AN ELASTOMERIC EJECTION SYSTEM

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ABSTRACT

The ability of elastomers to store large quantities of energy, which can subsequently be recovered very quickly, makes them attractive materials for propulsion devices. Recently the U.S. Navy has developed a torpedo ejection system based on an elastomeric mechanical capacitor. The criteria governing selection of a material for this application include high elastic energy, sufficient fatigue life, minimal creep, and resistance to deterioration by seawater. This paper describes various approaches to obtaining these material properties.

INTRODUCTION

The high elasticity of rubber can be exploited for energy storage applications, although it's not obvious that elastomers can offer very high levels of performance. Indeed, rubber is often distinguished from other polymeric materials by its low modulus; for example, the onset of rubbery behavior is commonly defined[1] as the temperature at which the storage modulus falls to 10 MPa. Typical elastomers have moduli even lower than this. While high compliance limits the magnitude of mechanical energy available from an elastomer, this energy can be acquired very rapidly. In natural rubber at room temperature, for example, segmental relaxation governing local motion transpires over time scales shorter than 10^{-8} s.[2] Hence, even a few cm^3 of soft elastomer can yield power levels exceeding one million watts.

One application of elastomers as energy storage devices is regenerative braking systems.[3] During braking a portion of the vehicle's kinetic energy is temporarily stored via elastic deformation of an elastomer, rather than being entirely dissipated as friction. Although not yet commercial viable, these devices offer the potential for significant increases in fuel economy.

Prestretched elastomers are currently in use as the propulsion mechanism for aerosol containers. Retraction of a cylindrical rubber sleeve[4-6] upon opening of a discharge valve evacuates the contents. The material properties of the rubber, along with its shape, determine the delivery pressure and volume characteristics. The main advantages of these self-pressurized containers is the environmental appeal of eliminating gaseous propellants and a reduced likelihood of explosions during incineration.

A more ambitious application of elastomeric propellants is for launching torpedoes.[7] Conventional launchers rely on 1.5 MW (2000 hp) turbine pumps for ejection of 2 ton torpedoes, which must achieve exit speeds of 50 km/hr in one second. The turbine pump systems weigh over 6000 kg, cost several million dollars, and occupy scarce volume inside a submarine. The advantages of an elastomeric launcher include a large reduction in weight, at least a ten-fold reduction in cost, and superior acoustic properties. Another important benefit is that the elastomeric device can be situated in seawater, outside the inner hull.

Although a spherical elastomer provides optimal strain to volume ratios, a disk geometry allows more flexibility in design and arrangements within the submarine. The current concept

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for an elastomeric torpedo ejection system (Figure 1) envisions a disk, two meters in diameter, comprised of one or more plies with a total thickness of as much as 20 cm. A small (*ca.* 50 kW) pump inflates the disk with seawater to a biaxial extension of 100%. Over the anticipated 15 year lifetime, the elastomer will experience more than 10^3 inflation cycles, as well as being maintained for extended durations in a pressurized condition. The latter "delivery-ready" condition is essential for aerosol containers, and, for that application, must be sustained over the entire product lifetime. For torpedo launchers, pre-inflation is only desirable, and even then for a duration of at most a few weeks. The creep properties of the elastomer govern whether and to what extent delivery-ready operation can be utilized.

The purpose of the present study was to determine the material requirements for an elastomeric torpedo launcher. Most of these considerations are relevant to energy storage devices in general. The main properties governing an elastomer's performance in this regard are (i) the magnitude of elastic (recoverable) energy, which, along with geometry, governs the attainable power, (ii) the propensity of the rubber to creep, which depletes the stored energy, and (iii) the failure properties, which determine the device's lifetime.

EXPERIMENTAL

Several dozen compounds were prepared, encompassing various material types. They are designated by their entry in Tables I–III (*e.g.*, IIC refers to compound C in Table II). Stocks were mixed in a Brabender Prepcenter mixer, with curatives introduced using a two-roll mill. Curing was carried out in a pressurized mold, typically at 160°C for 30 min.

