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The Viscoelastic Behavior of Isotactic Polypropylene Fibers

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INTRODUCTION

Increasing precision in the geometry of polymers as introduced by Ziegler and Natta has resulted in the preparation of isotactic polymers with outstanding mechanical properties when compared with the atactic materials. One of the more important results of this work has been the stereospecific polymerization of propylene gas by the Montecatini Group in Italy to yield a powder-like polymer melting at 175°C. which is suitable for melt spinning.[1]

Although atactic polypropylene was a low melting solid unsuitable for the preparation of fibers of any kind, the preparation of isotactic polypropylene has resulted in fibers with both high tenacities and high elongations at break, and as a consequence extremely high work-to-rupture values. Many important military end items such as parachutes and personnel armor vests can effectively utilize materials with high breaking energy densities. Unfortunately the stress-strain properties determined under static conditions are not necessarily indicative of the properties under the use conditions of high speed loading. It is therefore essential to determine the stress-strain properties of a new material over a wide range of strain rates in order to predict its utility for various applications.

In order to determine the properties of polypropylene over a wide range of strain rates using many different techniques, use was made of the testing equipment and skills available at Fabric Research Laboratories (FRL), Plas-Tech Equipment Corp. (P-T), Massachusetts Institute of Technology (MIT), and the National Bureau of Standards (NBS), as well as at the Quartermaster Research and Engineering Command (QM).

EXPERIMENTAL MATERIALS

The isotactic polypropylene used for this testing was a 230-denier 70-filament yarn obtained from Industrial Rayon Corp., Cleveland, Ohio and identified as TC-170-p70. A second cone of yarn previously obtained from the Industrial Rayon Corp. and identified as TC-170-p4 was a 235-denier 34-filament yarn. This second yarn was less uniform; therefore, it was only used for a few confirmatory tests.

EXPERIMENTAL TECHNIQUES

The apparatus and techniques used to determine the stress-strain properties of polypropylene yarn and fiber are discussed briefly in the following paragraphs.

Tests Using the Instron—QM Research and Engineering Command

The Instron tensile tester, Model TT-B, was used to conduct stress-strain studies at rates of elongation of 1.0 and 12 in./min. which for a gage length of 5 in. corresponded to 20 and 240% per minute. The Instron has a weighing system utilizing a bonded type of resistance wire gage to motivate the recorder pin. The machine has a wide range of load sensitivities and is operated at a constant rate of elongation.[2] Although the mechanics of the Instron machine would allow testing speeds as high as 20 in./min., the response time of the recorder available (1.3 sec. full scale) prohibited such rapid straining. The testing was conducted under standard conditions of 70°F. and 65% R.H.

Mitex High Speed Tester—QM Research and Engineering Command

The Mitex is a pneumatic-hydraulic test unit prepared by the Textile Division of MIT for the

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Textile, Clothing and Footwear Division of the QM. The specimen is pulled by a rod attached to the main cylinder piston. The load cell is a piezoelectric type and registers load increases via voltage output to an oscilloscope screen. The strain reading on the specimen is accomplished by attaching a premarked magnetic tape either to specimen or to lower jaw and registering its movement through a recorder head which shows the passing of premarked tape peaks as impulses on the scope screen. This unit operates at a load capacity of up to 500 lb. with testing rates available varying from 1 to 25 ft./sec.

Plastechon High Speed Tester—Plas-Tech Equipment Corporation

The Plastechon model 581 (8 in. stroke machine) is a universal testing machine in which the load is applied to the test specimen by the action of an air-oil system. An operating pressure of 150 lb. was used. The speed of testing was varied by the use of an adjustable orifice in the exhaust line. Extension rates of up to 15,000 in./min. can be obtained depending upon the oil orifice opening and the modulus of elasticity of the material being tested. The Model 581 Plastechon is shown in Figure 1 with a metal stop which can be used for high speed stress relaxation.

