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A Study of Polymer Film Brittleness*

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INTRODUCTION

For the past several years, polymer resin producers, film fabricators, and consumers have shown a growing concern over the effect of loading rates on many of the mechanical properties of plastic films.[1-4] Brittleness has been manifest in numerous polymers and in film fabrication, testing, and end use applications. The term brittleness has been used to denote, in a polymer type or film, a lack of ductility or stretchability, low elongation, low impact resistance, poor flexibility, or, generally speaking, a lack of "toughness."

The experimental work undertaken and reported herein was an effort to determine the relationship between brittleness and the chemical and physical structural features of various polymer films.

The study included use of several conventional testing techniques in addition to novel, high-speed tests.

MANIFESTATIONS OF BRITTLENESS

Many potentially attractive polymers have been excluded from commercialization as self-supporting films because of their brittleness, usually evidenced by low elongation or lack of ductility. Some polymeric films are so shock-brittle they are difficult to handle without breaking, while still others exhibit vast differences in their processability.

Many self-supporting films do not appear to be brittle under conventional testing rates of 0.05 to 20 in./min. However, at higher testing rates or at lower temperatures, lack of ductility is quite apparent.[5,6] For example, amorphous polyethylene terephthalate film, when tested at a conventional rate of 100%/min. on the Instron tester has an elongation of 400%, but at five times this rate, the breaking (ultimate) elongation is reduced to 15% or less.

The temperature and humidity effect is evident in cellophane, where the effectiveness of softener is destroyed by the lack of water. Many films fail in the ultimate test, i.e., packaging applications. In shipping and handling, where the film is subjected to impact, many films fail. An example of this is linear polyethylene, which at conventional testing rates appears to be tough and ductile as evidenced by ultimate elongations of 600–700%; however, under bag drop tests it fails to exhibit the ductility predicted from tensile tests at conventional rates. From some of the early work on the brittleness of elastomers, the brittle point was associated with the glass-transition temperature. However, there are differences between brittle temperature and glass-transition temperature. The former can not be specified uniquely, since it varies with rate of testing. Many polymeric films are not brittle below their glass-transition temperature. For example, Mylar polyester film (Du Pont trademark), whose glass transition temperature is 65°C., is not brittle at −196°C. Brittleness may be defined as the inability of a material to deform the required amount within the time permitted by the test at a specific test temperature.

MOLECULAR INTERPRETATION OF POLYMERIC BRITTLENESS

In response to an applied external force polymeric films possess the properties of viscous liquids and elastic solids.[1,7,8] The degree to which each is evident depends upon the manner in which the stress is applied. High polymer molecules respond to stress not only by lattice deformation and slippage past one another, as do molecules of ordinary solids and liquids, but also by changing

* This paper is a corollary to the paper by G. D. Patterson and W. H. Miller, Jr., presented at the Second Annual Symposium on High Speed Testing (see p. 291). The equipment used for this work was essentially the same as that described at the symposium.

their configuration. The polymer molecules tend to diffuse back to molecular configurations of maximum entropy. If the test is performed at a rate which is rapid compared to the rates of molecular diffusion, polymers behave like elastic solids or rubber. In relatively slow rates of stress application (steady-state conditions), polymeric films behave like viscous liquid. Thus the interaction between molecular chains depends upon the valence bonding between atoms along the chain and also upon the steric effects introduced by branching, side groups, dipole effects, etc.

The total deformation endured by a polymeric film under a tensile stress may be expressed as the sum of deformation from three distinct mechaisms.

(*a*) Initially the bond angles along the polymer chain respond to the stress. This is the most rapid response and is essentially time-independent, being represented as the elastic or Hookean portion of the stress–strain curve. Deformation in this region is recoverable.

(*b*) Uncoiling of polymer chains and chain segments results in a time-dependent deformation. When the stress is applied the uncoiling is restricted by secondary bonds between chain segments. Since there may be several different bonds resisting the uncoiling of chain molecules, each will require its own orientation time and the nature of the overall strain on the specimen will not be a simple function of time.

(*c*) A nonrecoverable deformation results from chain–chain slipping. This also is resisted by secondary valence forces.

It can not be said *per se* that crystalline polymers are brittle, for both polyethylene (low density) and Mylar polyester film are highly crystalline and ductile. As the crystallinity of polyethylene is increased, the polymer does become more brittle, so that for a given system there are limits within which a crystalline polymer is ductile and "tough." Polyethylene terephthalate, unoriented but crystallized, is extremely brittle; on the other hand, we have amorphous polymers such as polystyrene and amorphous polyethylene terephthalate which are also brittle. In general, orientation of polymeric films reduces their rate sensitivity and markedly increases their ductility and "toughness," as shown by Mylar polyester film (oriented, crystalline polyethylene terephthalate). Thus it appears that a knowledge of the molecular changes brought about by orientation will give an insight into the factors responsible for brittleness.

EXPERIMENTAL AND DISCUSSION

Time to Failure of Films in Bag Drop Tests

To determine the order of magnitude of the time and the rate of deformation involved in film failure in rice bag drop tests, high-speed motion pictures of bag drop tests were taken with a Fastax Camera at 6000 frames/sec.