Tensile testing at room temperature employed an Instron 4206, along with a Wallace optical extensometer. Sample dimensions corresponded to ASTM D638 and D412 for strength and modulus measurements respectively. Recoverable energy determinations consisted of uniaxial extension of the sample at a 5 mm/min cross-head velocity (nominal strain rate equal to 0.001 s^{-1}). At a given strain (typically 100% elongation), the cross-head was instantly reversed, and the sample returned to zero strain at the same velocity. The slight lag in the
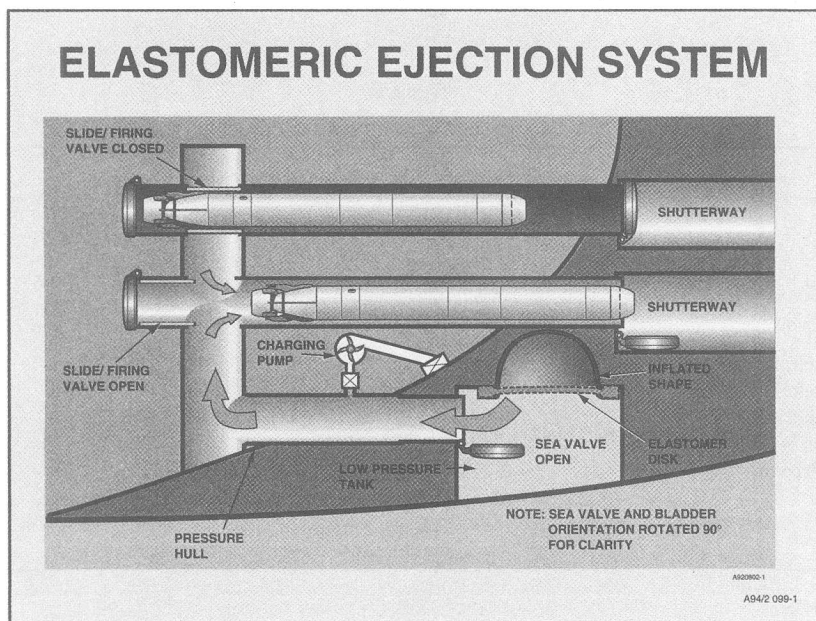

FIG. 1.—Schematic of elastomeric torpedo launching system. At launch the firing valve opens, allowing the elastic energy of the bladder to discharge the launch fluid. The resulting pressure differential accelerates the torpedo out of the tube.

TABLE I

COVALENTLY CROSSLINKED COMPOUNDS WITHOUT FILLER

	IA	IB	IC
NR[a]	100	100	—
SBR[b]	—	—	100
Antioxidant	0.5	—	0.5
Zinc oxide	—	5	3
Stearic acid	—	2	2
Dicumyl peroxide	0.7–3.0	—	—
Sulfur	—	2.5	1.5
CBS[c]	—	0.6	1.2

[a] SMR-L.
[b] 1500 type.
[c] N-cyclohexyl-2-benzothiazolesulfenamide.

reversal of the cross-head introduces negligible error. An elastomeric torpedo launcher would operate under biaxial extension, but for the evaluation of stiffness and strength, the more convenient uniaxial extension geometry was used. The breaking stresses and strains are actually higher under biaxial tension than under uniaxial tension,[8,9] while fatigue lifetimes are not significantly different.[10]

Creep experiments were carried out in a pure shear geometry (sample dimensions = 2 mm × 1 mm × 13 mm) at 26°C using a Imass Corp. Dynastat instrument. Following imposition of a stress, the deformation was monitored over a time period of from 10^{-1} to 10^3 seconds. The stress was either maintained constant during the creep, or periodically removed and reapplied.