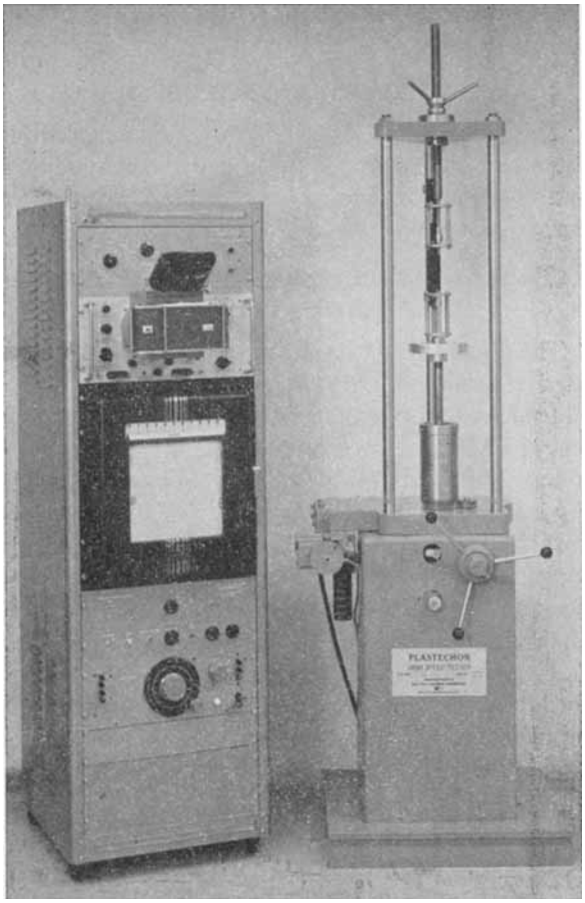

Fig. 1. Model 581 Plastechon high speed testing unit.

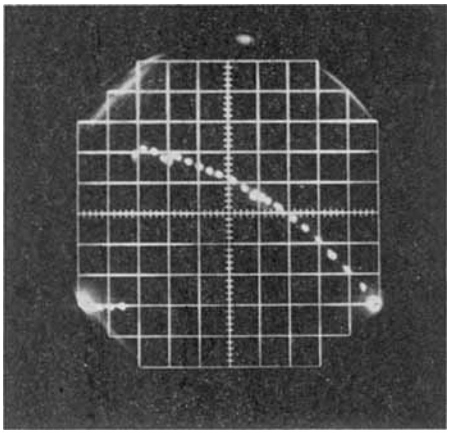

Fig. 2. Stress-strain curve obtained with the Plastechon tester.

A linear potentiometer-type transducer is used to measure displacement which is fed into the horizontal axis of the oscilloscope. This signal is modulated at different frequencies to give appropriate time pulses. Load is measured by a dynamic nonbonded load cell, the signal from which is fed into the vertical axis of the oscilloscope.[3] For the polypropylene tests a gage length of 5 in. was used. The stress-strain pattern was measured on an oscilloscope and a permanent record obtained with a Polaroid Land Camera. A sample test is shown in Figure 2.

Compressed Air Cylinder—Fabric Research Laboratories

Yarns were tested at moderately fast speeds, 1000–12000 in./min. with a tester developed at FRL.[4] The moving crosshead is attached to the piston of an air cylinder in which the pressure is applied rapidly through a fast acting valve. The velocity is controlled by both the applied pressure and the throttling of the exit port to the exhaust chamber of the cylinder. Velocity and displacement are measured by the output signal of a prerecorded tape attached to the moving piston.[5] Loads are measured with a piezoelectric transducer (Endevco force gage-model 2103-500). Both signals are fed to a Tektronix-type 502 dual beam oscilloscope.

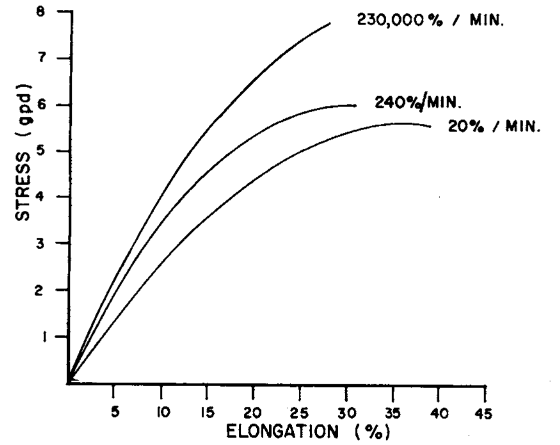

Fig. 3. Stress-strain behavior of isotactic polypropylene at different strain rates.

Falling Weight Method—Massachusetts Institute of Technology

The yarn sample is mounted in rubberized jaws separated a distance of 8 in. A 25-lb. weight is dropped from a height of 10 ft. and accelerates the jaw to a speed of up to 40 ft./sec.