A grid pattern was printed on several representative films with an opaque ink. The pattern was stamped on manually with a rubber stamp cut from a die patterned from graph paper. The bags, fabricated by hand, were of two types, a fin-seal pouch containing 550 g. of rice and a bag of rectangular cross section containing 1000 g. of rice. The latter type was fabricated by wrapping the film around a wood block 4 in. × 7 in. × 1 in. In both types, seams, edges, tops, and bottoms were sealed with pressure-sensitive tape made from Mylar polyester film.

The bags were released from a spring-loaded trap door from a height of 9 ft. onto a Lucite plate. From the known film speed and the measured change in dimensions between grid lines, it was possible to determine both the amount and rate of deformation of the bags. The speed of the motion picture was not sufficient to catch the exact instant of failure, since one frame would show the bag to be still intact, whereas in the next frame, a break, ranging anywhere from 0.5 to 3.0 in. in length would appear. While an attempt was made to design the bag and its load so that it would fail on the first drop, it was not possible to get all film types to do so with the available drop height.

The time interval between contact of the bag with the impacting surface and the detection of film failure was shortest for the films generally considered to be brittle. The more durable films had longer time intervals (absorption of more energy and greater deformation) before failure. The time was in the range of 3–4 msec. for linear polyethylene. The more durable films, such as 0.5-mil Mylar (50 Mylar), and saran-coated, 1-mil cellophane, had time intervals in the 5–7 msec. range. Saran-coated Mylar had a failure time of 12 msec. The results are summarized in Table I.

From the amount of deformation and the time interval, the rates of elongation were found to cover the range 130,000–230,000%/min. Rate of tearing ranged from 60 to 500 m./sec. These results indicate the range of rate of deformation to be considered in studying film properties related to brittleness. This also points up the need for

higher testing rates where routinely measured film properties are to be correlated with film durability.

The ability of saran-coated 50 Mylar polyester film, to deform without rupture was evidenced.

TABLE I
Time to Failure of Films in Rice Bag Drop Tests

Film	Time interval, msec.
Amorphous polyethylene terephthalate	3–4
Linear polyethylene	3–4
High density polyethylene (du Pont)	3–4
Mylar polyester film (0.5 mil)	5–7
Cellophane, saran-coated (1.0 mil)	5–7
Mylar, saran-coated (1.0 mil)	12

It took four drops from the 9-ft. height before the bag finally failed. However, it was deformed considerably before failure. Measurement of the grid lines indicated elongation of over 100%.

Critical Strain Rate

The ability of a polymeric film to absorb and dissipate the energy of externally applied stresses depends strongly upon the temperature of the material and the rate of application of the stress. At too low a temperature or at a too rapid application of the stress the polymer chains are essentially reduced in mobility, the viscous elements cannot come into play, the energy is concentrated, and a brittle failure results. This inability of the polymer segments to respond to stress results in film failure with elongations of only a few per cent. The rate at which this low elongation failure takes place is referred to as the critical strain rate (CSR). The most brittle films had critical strain rates below the routine 100%/min. rate used on the Instron tensile tester. Figure 1 illustrates the marked decrease that occurs in ultimate elongation when the CSR has been reached. In general, specimens tested were 2 in. in length and 1 in. in width; however, to extend the strain-rate range to the order of 10^6%/min., specimens 1 in. in length and 0.5 in. in width were used in some cases. The most ductile film, Mylar polyester film, has a value beyond the maximum available, approximately, 1×10^6%/min. To cover this wide range of testing rates, two instruments were used. From 1 to 1000%/min. the Instron tester was utilized. For the higher rates the impellent-wheel (crosshead-driving flywheel) tester was used.

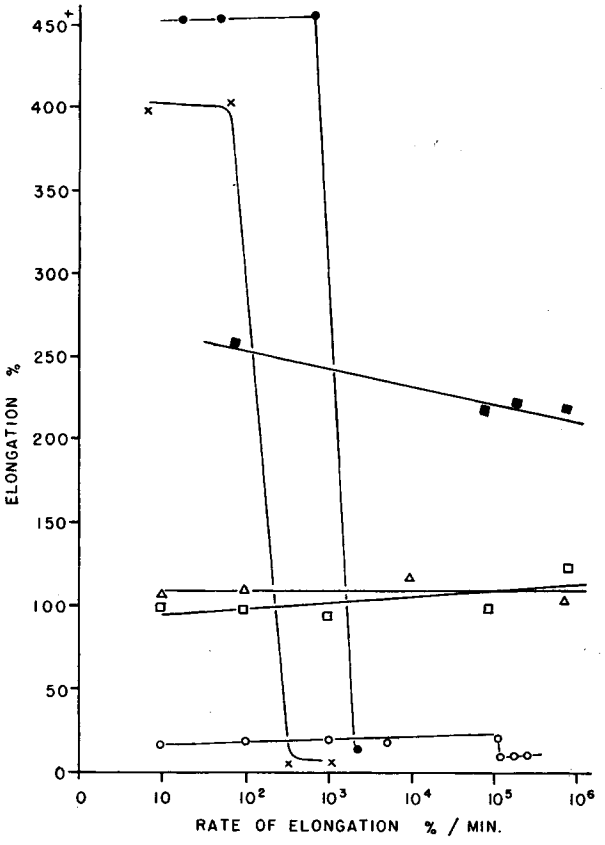

Fig. 1. Critical strain rate: (×) amorphous polyethylene terephthalate; (○) cellophane, saran-coated; (△) Teslar PVF film; (□) Mylar polyester film; (●) linear polyethylene; (■) low-density polyethylene.