Seawater aging experiments were carried out in the lab using a commercial seasalt preparation (Aquarium Systems Instant Ocean), with the exception of one year-long immersion

TABLE II

COVALENTLY CROSSLINKED COMPOUNDS WITH CARBON BLACK

	IIA	IIB	IIC	IID	IIE	IIF
NR[a]	100	100	—	—	100	100
SBR[b]	—	—	100[c]	100	—	—
Antioxidant	0.5	0.5	—	—	0.5	0.5
Zinc oxide	—	—	—	—	4	4
Stearic acid	—	—	—	—	1	1
Carbon black, N110	45	—	—	40	—	—
Carbon black, N326	—	45	—	—	40	40
Carbon black, N339	—	—	82.5[c]	—	—	—
Aromatic oil	—	—	62.5[c]	5	—	—
Dicumyl peroxide	0.7–3	0.7–3	1–6	0.5–3.2	—	—
Sulfur	—	—	—	—	1–3	0.5
MBS[d]	—	—	—	—	—	0.3
DTDM[e]	—	—	—	—	—	0.5

[a] SMR-L.
[b] 1500 type.
[c] Carbomix 1848R (Ameripol Synpol Corp.).
[d] 2-(Morpholinothio)benzothiazole.
[e] Dithiodimorpholine.

COMPOUNDS WITH MIXED COVALENT AND IONIC CROSSLINKS

	IIIA	IIIB	IIIC	IIID	IIIE
NR[a]	100	100	—	—	—
XNBR[b]	—	—	100	100	—
HNBR[c]	—	—	—	—	35
XHNBR[d]	—	—	—	—	65
Antioxidant	1	1	0.5	0.5	0.5
Zinc oxide	20.5	20.5	7.5	7.5	—
N110	45	—	—	40	—
Methacrylic acid	20.5	20.5	—	—	—
Dicumyl peroxide	1–3.2	0.5–4	0.2–1.5	0.2–5	0.7–4.5

[a] SMR-L.
[b] Nipol 1072-EP (Nippon Zeon Co.).
[c] Zetpol ZPL-2020 (Nippon Zeon Co.).
[d] Zetpol ZSC-2295 (Nippon Zeon Co.).

of samples in flowing water pumped from a depth of 6 meters off the coast of Key West, Florida.

RESULTS AND DISCUSSION

RECOVERABLE ENERGY

At least for small strains and thus linear behavior, the elastic (stored) energy is proportional to the equilibrium modulus[1]; moreover, all rubber elasticity theories indicate that this modulus is directly proportional to the crosslink density. Hence, even at large deformations, for which stress is no longer directly proportional to strain, one still expects a monotonic increase in recoverable energy with increasing concentration of network junctions.

On the other hand, it is well known[8,11] that the failure properties of rubber exhibit a maximum as a function of crosslink density. Beyond the low levels necessary for mechanical integrity of the network, further crosslinking occasions embrittlement due to the loss of energy dissipative mechanisms. Such mechanisms underlie the strength of an elastomer, primarily by alleviating stress concentration. The decrease in an elastomer's durability with increasing modulus is seen in measurements of tensile strength, fatigue life, tear resistance, etc., although different failure properties differ in their quantitative dependency on crosslink density. In order to avoid excessive creep, practical elastomeric materials have crosslink densities well past the level corresponding to the maximum in failure performance. Thus, a compromise invariably exists between the modulus and durability of an elastomer. Achieving higher levels of stored energy necessarily means a reduced mechanical lifetime.

Selection of a material for energy storage thus involves determination of the elastomer having the most favorable relationship between recoverable energy and failure properties. The present study focussed on three material variations: (i) the polymer type, particularly with respect to capacity for strain-induced crystallization, (ii) the mechanical lability of the crosslinks (e.g., covalent versus ionic junctions), and (iii) the extent of filler reinforcement. Although fatigue life and the other failure properties will differ in the details of their dependence on crosslink density, only tensile strength was assessed for the initial screening described herein.