A piezoelectric crystal is used as the load cell and is calibrated by striking a 3-lb. weight with a hammer. This system must be used for calibration because the natural frequency of the load cell is approximately 20,000 cycles/sec. and is therefore only operable under dynamic conditions. The strain is measured by means of a magnetic tape which is attached to the moving jaw. Every 0.080 in. there is a pip which for a 8-in. gage length represents 1% strain. The outputs of these devices are fed simultaneously to a dual beam oscilloscope and camera recorded to give a permanent load-elongation output record.[5]

Ballistic Method—Fabric Research Laboratories

Polypropylene yarns were marked with a special typewriter key at intervals of 6 marks/in. and with identifying double lines after each 10 marks. The yarns were then mounted vertically and impacted with a missile traveling at speeds of from 1000 to 2000 ft./sec. The exact speed of travel is determined with a ballistic pendulum. A high speed stroboscopic light allows up to 15 photos to be taken in the same picture as the bullet passes through the fiber sample. The elongation of the yarn can be determined from the changes in the distances between marks. Estimates of the stress in grams per denier corresponding to each elongation were obtained from the equations of motion of the bent portion of the yarn as developed by Lee of Brown University.[6] The stress values were also obtained independently by the use of a strain gage at the upper end of the yarn. The signal from the strain gage was fed into an oscilloscope and a permanent record obtained with a Polaroid Land Camera. This technique is discussed in detail in a paper to be published by one of the present authors.[7] An upper speed limit for testing polypropylene is reached at transverse striking velocities of about 1500 ft./sec. At this speed, a critical velocity failure occurs,[8] where the sample breaks immediately upon impact.

Rotating Disc Longitudinal Impact Machine—National Bureau of Standards

The yarn specimen $^2/_3$ of a meter long is attached at one end to a head mass and at the other end to a small tail mass.

TABLE I
Mechanical Properties at Various Strain Rates

Laboratory	Speed of testing, in./min.	Speed of testing, %/min.	Rupture load, g./denier	Rupture extension, %	Work to rupture, joules/g.
QM	1	20	5.7	38.0	126
QM	12	240	6.0	32.2	118
P-T	300	10,000	6.1	32.1	119
FRL	2,400	96,000	6.7	29.8	113
P-T	3,300	110,000	7.0	30.7	120
QM	12,000	200,000	6.9	28.0	111
FRL	5,760	230,000	7.1	27.0	105
MIT	21,600	270,000	7.0	28.0	107
FRL	9,400	370,000	8.0	27.7	113
NBS	—	400,000	—	—	69
FRL	12,500	500,000	8.4	28.4	115
FRL	432,000 to 650,000	>1,500,000	5.5	13.5	34
FRL	940,000	>2,000,000	9.6	12.0	40

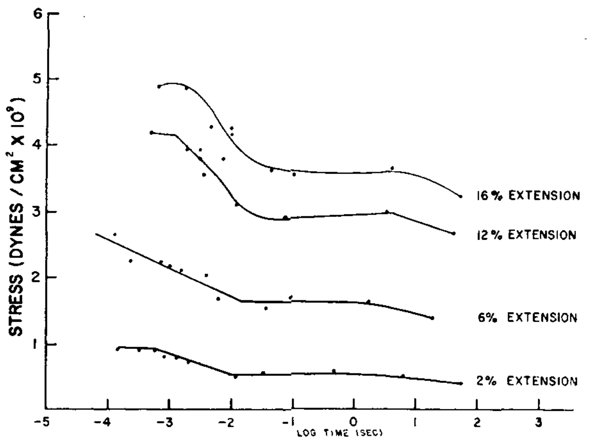

Fig. 4. Stress–log time plots in the form of stress relaxation curves.

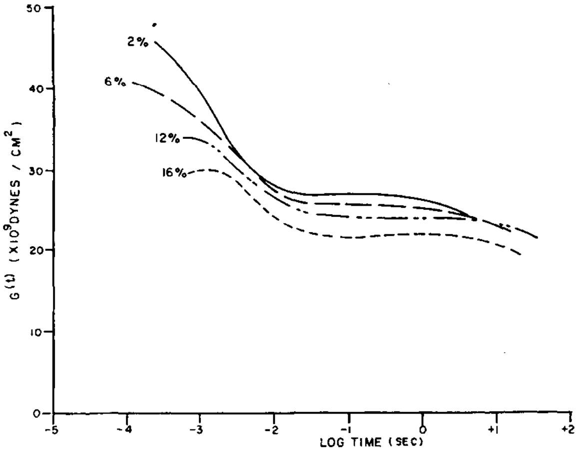

Fig. 5. Modulus as a function of log time for four different extensions.