Description of the High-Speed Tensile Tester

Many methods have been used in the past to impart a constant velocity to one end of a specimen during a tensile test. In the case of conventional low-speed testers, up to 50 in./min., screws are used; however, these devices are impractical for use at higher velocities.

Accordingly, a high-speed tester was designed, built, and used in this study to provide a velocity range from 50 to 10,000 in./min. Velocities over this range are constant, and the unit is simple to construct. The tester consists of a 1-hp. motor coupled directly to a 69-lb. machined flywheel, (energy bank). Energy stored in the flywheel is transmitted through a variable speed drive, then to a second flywheel fitted with a lead tire (impellent flywheel), which is made to engage a steel tape attached to the specimen under test. Shown in Figure 2 is a schematic drawing of the test unit with a section through the impellent flywheel.

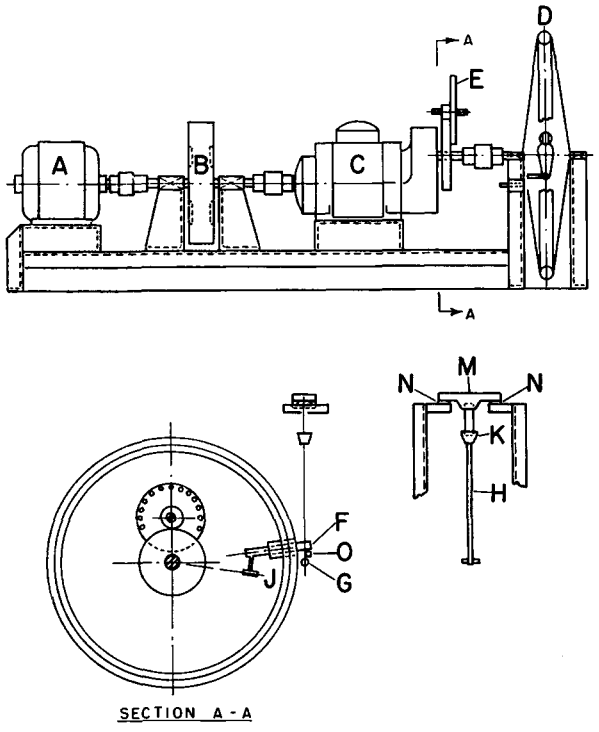

Fig. 2. High-speed tensile tester.

The drive motor (A), 1 hp., rotates at 1750 rpm and is coupled directly to the energy bank (B), a machined flywheel which is 11.5 in. in diameter and weighs 69 lb. The flywheel, tooled from steel plate, was balanced both statically and dynamically. A 1-hp. Graham variable-speed transmission (C), input 1750 rpm, output 0—130 rpm, is used to control the velocity of the impellent wheel (D), which was constructed from a 25-in. diameter sulky wheel fitted with a lead tire weighing approximately 39 lb. The impellent wheel, in addition to receiving energy stored in the energy bank, is in itself a source of energy during the tensile test cycle. Since the rate of stressing or velocity must remain constant during the testing cycle, energy stored in the energy bank and the impellent wheel must be much greater than the energy required to break the specimen. This is accomplished by the tandem effect of the two flywheels. Shown in Figure 3 is a plot of the available energy versus speed of the impellent wheel.

The distance marker unit (E) located on the output shaft of the Graham transmission is a 96-tooth steel spur gear which engages a 24-tooth fiber gear