In Figure 2 are shown representative results for the dependence of tensile strength on recoverable energy. These data reflect the general trend that the elastomers divide into two categories, covalently crosslinked elastomers having substantially worse properties than those in which a portion of the crosslinks are ionic (e.g., zinc salts of carboxylic acids). This
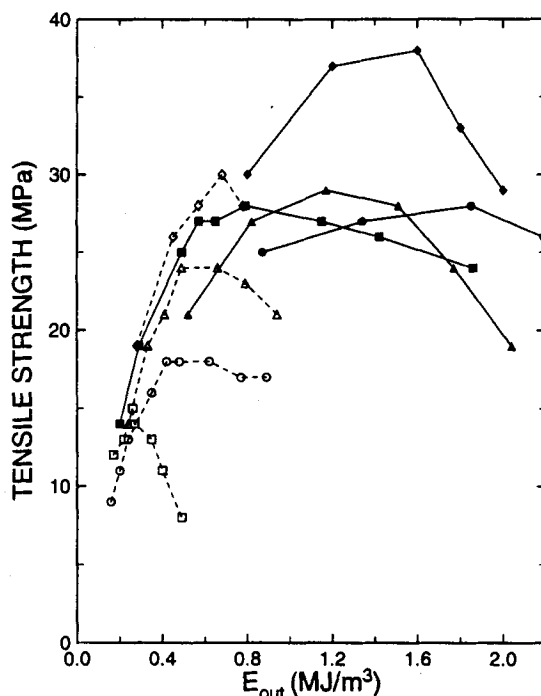
FIG. 2.—Representative results for the variation of tensile strength with the recoverable energy obtained at 100% elongation for compounds of varying crosslink density. The solid curves correspond to elastomers containing ionic crosslinks (IIIB - ▲; IIID - ■; IIIA - ●; IIIE - ◆), while covalently crosslinked rubbers are denoted by the dashed lines (IA - □; IIC - ○; IIB - △; IIE - ◇).

result reflects the lability of the ionic linkages.[12] At low strain the total crosslink density is high, yielding high modulus and recoverable energy. At higher strains, particularly approaching the point of failure, the mechanically labile ionic bonds dissociate. This alleviates stress, delaying macroscopic rupture. Since significant bond dissociation only occurs at stresses near the point of rupture, and moreover the ionic crosslinks can reform upon removal of the stress, high recoverable energy is reobtainable. Effectively, the concentration of ionic crosslinks is strain dependent in an advantageous fashion.[13] To a much lesser degree, this same mechanism accounts for the higher strength of rubber networks with polysulfidic linkages in comparison to peroxide cured rubbers, in which the carbon–carbon bonds comprising the junctions are impervious to stress.[14,15]

The mechanical dissociation of the ionic bonds (which can also be effected thermally[16]) is reflected in a substantial energy loss accompanying reversing deformations. This is illustrated in Figure 3, in which the hysteresis for cyclical deformation of an ionically crosslinked elastomer greatly exceeds that for a covalently crosslinked compound having the same recoverable energy. Thus, increasing the proportion of covalent bonds in the network lowers the hysteresis. Elastomers containing ionic crosslinks were always observed herein to have higher hysteresis than the corresponding rubbers with only covalent linkages (Figure 4). While a preferred compound for energy storage applications would offer the most recoverable strain energy for a given strength, the efficiency of the device will suffer if there is too high a proportion of ionic crosslinks. From measurement of the modulus change after extraction of the zinc ions with mineral acid, it was estimated that in Compound IIIB one-third of the crosslinks were ionic.

It is commonly accepted that hysteresis is responsible for the "toughness" of elastomers. Quantitative relationships between hysteresis and various failure properties have even been
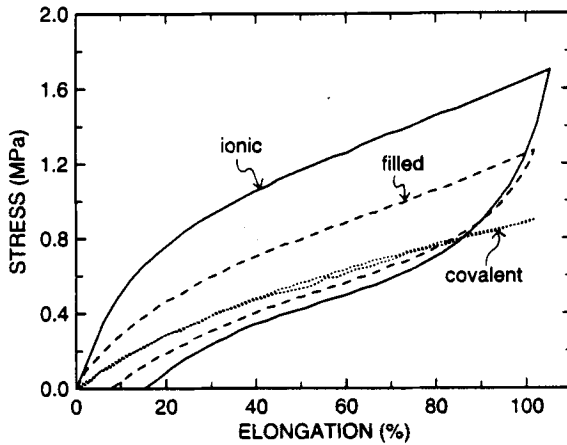
FIG. 3.—The mechanical hysteresis for NR extended to 100% and immediately retracted: dotted line - Compound IA (covalent crosslinks, no carbon black); dashed line - Compound IIA (covalent crosslinks and 45 phr N110); solid line - Compound IIIB (mixed ionic and covalent crosslinks without carbon black). All three elastomers yield equal recoverable energy; however, the strain energies necessary to achieve 100% extension are very different.

