order in the interlamellar regions can be expected. On extension, only a few weak, interlamellar regions are opened, then deform elastically as expected; however, now, because of the few regions involved, the limit of reversible extensibility on a macroscopic scale is reached very soon and permanent deformation takes place at lower extensions.

During the relaxation cycle, the lamellar deformation (range b) is immediately recoverable to the point of complete lamellar contact. Beyond this point, the complicated rearrangement of the lamellar interface to its original order obviously is a much slower and probably an always incomplete process.

The above mechanisms readily interpret the small angle x-ray diffraction and electron microscopic observations and the different elastic characteristics of ranges (a) and (b).

Stress relaxation of polypropylene fibers

Stress-relaxation curves of elastic and non-elastic polypropylene fibers at 100% extension are shown in Fig. 14. The changes in elastic recoveries of these fibers introduced by stress relaxation are given in Table 5.
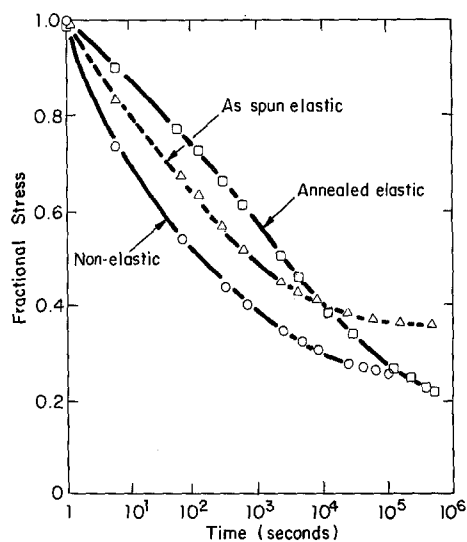

Fig. 14. Stress relaxation curves of polypropylene fibers. Temp.: 23 °C, extension 100%. △ "as spun" elastic, initial stress 0.85 g/den; ☐ annealed elastic, initial stress 1.15 g/den; ○ non-elastic, initial stress 0.27 g/den

Table 5. Effect of stress relaxation at 100% extension at 23 °C on elastic recovery of polypropylene fibers

Fiber	dpf	ER$_{100}$, %	Relax. Time (hr.)	ER$_{100}$, %, after str. relax
Elastic	13	80	92	50
Annealed elastic	13	95	93	85
Non-elastic	41	35	24	5

The initial rate of stress decay decreases with increasing (original) elastic recovery of the fiber. By means of suitable translations along the time scale and the stress axis, the curves of these samples can be made to superpose, exclusive of the initial portion of

the curves. This indicates that the stress relaxation of these fibers is largely controlled by one visco-elastic mechanism which involves changes in intercrystalline regions of the materials. The number of such changes decreases with increasing perfection of the particular crystalline structure responsible for the elastic recovery property. In the annealed sample, both the uniformity of the morphology essential for elasticity, and the high crystallinity cooperate to decrease stress decay. The decrease in stress with time was measured up to 93 hours (3.3 × 10^5 sec.).

The final stress levels observed for these fibers represent approximately 30% of the initial stress. In spite of the magnitude of this stress decay, the resulting decrease in elastic recovery is remarkably small for the annealed sample. This emphasizes the stability of the structure during stress relaxation and also the importance of the reversible deformation of the lamellar crystallites.

Creep behavior of polypropylene fibers

Creep curves for an elastic annealed polypropylene fiber (ER_{100} of 95%) and a cold-drawable non-elastic fiber (ER_{100} of 35%) are shown as log-log plots in Fig. 15.

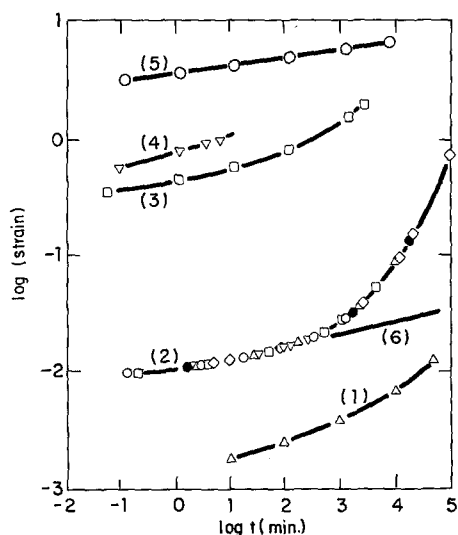Fig. 15. Creep curves of polypropylene fibers at 23 °C. Elastic fiber: (1) △ creep stress 0.15 g/den; (2) ● creep stress 0.38 g/den also master curve for elastic fiber; (3) □ creep stress 0.76 g/den; (4) ▽ creep stress: 0.91 g/den; (5) ○ non-elastic fiber at creep stress 0.76 g/den; (6) —— high tenacity fiber at creep stress 0.5 g/den