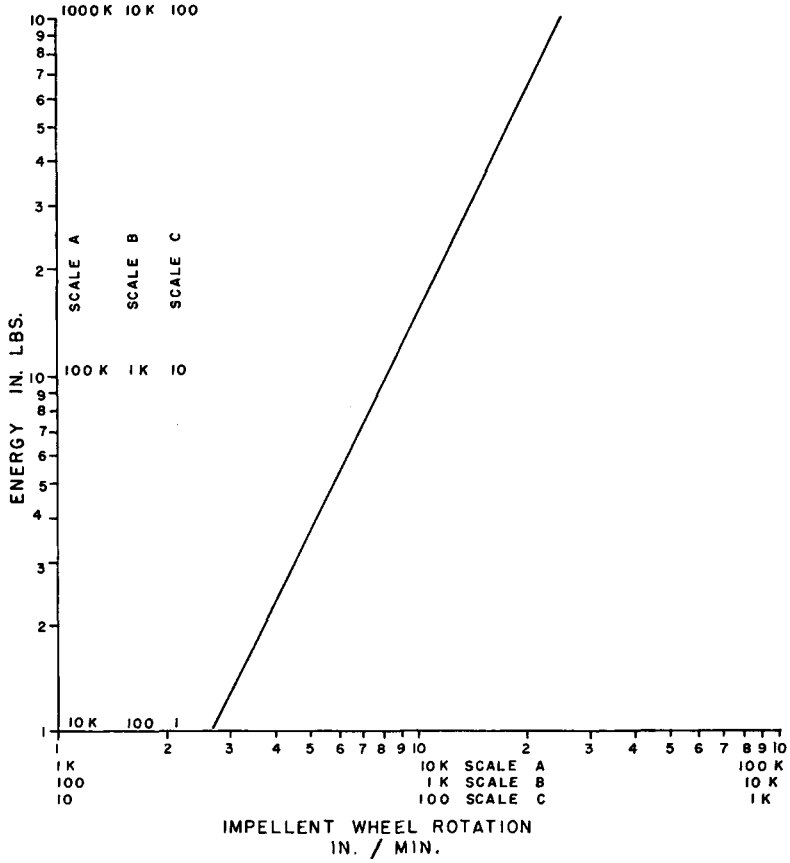

Fig. 3. Plot of energy vs. impellent wheel speed; $E = (I_1W_1^2) + (I_2W_2^2)$.

attached to a 9-in. diameter black Lucite disk. The disk has 90 precision-drilled holes on a circumference which is $^1/_2$ in. from the disk periphery. A light source and photoelectric system is used to detect the holes. Detection of light through the holes develops a signal which is amplified and shaped for display on the oscilloscope as the time or distance axis on the stress–strain curve. Each signal so displayed represents a lower specimen grip travel of 0.25 in.

On the periphery of the impellent wheel is a spring-loaded steel fork (F) which is retained by a ratchet and which normally does not project beyond the periphery of the lead tire. When the preset test speed has been reached, the fork is released on signal to engage the cross bar (G) at one end of a $^1/_2$-in. wide steel measuring tape (H). (Adjustments to length of this tape can be made, depending upon specimen length under test.) The opposing end of the steel tape is connected to the lower specimen grip (K), which holds the bottom end of the specimen. The upper end of the specimen is clamped in a low-mass upper grip (M) which rests on a pair of piezoelectric crystals (N) used as the load-sensing system. When the fork on the impellent wheel engages the cross bar, it wraps the steel tape around the impellent wheel circumference until the film breaks, at which time centrifugal force throws the cross bar and tape free of the fork and to the floor below.

Activation of the fork mechanism is accomplished manually by pushing a lever into the path of a ball race (J) fitted on the end of the spring loaded ratchet to release a dowel from the detent in the fork body. The fork release mechanism is located in such a way that the impellent wheel makes greater than seven-eighths of a revolution before it engages the specimen tape cross bar.

Specimens are mounted in the grip in a jig so shaped as to accommodate both the upper and the lower grip and approximately 1 in. of the steel tape to assure the proper alignment of the entire specimen clamping system with regard to the impellent wheel and its fork mechanism. At the higher rates of impellent wheel rotation it was found that air currents were generated that caused misalignment of the specimen cross bar as it hung freely at the fork engagement point. Use of a small bar magnet (O) mounted on the instrument frame cross member and then contacting the steel tape above the cross bar alleviated this condition.

This entire assembly described was firmly bolted to the floor and completely separated from the force-detecting piezoelectric load-sensing elements.

Force Detection

To measure the forces developed during the stressing of the test specimen a pair of barium titanite, $^1/_2$ in. diameter, $^1/_{10}$ in. thick piezoelectric crystals were used. Connected in series, output of the crystals during film stressing was fed into a high-impedance electrometer and then to an oscilloscope for display and ultimate photographing by a Polaroid-Land camera.

For assurance of an absolute minimum in motion of the load-sensing device and, further, that the record of small and rapid fluctuations in the forces developed would not be lost during a stressing event, a massive support, completely separated from the impellent flywheel arrangement was bolted to the floor. On this support were placed the load-sensing elements which supported the vertically mounted grip-specimen-steel tape assembly.

Forces exerted through the film to the upper grip and then to the crystals results in a charge which is proportional to the applied force; consequently, a potential is developed between the surfaces of the crystals whose magnitude is inversely proportional to the capacity of the system. The potential difference developed will remain as long as the force is maintained only if the resistance between the crystal surfaces is sufficiently high. The electrical capacity of the crystals is small and must be kept small to be sure that the voltages developed are large enough for easy and precise measurement. Voltages which are strictly proportional to the applied force are obtained by keeping the resistance in parallel to the piezoelectric crystals sufficiently high (10^{12} megohms) to make the time constant of the measuring system many times the duration of the force developed at any instant of specimen stressing.

Calibration of the system is accomplished by placing weights in a pan suspended from the upper specimen grip which is resting upon the crystals.