proposed.[17-20] Herein it was generally observed that for a given compound, systematic alterations in hysteresis, for example from changes in crosslink density, effected systematic changes in tensile strength (*viz.* Figure 2). However, for the ionically crosslinked samples taken *in toto*, there was no correlation between these two properties (Figure 5). The elastomers containing only covalent crosslinks exhibited a weak proportionality between hysteresis and strength, about which individual samples exhibited large scatter (Figure 5). The tenuous connection between hysteresis and strength means the former is of importance for the launcher application only because it reduces the efficiency of the energy storage.
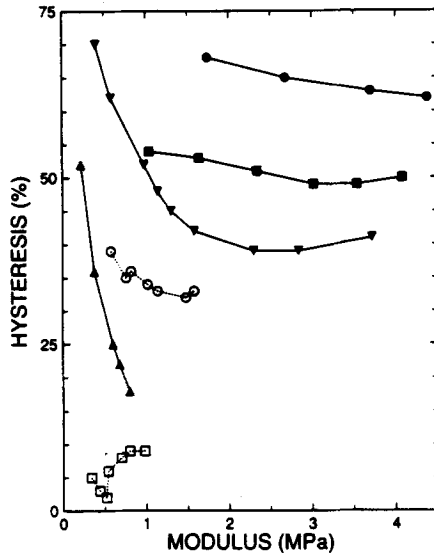

FIG. 4.—The hysteresis measured at 100% elongation for NR with 0 (squares) and 45 phr (circles) N110 carbon black. The unfilled symbols denote covalent crosslinks, while the filled symbols refer to compounds with both covalent and ionic linkages. Also shown is data for ionically crosslinked NBR unfilled (▲) and with 40 phr N110 carbon black (▼).
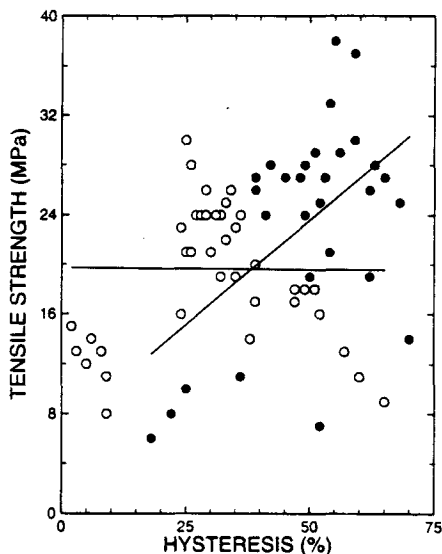
FIG. 5. — The relationship between tensile strength and hysteresis (measured at 100% elongation) for various elastomers containing covalent (O) or mixed covalent and ionic crosslinks (●). The lines are the linear least squares fits to the respective data sets. There is no correlation between hysteresis and strength for the ionically crosslinked rubbers, while the covalent elastomers show a weak proportionality between these two properties.

CREEP

The lability of ionic crosslinks, which underlies their better mechanical properties, is a potential liability beyond hysteresis considerations. While reversible crosslink dissociation at extensions near to failure is desirable, even low stresses applied for an extended duration may disrupt the network bonds, with the presence of a diluent having some ionic strength exacerbating the problem. Since the torpedo launcher is intended to be submerged in seawater, this aspect of the performance of ionically crosslinked rubber was investigated.