As shown in Fig. 15, the curves (1) through (4) for the elastic fiber possess the same general shape, and have been successfully superposed through suitable translations of the curves along both the strain and time axes. The extended version of curve (2) in Fig. 15 represents the so-called master curve obtained by such a procedure, with respect to a nominal stress of 0.38 g/d.

A detailed analysis of the master curve (curve (2) of Fig. 15) revealed that the creep up to 600 min. is proportional to the cubic root of time (i.e., *Andrade Creep*) indicating a mechanism of retarded elastic deformation. This deformation is recoverable. Possible molecular mechanisms are a deformation due to the effects of chain entanglement in the intercrystalline regions and also viscous flow, together with an elastic deformation such as the reversible translation or deformation of the crystals and also possible rubber-like elasticity of the intercrystalline regions. In the region between 600 and 10,000 min. viscous flow becomes increasingly important with increasing time, and, towards the end of the range, the flow effect dominates. At longer times creep proceeds at a rate faster than can be accounted for by the flow effect. A reasonable explanation is that the material starts to deform inhomogeneously at this stage.

From the projection of the various visco-elastic regions identified in the master curve, one can predict the types of deformation the sample undergoes at different stresses and times. For example, the curve (3) of Fig. 15 corresponding to creep at 0.76 g/d, involves only the retarded elastic deformation up to 170 min (strain of 110%), and viscous flow becomes important just prior to the sudden break of the sample. An important conclusion deduced here is that after the initial extension involving separation of the lamellar crystals, the creep process does not introduce any new lamellar separation and is governed by the mechanism of homogeneous viscoelastic deformation until the fiber breaks.

Also in Fig. 15, creep behavior of a non-elastic polypropylene fiber is compared with that of the elastic fiber under a comparable stress. Due to the necking of the fiber during the initial stage, the non-elastic sample exhibits a relatively large creep strain while the creep rate is somewhat lower than that of the elastic

fiber. The creep rate of the former is more comparable to that of a high tenacity fiber (melt spun and drawn, 3.25 dpf, tenacity 5.7 g/d). Long-term creep properties of the high tenacity fiber seem to be superior to those of the elastic fiber.

The effect of rate of extension on the elastic recovery is shown in Fig. 16. An increase in
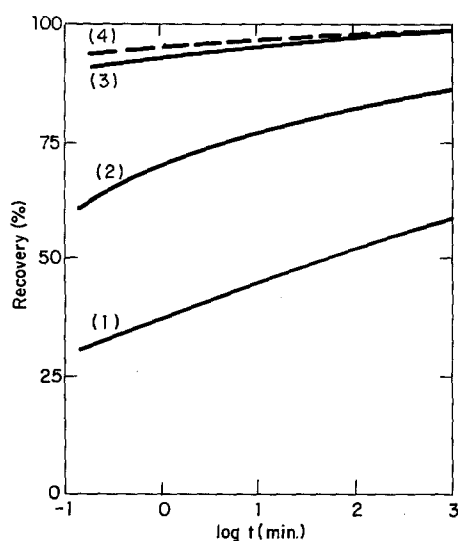
Fig. 16. Dependence of length recovery on rate of extension. (1) creep to 110% extension, 7×10^4 min.; (2) Creep to 38% extension, 1×10^4 min.; (3) Creep to 108% extension, 6 min.; (4) Stretch to 100% extension, 1 min.

rate of deformation results in a higher instantaneous recovery of the sample length. The variation in instantaneous recovery with strain and strain-history provides an estimate of the

contribution of reversible bending of the lamellar crystals to the observed elongation of the sample. As expected, at high rates of deformation, the lamellar deformations occurs preferentially.