During preliminary testing it was found that high-frequency oscillations were superimposed on the stress–strain curve. This we found was due to vibrations in the upper jaw. Dampening was affected by preloading the upper jaw with a weighted rubber stopper fixed on a pivoted arm and resting on the grip during a test cycle. Shown in Figure 4 are typical stress–strain curves for poly-

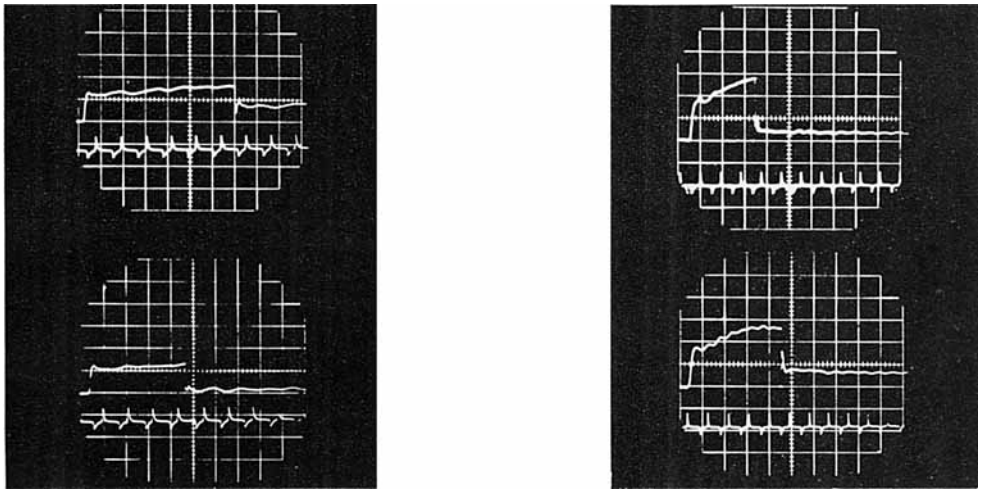

Fig. 4. Typical stress–strain diagrams, strain rate 5.0×10^5%/min.: (*a*) low density polyethylene; (*b*) Teslar PVF film.

ethylene and Teslar PVF film (Du Pont trademark) obtained at strain rates of 5.0×10^5%/min.

Values for the critical strain rate (CSR) for a variety of films are given in Table II. Some films exhibit critical strain rates which differ significantly with the principal direction of test. In such cases, the lower values of CSR are quoted, since in actual use, films are generally stressed biaxially, and their durability is limited by the lower value of CSR.

TABLE II

Critical Strain Rates (CSR) for Representative Films at 23.5°C. and 50% R. H.

Film	CSR, %/min.	$\tau_{minimum}$, msec.
Terephthalate copolyester film	5	2.5×10^6
Amorphous polyethylene terephthalate	100	2.4×10^5
Linear polyethylene	4,000	9.0×10^3
Cellophane, saran-coated	200,000	1.2
Teslar PVF film	>900,000	<6.0
Polypropylene	400,000	2.0
Polyethylene	>900,000	<1.8
50 Mylar polyester film	>1,000,000	<6.0

The effect of rate of stressing on the tensile properties was determined for several polymers. In general, the tensile strength and the initial tensile modulus increase with increased rate. There was some indication that perhaps in a particular region of strain rate (1000%/min.) there may be a decrease in the initial tensile modulus. However, accurate measurement of the initial portion of the stress–strain curves at high rates was not possible, as these tests resulted in much variation. In Table III are shown the values for property changes with change in strain rate. The ultimate elongation shows no significant change with rate until it approaches the critical strain rate and then abruptly decreases.

Consider the critical strain rate in terms of molecular orientation times. When a polymer is stressed beyond the yield point it takes a finite time for the macromolecules to respond to the stress. This depends not only upon the type of polymer molecules but also the environment, which includes many factors such as the order, crystallinity, and steric effects. This time of orientation is actually the distribution of orientation times for the various groupings, segments, and configurations which respond to the stress. From the maximum breaking elongation at room temperature (at slow rate of deformation) as the "normal" elongation and the maximum rate of deformation at which this elongation is realized (approaching the CSR), a minimum orientation time was calculated. This is the minimum time required for a polymer to elongate to its "normal" elongation. These values are given in Table II for several films. In cases where the CSR exceeded the available test rate, the minimum orientation time, $\tau_{minimum}$ is given as "less than" a certain value. There is a sharp division between polymers which are brittle (above 1000 msec. for $\tau_{minimum}$) and the tougher films which have values of less than 10 msec. We might arbitrarily select a value of 10 msec. as the value above which films exhibit brittleness at room temperature.

TABLE III
Effect of Rate on Tensile Properties at 23.5°C. and 50% R.H.