TABLE II

Mechanical Properties of Cone 2 (TC-170-p4)

Laboratory	Speed of testing, %/min.	Rupture load, g./denier	Rupture extension, %	Work to rupture, j./g.
QM	240	7.3	26.0	89
P-T	10,000	6.9	26.6	81
NBS	520,000	—	—	71

TABLE III

Effect of Extension Rate Upon Stress at Equivalent Strain

Strain rate, %/min.	Stress × 10⁹ dynes/cm.				
	At 2%	At 6%	At 12%	At 16%	Source
20	0.48	1.36	2.65	3.20	QM
240	0.56	1.60	2.96	3.58	QM
4,000	0.56	1.68	—	—	P-T
10,000	0.48	1.52	2.86	3.50	P-T
60,840	0.71	1.68	3.11	3.83	P-T
96,000	0.79	2.02	3.40	4.15	FRL
200,000	0.78	2.01	3.50	4.25	QM
230,000	0.94	2.10	3.76	4.56	FRL
370,000	0.88	2.14	3.90	4.79	FRL
500,000	0.93	2.22	4.10	4.87	FRL
1,500,000	0.71	2.24	4.15	4.87	FRL
2,000,000	0.79	2.64	7.32	—	FRL

The assembly is then mounted in the longitudinal impact machine and the head mass impacted by a hammer on a rotating disc. The head is impacted at velocities between 10 and 100 m./record. The corresponding rates of straining at impact range from 50,000 to 500,000 %/min. The positions of the head and tail masses in free flight are recorded by a high speed camera. The work to rupture is calculated from the general formula $W = kV^2$ where W is the breaking energy density, k is an instrumental constant dependent upon the head and tail masses, and V is the impact velocity.[9]

EXPERIMENTAL RESULTS

As pointed out in the section entitled "Experimental Materials," except where otherwise indicated,

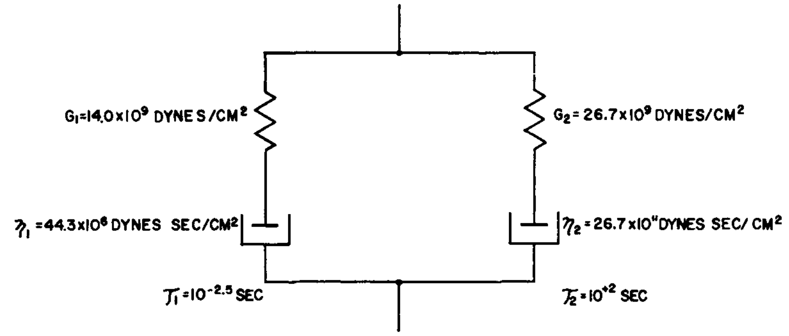

Fig. 6. Mechanical model representing isotactic polypropylene (6% extension).

TABLE IV
Relaxation Parameters for Isotactic Polypropylene

Strain, %	Log test time	E, dynes/cm.^{2} × 10^9				
		E_0	E_2	E_{total}	E_1	
2	1	1.71 × 10^9	2.72 × 10^9	24.0 × 10^9	23.9 × 10^9	0.110
2	−1	0	0	28.2	28.2	0
2	−2.5	6.50	10.2	35.3	33.6	0.304
6	1	1.71	2.72	23.5	23.4	0.120
6	−1	0	0	27.8	27.8	0
6	−2.5	3.01	4.72	31.8	31.4	0.151
12	1	1.10	1.57	23.5	23.4	0.067
12	−1	0	0	23.5	23.5	0
12	−2.5	3.27	5.14	32.0	31.6	0.163
16	1	1.03	1.56	21.7	21.7	0.072
16	−1	0	0	22.0	22.0	0
16	−2.5	2.52	3.93	28.2	27.9	0.141

only the 230-denier 70-filament yarn was used for the determination of viscoelastic properties.

The ultimate properties (elongation, tenacity, and work to rupture) obtained at the different testing speeds are summarized in Table I.

The less uniform cone of polypropylene yarn was subjected to a few tests for comparison with the first cone. The results obtained at three different testing speeds are shown in Table II.

No other work was conducted with this cone because of fairly large denier variations. Note that with both cones the results using the rotating disc apparatus at NBS show a sharper drop in the work-to-rupture value at high speeds than would be indicated from the results of other work.