Sonic modulus

The sonic velocity-extension curves for elastic "hard" fibers and a cold-drawable fiber of polypropylene and "*Lycra*" spandex fiber are shown in Fig. 17. All the polypropylene
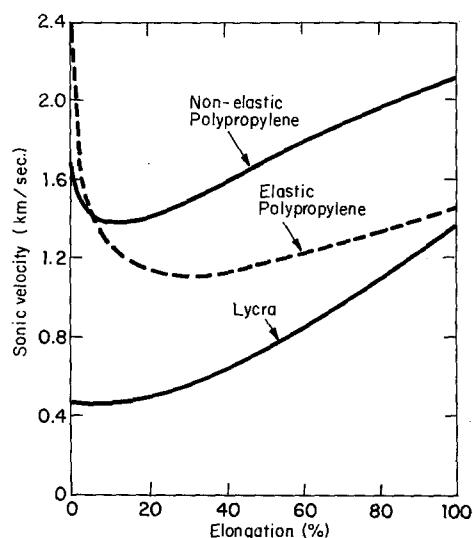
Fig. 17. Variation of sonic velocity with elongation for polypropylene and Lycra fibers

fibers show a minimum in the curve in the range of about 15 to 30% extension. The elastic fibers characteristically undergo a large

Table 4. Tensile properties and density of *Celcon*, polypropylene and spandex fibers (Elongation rate: 100%)

Sample	DPF	Elastic Recovery from 100% Extension %	Volume[a] Density g/cc	Tensile Mod. g/d	Sonic[b] Mod. psi
Polypropylene Elastic Fiber (Annealed at 150 °C for 60 min.)	13	96	0.922	22	8.1×10^5
Non-elastic fiber	42	35	0.902	7	3.6×10^5
Elastic *Celcon* fiber (Annealed at 160 °C for 60 min.)	5.2	97	1.422	27	5.5×10^5
Lycra Type 125	120	99	—	0.08	—

[a] Determined by pycnometry.
[b] At zero extension.

initial decrease compared with the non-elastic fiber. This is partly due to a relatively high value of sonic velocity of the elastic fibers in the unextended state, and this trend agrees with that observed for the tensile moduli, as indicated in Table 4.

The initial decrease in sonic velocity for the non-elastic, unoriented polypropylene fiber is believed to be due to disorientation and disruption of the crystals and polymer chains accompanying the strain-softening process preceding necking, as previously reported for such crystalline polymers as polyethylene (2), polypropylene (10, 11), nylon (3), and protein fibers (4). The steady increase of sonic velocity observed at higher extensions co-incides with the birefringence behavior of the fiber as shown in Fig. 20, where an increasing degree of chain orientation along the fiber direction introduces a steady increase of birefringence with extension in this range of extension.

In the case of completely amorphous polymers, the statistical theory of rubber elasticity predicts an initial decrease in tensile modulus with extension for materials with an ideal network structure, due to the effect of internal pressure during the deformation (5). However, elastomers with non-ideal network structure such as some butyl rubbers (6) and *Lycra* (shown in Fig. 17) do not exhibit a reduction in modulus with initial extension.

Interpretation of the observed changes in sonic velocity with extension for an elastic "hard" material should include consideration of the physical changes in the internal structure of the material with extension. The principal changes are the reduction in bulk density of the material and the tilting of the crystalline lamellae during extension (13). The normalized sonic modulus calculated by using the bulk density of the materials (as determined from the diameter change with extension) is shown as a function of extension for highly elastic fibers of polypropylene and *Celcon*® in Fig. 18 and 19, respectively.

The large initial decrease observed in the normalized sonic modulus can be largely attributed to the mechanical transition from the closed to the open internal structure of the material, which involves disruption of the interlamellar bonding forces, including the *van der Waals* forces between lamellar surfaces,
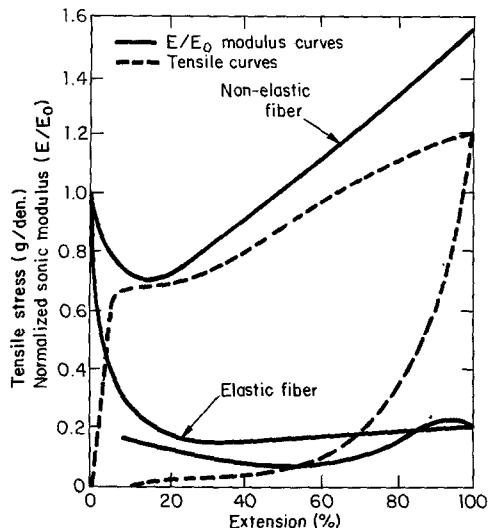