Film	Rate, %/min.	Tensile strength, psi	Elongation, %	Initial tensile modulus, psi	Yield strength	
					Stress *t*, psi	Elongation at yield, %
Polyethylene MD[a]	2	—	—	21,800	930	4
	10	—	—	24,800	1,000	4
	100	3,100	260	29,900	1,100	4
	500	3,300	290	33,500	1,400	7
	1,000	—	—	—	1,400	9
	200,000	—	220			
	400,000	3,900	210			
	860,000	—	210			
Linear polyethylene MD	2			73,200	1,500	2
	10			72,600	1,800	2
	100	3,700	550	84,800	2,100	3
	1,000	3,500	480	—	2,800	5
	2,000	5,600	590	—	3,400	6
	4,000		10	—	—	—
Amorphous polyethylene terephthalate MD	2	—		336,000	7,000	2
	10	7,200	390	296,000	7,700	2
	100	9,500	460	316,000	7,800	3
	500	7,600	5	—	7,600	3
	1,000	3,500	5			
	2,000	1,800	10			
Mylar C polyester film MD	2	21,500	70	628,000	11,800	2
	10	25,700	100	632,400	12,600	2
	100	25,800	90	616,000	13,700	2
	500	24,800	90	—	14,200	4
	1,000	—	80	—	15,600	9
	2,000	—	120	—	—	—
	462,000	23,400	110	—	—	—
	924,000	24,000	130	—	—	—
Mylar, saran-coated MD	2	16,500	120	458,500	9,200	2
	10	17,000	130	457,900	9,700	2
	100	16,400	110	437,000	10,400	2
	500	16,300	120	—	11,200	4
	1,000	17,000	140	—	11,300	5
	8,000		110			
	946,000		100			
Saran-coated cellophane, MD	0.2				2,900	0.5
	2	10,000	14	445,000	4,400	1
	10	10,700	17	507,000	5,500	1
	100	12,100	15	458,000	6,900	2
	500	13,000	18	—	7,600	2
	1,000	12,700	17		10,000	6
	2,000	12,200	18			
	17,200	11,000	14			
	140,000		16			
	200,000	19,100	7			
	300,000		2			
	442,000		2			

TABLE III (*continued*)

Film	Rate, %/min.	Tensile strength, psi	Elongation, %	Initial tensile modulus, psi	Yield strength	
					Stress *t*, psi	Elongation at yield, %
Teslar PVF film, MD	2	10,100	100	315,800	5,200	2
	10	10,000	110	300,200	5,700	2
	100	11,700	120	317,000	6,500	2
	500	12,400	130	—	7,100	5
	1,000	11,700	150	—	7,700	6
	2,000	11,300	140	—	8,600	19
	11,500	12,800	100			
	25,000	14,400	80			
	100,000	14,600	130			
	900,000	18,700	90			
Polystyrene (oriented) MD	2	8,290	9	453,500		2
	10	8,650	8	402,400		3
	100	11,200	6	408,800	11,240	3
	500	9,200	5		9,200	5
	1,000	4,900	6		4,900	6
	7,500	10,800	2			
Amorphous copolyester film	2	5,000	8			
	5	7,300	2			
	10	6,500	3			

[a] MD = machine direction.

TABLE IV
Effect of Temperature and Rate on Properties

Film	Temp., °C.	Strain rate 1000%/min.		Strain rate 100%/min.			Strain rate 10%/min.	Strain rate 2%/min.
		Tensile, psi	Elongation, %	Tensile, psi	Elongation, %	Modulus, psi	Modulus, psi	Modulus, psi
Polyethylene MD[a]	−20	5,600	75	5,100	280	66,600	51,100	49,400
	−10	5,000	240	4,500	250	46,000		
	0	4,300	220	3,500	180	36,400	32,500	34,400
	10	4,200	290	3,800	270	35,800		
	23	3,400	230	3,100	260	29,900	24,800	21,800
	40	2,500	260	2,300	270	10,100	8,400	7,900
	60						5,000	5,300
Mylar C polyester film MD	−20	31,900	70	31,800	85	611,300	514,300	510,500
	−10	35,300	105	32,300	95	497,300		
	0	23,900	60	23,300	55	639,100	478,000	567,200
	10	29,500	90	25,800	75	514,700	632,400	628,000
	23	22,900	80	25,700	90	616,600	409,500	424,200
	40	24,700	90	26,900	110	542,700	393,800	414,500
Polystyrene (oriented) MD	−20	7,800	4	14,100	4	428,100		
	−10	8,800	4	13,900	4	414,000		
	0	8,300	4	11,000	3	468,500		
	10	8,400	4	12,300	4	413,000		
	23	4,900	6	11,200	6	408,800		
	40	4,600	6	7,600	9	355,100		
Linear polyethylene MD	−20						148,700	95,100
	−10							
	0	3,850	65	3,400	50	167,800	106,800	91,700
	10							
	23						72,600	73,200
	40						38,200	28,500
	60						21,000	17,100

[a] MD = machine direction.

Effect of Temperature

The high-speed tensile tester is not equipped to permit testing over a temperature range. Limited temperature–rate studies were carried out on the Instron tester, the maximum rate of elongation used being 1000%/min. At this rate and a temperature of −20°C., low-density polyethylene approaches the critical strain. Data for several films are shown in Table IV.