In Figure 3 the load-extension curves for strain rates of 20, 240, and 230,000% per minute are compared. In order to evaluate the viscoelasticity of isotactic polypropylene, the concept of stress relaxation during a constant extension rate test is applied.[10] The load values at 2, 6, 12, and 16% extension are given in Table III in stress units of dynes/cm.^{2}.

The data in Table III and the times required to reach these strains at the strain rates involved are used to prepare curves of stress against logarithm of time in seconds. The points of equal extension have been connected to give curves reminiscent of stress relaxation experiments in Figure 4.

The stress values have been converted to moduli and the moduli have been plotted against log time in seconds in Figure 5.

DISCUSSION

Isotactic polypropylene yarn has been investigated over five decades of testing time from 10^{-4} to 10^1 sec. and the stress-strain properties determined. This particular yarn was reported by the manufacturer to have a crystallinity of 65% and an orientation of 90%. Relaxation in formation was obtained at 2, 6, 12, and 16% extension. In addition, whenever possible the complete stress-strain curve was investigated to yield information on rupture tenacity, rupture elongation, and work to rupture.

The tensile strength of polypropylene increased from 5.7 g./denier at 20% per minute to 8.4 g./denier at 500,000 %/min. For the same change in strain rate (25,000-fold) the rupture strain decreased from 38% at the slowest rate to 28% at the 500,000 %/min. If we consider the ballistic tests the changes are more pronounced with the tenacity increasing to 9.6 g./denier and the rup-

TABLE V
Parameters for the Mechanical Model at Different Extensions

Extension, %	G_1, dynes/cm.^{2} × 10^9	η_1, dyne-sec./cm.^{2} × 10^7	τ_1, sec.	G_2, dynes/cm.^{2} × 10^9	η_2, dyne-sec./cm.^{2} × 10^{11}	τ_2, sec.
2	21.1	6.69	$10^{-2.25}$	26.0	26.0	10^{+2}
6	14.0	4.43	$10^{-2.5}$	26.7	26.7	10^{+2}
12	10.2	10.2	10^{-2}	24.2	24.2	10^{+2}
16	8.1	8.1	10^{-2}	21.8	21.8	10^{+2}

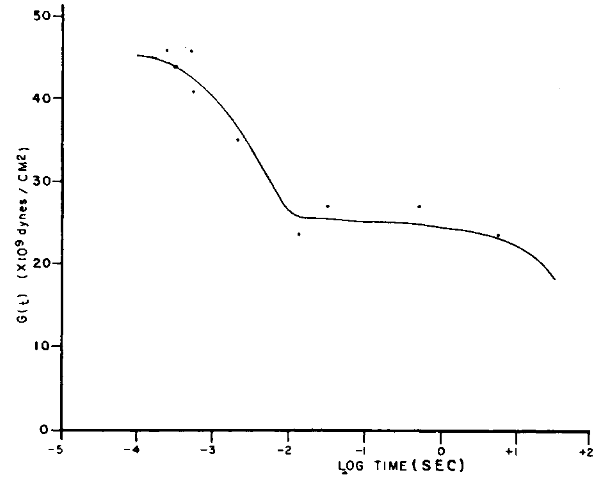

Fig. 7. Comparison of experimental points with curve for mechanical model (2% extension).

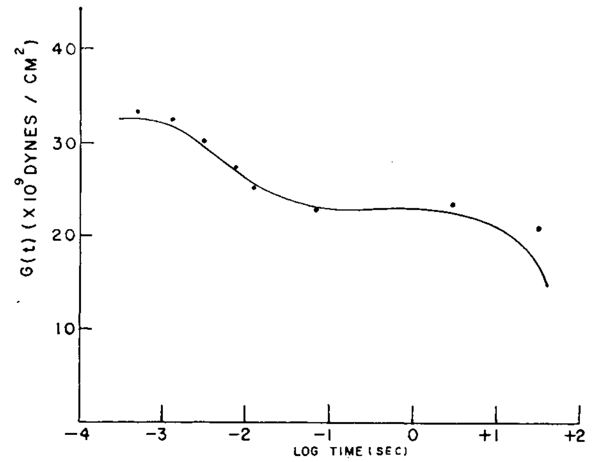

Fig. 9. Comparison of theoretical curve from proposed model with experimental data (12% extension).

ture elongation decreasing to 12%. Due to the nature of the ballistic tests less certainty can be ascribed to the ultimate properties obtained in this manner.