Fig. 18. Variation of sonic modulus and tensile stress with elongation for polypropylene fiber. Elongation rate: 100%/min.; —— E/E_0 modulus curves, ----- tensile curves
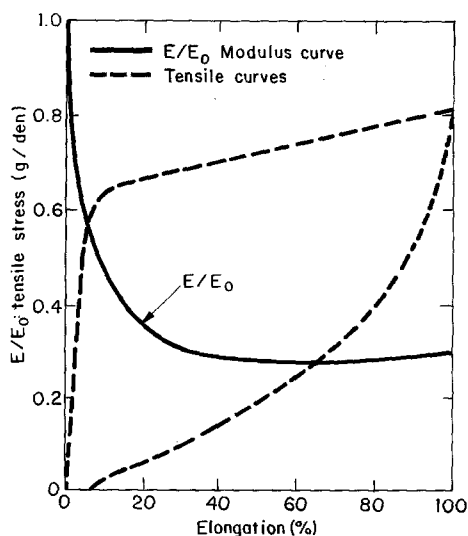

Fig. 19. Variation of sonic modulus and tensile stress with elongation for elastic *Celcon* fiber. Elongation rate: 100%/min.; —— E/E_0 modulus curve; ----- tensile curves

tie molecules, and entangled chains. After the rapid initial decrease, the modulus remains essentially constant above about 25% elongation. This feature of the variation in sonic modulus with extension marks a characteristic difference between the elastic and non-

elastic fibers. The non-elastic polypropylene fiber shows a steady increase in the modulus after the initial stage of extension due to increasing molecular orientation. A similar trend in sonic modulus-extension behavior as in the elastic materials was observed for certain melt spun polypropylene fibers by *Samuels* (12).

The type of sonic modulus-extension relationship observed for the elastic materials is similar to that of a linear spring, where the mass per unit length of the spring decreases linearly with extension, and its extension increases proportionally with the applied force. When the spring is closed, the sonic modulus is relatively high because the spring constitutes essentially a solid medium. When the spring is initially stretched uniformly in such a way as to introduce a sequential separation of the repeat units of the spring, the sonic modulus of the spring would decrease with extension and reach a steady value when the spring undergoes a uniform extension. The constant value would correspond to the force constant of the spring in uniform extension. The sonic velocity of the spring is equal to the square root of the ratio of the force constant to the mass per unit length (7).

As shown in Figs. 18 and 19 for elastic fibers of polypropylene and *Celcon®*, respectively, there exists a considerable degree of similarity between the elongation dependence of the sonic modulus and that of the slope of the tensile curve. In the extension cycle, at about 25% extension, the slope of the tensile curve seems to remain fairly constant with elongation up to 100%. The similarity between these two parameters also prevails in the retractive cycle, as shown in Fig. 18 for polypropylene fiber, considering the difference between the two types of measurements, such as the difference in the time scale. The observed differences in both sonic modulus and the slope of the tensile curve between the extension and retraction cycles indicate the dependence of the mechanical state of an elastic "hard" material on strain-history, as well as the viscoelastic relaxation times of the material.

Birefringence

The birefringence behavior of a highly elastic polypropylene fiber during extension
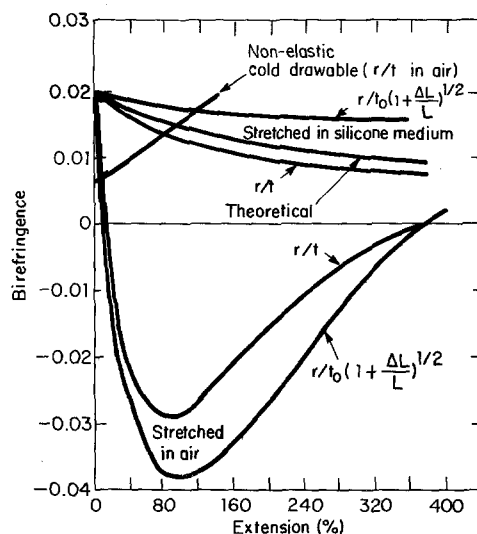