Effect of Rate on Impact Resistance

The tensile strength of polymeric films is known to increase with a decrease in the time of testing. The effect of rate on impact resistance was examined over a threefold range from 21.4 to 60.1 m./sec. The tester used to measure this effect has been previously described.[9] In principle, a 1/2-in. diameter steel projectile is mechanically accelerated from rest by pressurized air. The kinetic energy of the projectile is determined from precise velocity measurements in free flight. Impact strength of the film is determined from a measure of the residual energy in the projectile after rupture of the specimen. The rate of testing is changed by increasing or decreasing the pressure of the propellant gas. At a firing pressure of 20 psi the speed of the ball was 21.4 m./sec. and at 100 psi it was 60.1 m./sec. A 0.25-mil Mylar polyester film doubled in impact resistance over this range, while the 5.0-mil film showed only a 10% increase. The appearance of the fractures were of the ductile type, i.e., the film was drawn at the edges. A 4-mil polyvinyl chloride film behaved much like the heavy-gage Mylar, increasing about 10–15% in impact resistance over the range of test rates; it exhibited flow-type fracture except at 100 psi, where the failures in some cases were glasslike shatters. This is an indication of the approach of the brittle point for this film. It is interesting to note that Mylar does not exhibit brittle-type failure at the maximum rate available on the pneumatic impact tester (60 m./sec.), which is fifteen times the maximum speed used on the high-speed tensile tester (10^6%/min., equivalent to 4 m./sec. for a 1-in. sample).

Probe Burst Test

The pneumatic impact test imparts a biaxial stress which is representative of the type of stress encountered in packaging applications. Also available for stress application of this kind but at slower rates is a probe burst test performed on the Instron tensile tester. In this test, a 6-in. probe rounded at one end to a 1/4-in. radius is mounted vertically on a compression cell. The film specimen is suitably mounted in an annular clamp on the lower side of the moving cross head. The crosshead is allowed to fall at a constant rate until the probe bursts thru the film. Several representative films were tested at rates of 1 and 20 in./min. The more durable films, such as Mylar, polyethylene, and Teslar PVF film, had essentially the same resistance at the two rates. However, the brittle films, such as oriented polystyrene and a terephthalate copolyester film, showed the greatest rate dependence over this range of rates. This is shown in Table V by the high values of the ratio of the burst strength at the lower speed to the value at the higher speed.

TABLE V
Instron Probe Burst Test at 23.5°C. and 50% R.H.[a]

Film	Burst strength at various test rates, lbs./mil of thickness		Ratio of burst strengths at 1 in./min. per 20 in./min.
	1 in./min.	20 in./min.	
Mylar	26.8	26.6	1.0
Mylar, saran-coated	20.0	20.0	1.0
Teslar PVF Film	15.0	15.0	1.0
Polystyrene	12.4	3.8	3.3
Cellophane, saran-coated	8.3	8.3	1.0
Amorphous polyethylene terephthalate	6.6	7.9	0.8
Polyethylene	4.0	4.0	1.0
Linear polyethylene	3.5	3.2	1.1
Terephthalate copolyester film	3.4	1.3	2.6

[a] Rounded-end probe, 1/4 in. radius.

Mullen Burst Strength

Another test which was used to evaluate films with regard to brittleness is the Mullen burst test, ASTM D-774. It is a measure of the energy-absorbing ability of a film. The "tougher" films (greater area under the stress–strain curve) give the higher values. If "toughness" is rated by this test, polyethylene, because of its low tensile strength, does not rate high. A number of brittle films, such as amorphous terephthalate copolyester film and amorphous polyethylene terephthalate, rate relatively high because the test is done at a rate of deformation which is relatively slow, thus permitting those films to stretch. Little difference

was found between values obtained at 70 and 0°F., as shown in Table VI.

TABLE VI
Mullen Burst Strength

Film	Mullen burst strength, lb./mil. of thickness: 23.5°C., 50% R.H.	Mullen burst strength, lb./mil. of thickness: −18°C.
Mylar polyester film	68	68
Mylar, saran-coated	45	48
Polystyrene	27	23
Cellophane, saran-coated	22	26
Terephthalate copolyester film	13	14
Amorphous polyethylene terephthalate	11	12
Polyethylene	9	11
Linear polyethylene	8	10

Impact Resistance and Critical Strain Rate as Measures of Film Durability

The pneumatic impact test has been one of our standard tests for film brittleness. However, this test if performed at one rate of stressing, does not give a complete or accurate picture of film durability. We must consider the rate and temperature dependence as well as the strength characteristics. Combining the impact value and the CSR will better characterize a film with respect to durability. This should be done over a range of temperatures.

Examination of the impact values in Table VII reveals that the impact resistance of polyethylene is considerably below that of Mylar polyester film and saran-coated cellophane, but the CSR determined from high-speed tensile tests is among the highest. The relatively low tensile strength of polyethylene is reflected in this lower impact value. However, the film is not rate-sensitive. Thus, for example, polyethylene can withstand more rapidly applied stresses but smaller stress loads than can Mylar polyester film, which has high strength and low rate sensitivity. Plotted in Figure 5 are the impact and CSR values for representative films giving a smooth curve. The least brittle films are those with high CSR, while the best overall film from the standpoint of durability combines high values of both impact resistance and CSR.