Creep resistance is particularly important when the elastomeric launcher is to be maintained in a pressurized state. There are two aspects to creep which must be considered: time dependent, reversible creep transpiring under load, and permanent deformation effected by mechanical stress. The former may only preclude "delivery-ready" operation, while the latter results in a permanent decline of the launcher's effectiveness.

In Table IV a comparison is made of the permanent set developing in three unfilled elastomers, one covalently crosslinked, the other two containing some ionic crosslinks as well. Only the latter develop significant permanent set, which is worse in the presence of seawater. This reflects dissociation of the ionic junctions, whose reformation in the strained state

TABLE IV

PERMANENT SET AFTER 100% ELONGATION AT RT (SAMPLE THICKNESS = 1.5 MM)

	8 days in air	8 days in seawater[a]	One year in seawater[b]
IA	0	0	—
IIIB	5%	15%	—
IIIE	5%	15%	35%

[a] In laboratory.
[b] Coastal water in Key West, FL.

prevents complete recovery of the original dimensions after removal of the stress; that is, mechanical equilibrium is now associated with a longer specimen length. This phenomenon is intentionally utilized in "double-network" rubber technology.[21,22] The stress-induced deterioration of ionically crosslinked rubber is also seen in the decrease in recoverable energy after immersion in seawater (Figure 6). If there is no strain during the seawater exposure, the elastic energy measured subsequently is maintained. Note from Table IV that the decline in properties continues at least through one year of immersion. The water absorption after one year in seawater was equivalent (2% by weight) for the covalently crosslinked NR and compound IIIE containing ionic bonds. This uptake is half the value reported for two years immersion of NR in seawater,[23] indicating equilibrium was not attained.

From data of this type, it is evident that, at least if a stressed state is to be maintained for extended time periods, ionically crosslinked rubbers are ill-suited for energy storage applications. The problem is aggravated when the material will be exposed to seawater or other polar diluents. In contrast to the deterioration observed for the ionically crosslinked compounds, the covalently crosslinked rubbers should be relatively impervious to seawater. For example, sulfur vulcanized NR was found to survive with undiminished properties after four decades submersion in costal waters.[24,25] Although minor deterioration of some synthetic rubbers has been reported,[26,27] the expectation is that the network structure of sulfur or peroxide cured rubbers is unaffected by seawater.

In the present study it was found that, absent any carbon black, the covalently crosslinked elastomers exhibited no permanent set or loss of energy storage capability after prolonged deformation, either dry or in seawater. For those materials containing carbon black, as illustrated in Figure 7, stretching for an extended duration results in some decrease in recoverable energy (as subsequently measured on relaxed samples). The decrease, and the accompanying increase in sample length, are permanent, although not as severe as found for the ionically crosslinked materials. This behavior was unaffected by the presence of seawater.

After one year in seawater off the coast of Florida, compound IIF exhibited some pitting of its surface, apparently the result of biological attack. It is known that several microorganisms found in untreated water can cause biodegradation of rubber.[28] Although the deterioration was limited to the surface of the elastomer, this aspect of the performance of a launcher material is currently being studied.

In addition to the permanent set and permanent loss of energy storage capacity described above, there is a second form of creep which, although fully reversible, can impact on a launcher's performance. If the rubber is kept deformed for a period of time, creep will cause
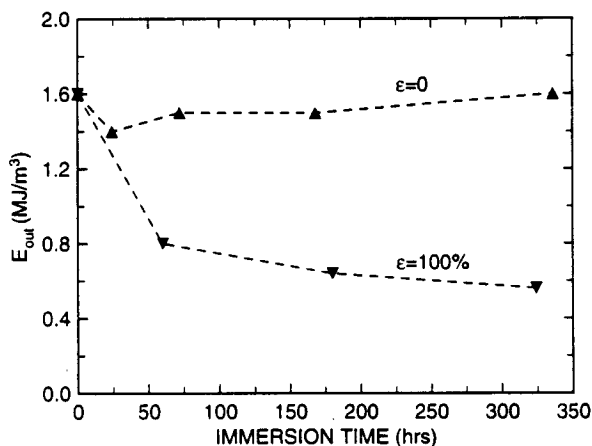