Fig. 20. Polypropylene fibers, birefringence versus extension

in air is significantly different from that during stretching in silicone fluid (Fig. 20). In air, the birefringence, initially positive, decreases rapidly with extension becoming negative at approximately 15% extension. It goes through a maximum negative value (at about 80–100% extension) and finally becomes positive just before breaking of the sample. However, when the fiber is extended in silicone oil, the birefringence is always positive. At any extension at which the birefringence was negative, the birefringence could be changed to a positive or a negative value by addition or removal of an immersion liquid. These observations are indicative of the influence of form birefringence. If one were to assume that there were no change in both fiber diameter and orientation of the morphological elements of mass during extension of the fiber, then the retardation would be a function primarily of the mass density. Based on these assumptions, one can calculate the theoretical curve of birefringence versus extension shown in Fig. 20. This curve is strikingly similar to that of the apparent birefringence (r/t) versus extension in silicone fluid. The similarity supports the view that the morphological elements, namely, the lamellar crystals remain transversely disposed without major disorientation.

The effect of the introduction of organic liquids of different refractive index on the birefringence of the elastic fiber at various degrees of extension is shown in Fig. 21. The
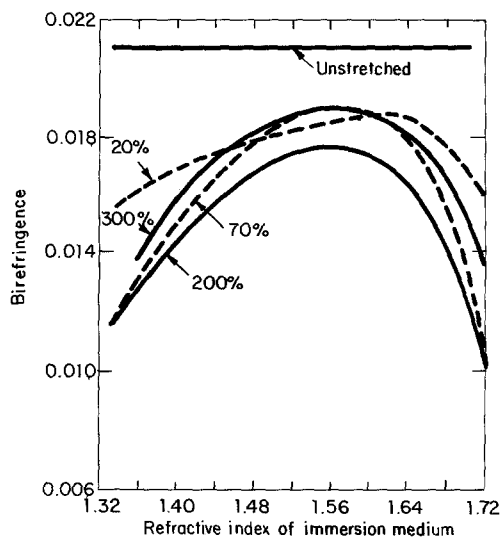

Fig. 21. Form birefringence; Birefringence of variously stretched elastic polypropylene fibers with refractive index of immersion medium

lack of change of birefringence of the unstretched fiber with change in the refractive index of the immersion medium indicates the absence of accessible voids. The convex upward shapes of the curves corresponding to different amounts of extension indicate an optical system of negative form birefringence (8) which may be due to the morphological arrangement of asymmetrically shaped voids with their long axes laterally disposed in the fiber. This interpretation agrees with the conclusion derived from small angle X-ray measurements (13). The shapes and relative dispositions of the curves for different extensions suggest differences in void content with extension, a factor involved in the birefringence/extension data presented in Fig. 20 and a fact also established by porosimetry (14).

In Fig. 20, the birefringence/extension in air behavior of a cold-drawable non-elastic polypropylene fiber is compared with that of the elastic fiber. Their characteristic difference is that the birefringence of the cold-drawable fiber increases steadily with extension

beyond the yield strain, reflecting an increasing degree of chain orientation along the fiber axis, a behavior which is well-known and easily checked by X-rays.

Conclusions

Since the characteristic mechanical and physical properties of "hard" elastic polypropylene and *Celcon®* are based on a specific morphology, it appears logical that similar elastic materials can be prepared from other polymers provided this basic morphology is duplicated. The primary requirements are good crystalline order and a uniform lamellar morphology, the lamellae being of large lateral dimensions, their surfaces being relatively flat and oriented normal to the direction of extension.

To summarize: The essential characteristics of "hard" elastic materials are as follows:
(1) High elastic recovery from 50–100% extension (90–97% length recovery).
(2) High elastic recovery over a wide temperature range (e. g., polypropylene from −190 °C to the annealing temperature) with considerably lower embrittling effects below the glass transition temperature.
(3) Repeated cycling considerably improves the work-recovery leading to a stable extension-retraction curve.
(4) The physical structure of the elastic material is comparatively stable under stress relaxation, is highly fatigue-resistant.
(5) Annealing "as produced" fibers or films in general improves their elastic characteristics.

The identification of this type of material by its characteristic superstructure (X-ray diffraction and electromicroscopy) is supported and complemented by the specific behavior in other physical measurements (tensile properties, sonic modulus, birefringence, surface and void measurements) during single and multiple elongation and retraction cycles to high extensions.

the technical staff at *Celanese Research Company* for numerous discussions. Also we want to thank *Celanese Corporation* for permission to publish this work.