TABLE VII
Pneumatic Impact Resistance of Representative Films at 23.5°C. and 50% R.H.

Film	Pneumatic impact resistance, kg.-cm./mil of thickness
Mylar polyester film	5.00
Mylar, saran-coated	4.54
Teslar PVF film	4.50
Cellophane, saran-coated	2.12
Polyethylene	1.23
Polystyrene	0.67
Amorphous polyethylene terephthalate	0.37
Linear polyethylene	0.35
Terephthalate copolyester film	0.12

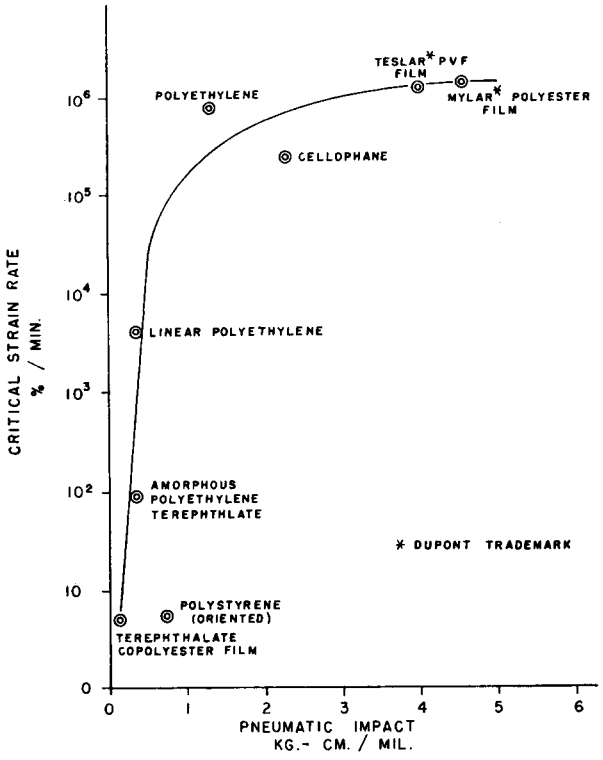

Fig. 5. Plot of pneumatic impact resistance vs. critical strain rate.

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Synopsis

The inability of polymer chains to deform the required amount within the time allowed by a stress-to-failure event results in brittle failure. Factors related to brittle behavior of films were investigated. By both conventional and novel testing techniques, stress–time–temperature relationships were studied to determine the brittle point. From high-speed tensile tests at strain rates up to 10^6%/min., the critical strain rate (incipient brittleness as indicated by failure accompanied by a marked decrease in ductility) was determined for representative films. High-speed motion pictures (6,000 frames/sec.) of film failure in rice bag drop tests, were used to ascertain the time of deformation to be related to brittleness. Deformation rates were calculated to be of the order of 130 to 230 $\times$ 10^3%/min.

Résumé

L'inaptitude des chaînes polymériques à se déformer durant la durée d'un étirement jusqu'à cassure éventuelle entraine une fragilité à la cassure. Les facteurs reliés à la friabilité des films ont été examinés. Les relations élongation—temps—température ont été étudiées à l'aide de techniques expérimentales nouvelles et conventionnelles en vue de déterminer le point de friabilité. La vitesse d'élongation critique (c.à.d. le début de friabilité indiqué par la cassure accompagnée d'une décroissance marquée de flexibilité) a été déterminée pour des films représentatifs au moyen de tests de tension à vitesse élevée allant jusqu'à 10^6%/min. Des images à haute vitesse (6.000/sec.) de l'apparition de la cassure des films lors des tests de chute de poids ont été utilisés pour vérifier la relation entre la durée de la déformation et la friabilité. Les vitesses de déformation calculées sont de l'ordre de 130 à 230 $\times$ 10^3%/min.

Zusammenfassung

Die Unfähigkeit von Polymerketten, sich in der Zeit zwischen Spannung und Bruch um den erforderlichen Betrag zu deformieren, führt zum spröden Bruch. Die Faktoren, die zum Sprödigkeitsverhalten von Filmen in Beziehung stehen, wurden untersucht. Zur Bestimmung des "Brittle points" wurden Spannungs-Zeit-Temperaturbeziehungen unter Verwendung konventioneller und neuartiger Prüfverfahren ermittelt. An ausgewählten Filmen wurde mittels Zugtests bei hoher Geschwindigkeit, Verformungsgeschwindigkeiten bis zu 10^6%/min, die kritische Verformungsgeschwindigkeit (einsetzende Sprödigkeit durch Bruch, begleitet von einer merklichen Duktilitätsabnahme, gekennzeichnet) bestimmt. Filmaufnahmen mit hoher Geschwindigkeit (6000 Bilder/sek) vom Filmbruch bei Falltests an Reissäcken wurden zur Festlegung der zur Sprödigkeit führenden Deformationsdauer verwendet. Für die Deformationsgeschwindigkeit wurden Werte in der Grössenordnung von 130 bis 230 $\times$ 10^3%/min berechnet.

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