FIG. 6. — The change in recoverable energy (measured at 100% elongation on relaxed samples) for Compound IIIE maintained unstrained (▲) and at 100% extension (▼) in RT seawater for the indicated time.
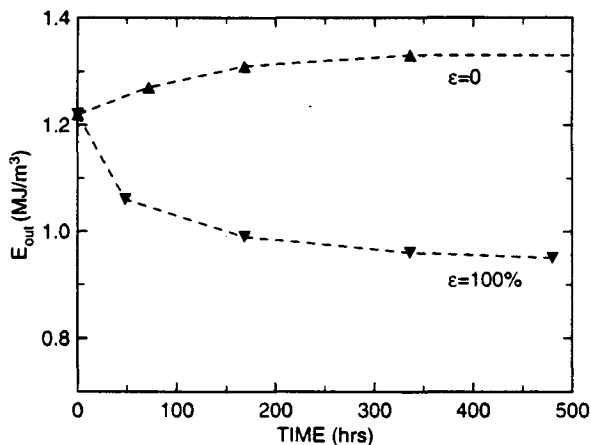
FIG. 7.—The change in recoverable energy (measured at 100% elongation on relaxed samples) for Compound IIF maintained unstrained (▲) and at 100% extension (▼) in air at RT for the indicated time.

a decrement in the propulsion energy immediately available. This loss can be completely recovered by retraction and re-extension of the elastomer, provided there has been sufficient time for recovery. However, this reversible creep limits "delivery-ready" operation of an elastomeric launcher.

The obvious means to minimize reversible creep would seem to be to minimize the duration of the stressed condition; this must be true for linearly viscoelastic materials. Limits for linearity are reputed to extend over a wider range for cross-linked rubber than for most materials,[29] and at the intended extensions (ca. 100%), elastomers appear "linear" in many experiments.[30,31] Notwithstanding this, neat cross-linked rubbers do exhibit subtle deviations from linear viscoelasticity at strains below 100%. A conspicuous example is the hysteresis for elastomers elongated to ca. 100% exceeding the amount predicted from stress relaxation experiments.[32-35] Another manifestation of nonlinear viscoelasticity is creep for cyclically applied stress sometimes exceeding that for a constant stress of the same magnitude.[36,37] These anomalies have been observed for both filled and gum natural rubber.

In Figure 8 the creep strain measured for Compound IB is shown for a constant applied stress of 1.22 MPa, along with the creep resulting from the same stress intermittently applied. At least when the periodic creep time exceeds the recovery time (i.e., duty cycle ≥ 50%), more creep occurs for intermittent stress than for constant stress. This is shown in Figure 9 for Compound IB (unfilled, covalently crosslinked natural rubber). The exact stress required to induce nonlinear behavior depends on the fraction of the cycle time for which the stress is applied.

Contrary to these results for NR, noncrystallizing SBR (Compound IC) was always found to creep more when statically loaded than when the stress was cyclically applied. This suggests that the mechanism giving rise to the reduced creep under constant stress is strain induced crystallization, as suggested previously.[36,37] This hypothesis is consistent with our finding (Figure 10) that the relaxation time of the NR markedly increases at strains for which the creep anomaly is observed. The increase in the time over which the stress decays is associated with the onset of crystallization.[38-40] Note in Figures 8 and 10 that effects arising from orientational crystallization appear at much lower strains for pure shear deformations (ca. 50%) than is generally found for uniaxial extension.[22,36,41]