Summary

"Hard" elastic materials are oriented, highly crystalline polymeric products (fibers or films) which show remarkable, long range elastic behavior on single and multiple extension over a very wide range of temperatures. They show a high elastic recovery from 50–100% extension (for example: polypropylene 68 to 97% length recovery from −190 °C to 140 °C) with a low embrittling effect below the glass transition temperature. Repeated cycling of annealed materials leads to a stable extension-retraction curve with high elastic and work recoveries. Their physical structure is comparatively stable to stress-relaxation and is highly fatigue resistant. The model and its elastic extension mechanism as proposed on the basis of X-ray diffraction and electron microscopic evidence (13) is supported by characteristic sonic modulus and birefringence data.

Zusammenfassung

„Hart"-elastische Materialien sind orientierte, hochkristalline Produkte (Fasern und Filme), die außerordentliches, elastisches Verhalten bei sehr hoher einmaliger oder wiederholter Dehnung in einem sehr großen Temperaturintervall aufweisen. Sie haben diese hohe Elastizität für 50–100% Dehnung (z. B. Polypropylen hat 68–97% Längenelastizität von −190 bis 140 °C) mit auffallend geringer Sprödigkeit unterhalb der Glastemperatur. Wiederholte Dehnung von getemperten Materialien führt zu einer stabilen Dehnungs-Entspannungskurve mit hohem Längen- und Arbeitserholungsvermögen, guter Entspannungsstabilität und hohem Ermüdungswiderstand. Charakteristische Schallmodulus- und Doppelbrechungsmessungen stimmen mit dem Modell der molekularen Überstruktur und dem elastischen Dehnungsmechanismus, der auf Röntgen- und elektronenmikroskopischen Daten (13) basiert ist, überein.

References

1) *Park, I. K.*, Paper DA 2 presented at the Durham, N. C. meeting of the American Physical Society, March 1966.

2) *Hillier, K. W.*, British J. Appl. Phys. 2, 167 (1951).

3) *Hamburger, W. A.*, Textile Research J. 18, 705 (1948).

4) *Woods, H.*, J. Colloid Sci. 11, 407 (1946).

5) *Flory, P. J.*, "Polymer Chemistry", Cornell Univ. Press, Ithaca, N. Y., (1953).

6) *Mason, P.*, J. Appl. Polymer Sci. 5, 428 (1961).

7) *Young, D.*, Handbook of Engineering Mechanics, Chap. 61, (New York, 1962).

8) *Bennett, H. S.*, in McClung's Handbook of Microscopical Techniques, p. 666-8, (New York, 1964).

9) *Quynn, R. G.* and *B. S. Sprague*, J. Poly Science, A-2 8, 1971 (1970).

10) *Ross, S. E.*, Textile Research J. 34, 565 (1964).

11) *Bryant, G. M.*, Textile Research J. 37, 552 (1967).

12) *Samuels, R. J.*, J. Poly Science C 20, 253 (1967).

13) *Noether, H. D.* and *W. Whitney*, Koll. Z. u. Z. Polym. 251, 991 (1973).

14) *Sobering, S.*, to be published.

15) See for example: *Kaswell, E. R.*, Textile Fibers, Yarns and Fabrics, (New York, 1953). *Booth, J. E.*, Principles of Textile Testing, (New York, 1961). *Morton, W. E.*, and *J. W. S. Hearle*, Physical Properties of Textile Fibers, (1962).

16) See for example: *Balta-Calleja, F. J.*, *B. Crist*, *N. Morosoff*, *A. Peterlin*, J. Macromol. Sci.-Phys. B7 (4), 705 (1973). J. Mat. Sci. 4, 722 (1969). J. Appl. Phys. 40, 4238 (1969). J. Macromol. Sci.-Phys. B4 (3), 519 (1970). Makromol. Chemie 141, 91 (1971). J. Poly. Sci. A-2 10, 1749 (1972). J. Poly. Sci. A-2, 10, 1237 (1972) etc.

Authors' addresses:

H. D. Noether
Celanese Research Company
Box 1000
Summit, New Jersey 07901
(USA)

I. K. Park
Parkim Enterprises Inc.
11 Melbourne Way,
Baskiry Ridge, New Jersey 07920
(USA)