Disregarding both the ballistic tests and those obtained by the rotating disc method (NBS), the work-to-rupture values for isotactic polypropylene decrease rather moderately as the rate of testing increases. The values at speeds of testing from 20 to 500,000 %/min. are vastly superior to any other synthetic fiber. If we place emphasis upon the results obtained by the rotating disc method and by the ballistic tests, the drop in work to rupture with increased speed of testing is very pronounced exceeding 50%.

One might expect the new isotactic polymers to be so highly oriented and crystalline that little time dependency would be exhibited. This is true at the intermediate strain rates for about 3 log cycles of time as shown by the flat portions of the stress-log time curve (Fig. 4). However, considerable time dependency is exhibited both at very low strain rates and very high strain rates as shown by the tan δ values in Table IV.

The stress-log time curves in Figure 4 suggest a relatively simple mechanical model. Two relaxation peaks are apparent, one at about $\tau = 10^{-2}$ sec. and the other a long time relaxation at $\tau = 10^2$ sec. A model is proposed in which two Maxwell models are connected in parallel as shown in Figure 6.

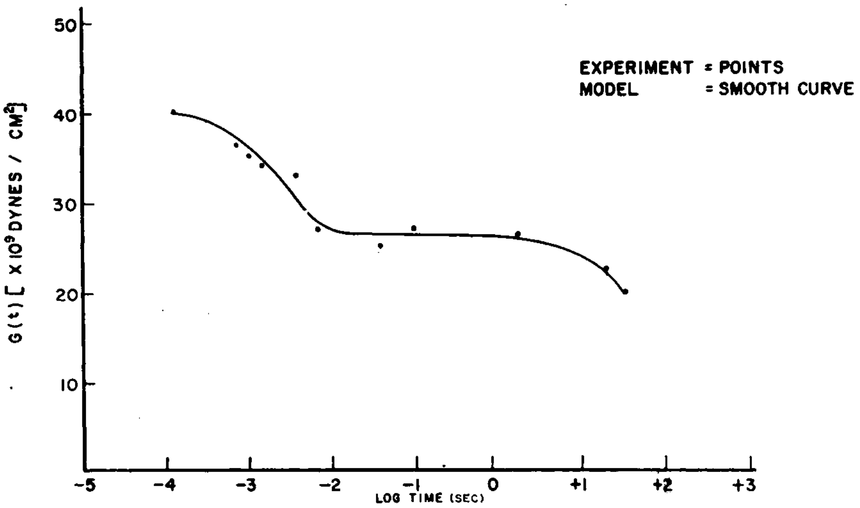

Fig. 8. Comparison of experimental data with mechanical model (6% extension).

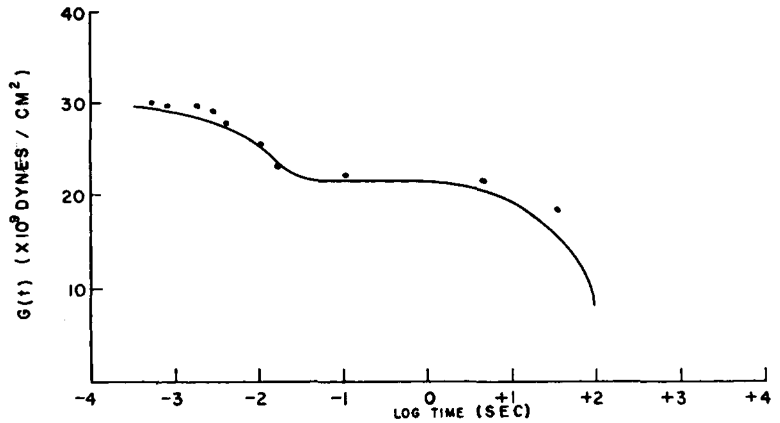

Fig. 10. Comparison of theoretical curve from proposed model with experimental data (16% extension).