SUMMARY

Its capacity for rapid recovery from large deformation allows even soft rubber to function as a high-power energy storage medium. The available energy and durability of such a
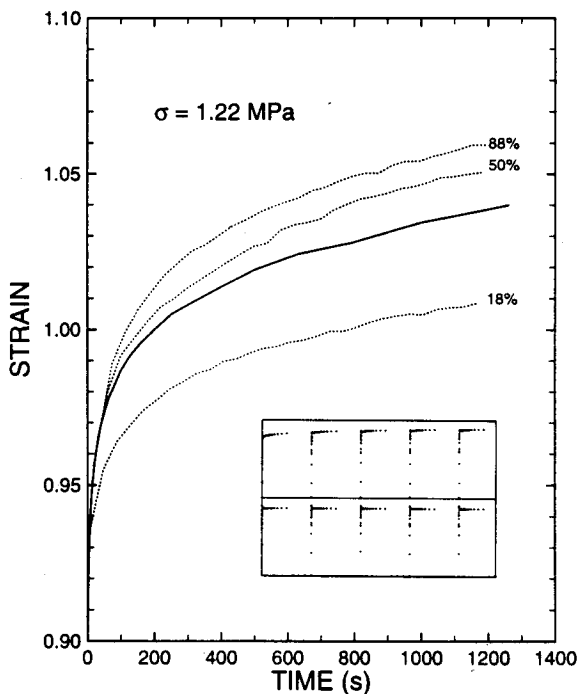
FIG. 8.—The creep strain of Compound IB for a static stress of 1.22 MPa (solid line) and for the same stress intermittently applied (dotted lines); for the latter, a cycle time of 30 s was used, with the indicated duty cycles. The inset shows the force (lower) and displacement (upper) for a 50% duty cycle (*i.e.*, 1.22 MPa stress for 15 s, followed by 15 s of zero stress).
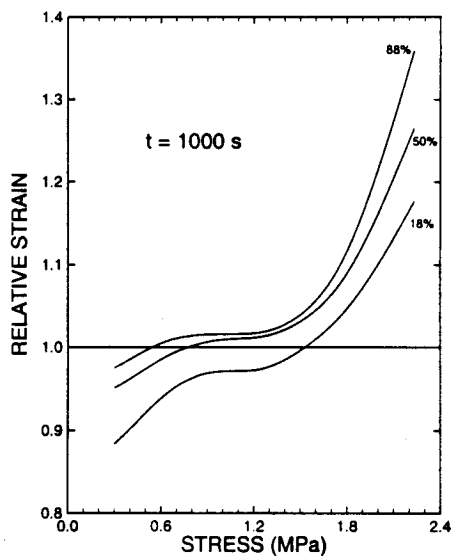

FIG. 9.—The creep strain of Compound IB after 1000 s for cyclically applied stresses; that is, the stress was repeatedly applied for the indicated portion of a 30 s time period, followed by zero stress. The data has been normalized by the corresponding strain obtained for a constantly applied stress of the same magnitude; hence, relative strains greater than unity imply more creep when the load is intermittent than when it is constant.
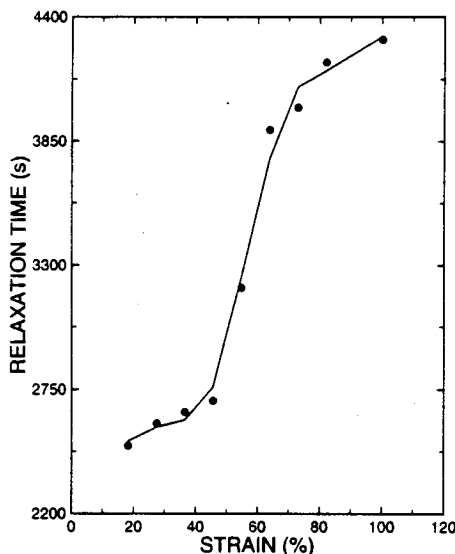
FIG. 10.—The time required for cessation of stress relaxation for Compound IB deformed in pure shear to the indicated strain. The large increase at strains beyond 50% (corresponding to stresses greater than 1 MPa) reflects the onset of orientational crystallization.

device are maximized by the presence of mechanically labile crosslinks in the rubber's network; however, this limits the duration over which the elastomer can be maintained in a stretched stated. While the performance is usually better if the elastomer is unstrained most of the time, at least for NR-based compounds, rapid cyclical operation can cause substantial creep, exceeding that transpiring under constant pressure.

ACKNOWLEDGEMENTS

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