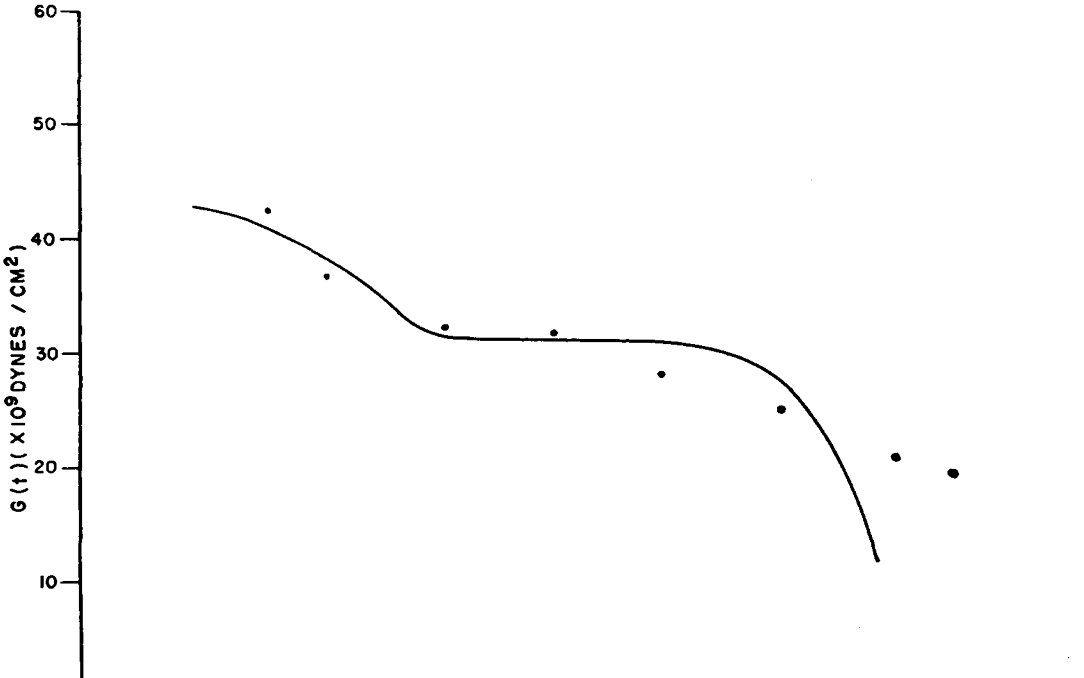

Fig. 11. Attempt to represent Hall's data by a simple mechanical model (15% extension).

The values of G_2 and G_1 were obtained from the 6% extension curve in Figures 4 and 5. The viscosity coefficients were calculated from the expression $\eta = \tau G$.

Theoretical modulus–log time curves can be constructed based upon this model by the use of the expression:

$$G_t = s/\epsilon = G_1e^{-t/\tau_1} + G_2e^{-t/\tau_2}$$

where G_1 is the total modulus, G_1 and G_2 are the spring constants for the model, τ_1 and τ_2 are the relaxation times, and t is the time of testing. The appropriate values of the constants in the model for 2, 6, 12, and 16% extension are given in Table V.

The curves constructed from the model and the figures given in Table V can then be compared with the actual values obtained at each extension. This has been done in Figures 7, 8, 9, and 10 where in each case the solid line represents the curve calculated from the mechanical model and the points represent the experimental data. The agreement is quite good, especially for the shorter relaxation time. Agreement with the long time region of the spectrum may be fortuitous and perhaps a box distribution of relaxation times may be more realistic for this region. This is even more apparent if we attempt to apply the same sort of model to data obtained by Hall at the British Rayon Research Association.[12] This has been done in Figure 11 where the tendency of the data to follow a box distribution at long times is shown by the straight line portion from 10^{0} to $10^{2.5}$ sec. Stress relaxation experiments by one of the present authors substantiates the nearly linear behavior at long times.[13]

It is interesting to calculate a value of the activation energy associated with τ, as suggested by Lyons.[14] Substitution in the formula given:

$$\tau = \frac{h}{2\pi^2 F^*} e^{F^*/kT}$$

yields a value of 18 kcal. indicative of molecular flow and the free volume effect. This is consistent with values obtained by Eyring et al. for polyamide monofils using forced vibration techniques.[15]

SUMMARY

The mechanical properties of isotactic polypropylene yarn have been studied over five decades of testing time. The mechanical behavior at 2, 6, 12, and 16% extension can be represented quite well by a mechanical model composed of two Maxwell units in parallel. However the long time (slow testing) area can be better represented by a box distribution. The ultimate properties of polypropylene yarn show generally increasing tenacity and decreasing elongation to rupture with increasing speed of testing. The breaking energy density values for polypropylene at most strain rates exceed those obtained with any other fibers to date.

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The isotactic polypropylene yarn was obtained from Mr. G. McFarren of Industrial Rayon Corp.

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Synopsis

The stress-strain properties of isotactic polypropylene yarn have been studied over a wide range of strain rates up to 2,000,000% per minute. The testing equipment used included the Instron, three pneumatic and pneumatic-hydraulic type of high speed testers, the falling weight method, the rotating disc longitudinal impact and ballistic techniques. Evaluation of the behavior of polypropylene at strains of 2, 6, 12, and 16% shows the existence of two relaxation peaks, one at $\tau = 10^{-2}$ sec. and the other at about 10^2 sec. with a plateau of little time dependency in between. The data, especially at the shorter testing times, can be well represented by a single mechanical model composed of two Maxwell units in parallel. Information concerning the ultimate properties of isotactic polypropylene yarn was also obtained. The work-to-rupture values for polypropylene at most strain rates exceed those characteristic of any other available textile material.

Résumé

Les propriétés tension-élongation d'un fil de polypropylène isotactique ont été étudiées dans un large domaine de vitesses d'élongation, supérieures à 2.000.000 %/minute. L'equipement servant à faire les tests comprenait un Instron, trois types d'appareils pneumatique et pneumatique-hydraulyque à vitesse élevée, le méthode de la chute d'un poids, les techniques du disque tournant à impact longitudinal et les techniques balistiques. L'évaluation du comportement du polypropylène à des élongations de 2, 6, 12 et 16 % montre l'existence de deux pics de relaxation, un à $\tau = 10^{-2}$ seconde et l'autre à environ 10^2 secondes avec un plateau ne dépendant que peu du temps entre les deux.

Les résultats, spécialement ceux effectués pendant les durées plus courtes, peuvent très bien être représentés par un modèle mécanique simple composé de deux unités de Maxwell en parallèle. On a également obtenu des informations concernant les propriétés définitives du fil de polypropylène isotactique. Le travail à fournir pour atteindre la rupture du polypropylène isotactique pour la plupart des vitesses d'élongation dépasse les valeurs caractéristiques de tous les autres textiles disponibles.

Zusammenfassung

Das Spannungs-Dehnungsverhalten von isotaktischem Polypropylengarn wurde in einem weiten Bereich der Verformungsgeschwindigkeit bis zu 2 000 000 %/Minute untersucht. Zu der verwendeten Testaurüstung gehörte das Instrongerät, drei Hochgeschwindigkeitstester vom pneumatischen und pneumatisch-hydraulischen Typ, die Fallgewichtsmethode, der Longitudinalschlag mit rotierender Scheibe und ballistische Verfahren. Das Verhalten von Propylen bei Verformungen von 2, 6, 12 und 16% zeigt das Vorhandensein von zwei Relaxationsspitzen, eine bei $\tau = 10^{-2}$ Sekunden und die andere bei 10^2 Sekunden und dazwischen ein Plateau mit geringer Zeitabhängigkeit. Die Ergebnisse können, besonders bei den kürzeren Testdauern, gut durch ein einziges, aus zwei parallelgeschalteten Maxwelleinheiten aufgebautes, mechanisches System wiedergegeben werden. Auch Angaben über die Reisseigenschaften von isotaktischem Polypropylengarn können erhalten werden. Die Werte für die Zerreissarbeit von Polypropylen liegen bei den meisten Verformungsgeschwindigkeiten höher als die für irgend ein anderes bekanntes Textilmaterial.

Discussion

Question: Is it possible that the sharp rise in modulus with decreasing test time is associated with the glass transition temperature?

Answer (Mr. Laible): The glass transition temperature for polyethylene would be about −85°, but I think for polypropylene it would be much higher, probably above zero. Using the rough rule of 0.67 times the melting point, a T_g of about 20°C. would be obtained. It is actually between 0 and 5°C.

It is quite true that the rise in modulus is very pronounced at the short testing times, just as if it were a glass transition temperature region. It would be very interesting if we had data not only for different testing times but also for different temperatures. Although we usually restrict time–temperature superposition to amorphous materials, some time–temperature studies of crystalline materials would increase our understanding. We usually find that time–temperature superposition does not work very well with crystalline materials.

Question: You mentioned a 90% orientation in the polypropylene materials; will you explain this a little bit more?

Answer: Actually, to have been sure of the accuracy of the crystallinity and orientation values, we should have conducted some measurements of density and birefringence, respectively. In general we accepted the values given by Industrial Rayon Corporation.