

MECHANICS OF ELASTOMERS AT HIGH TEMPERATURES

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ABSTRACT

"Among elastomers commercially available, several are reasonably stable for prolonged periods at temperatures above 200°C (392°F); but at such temperatures, their strength characteristics are inadequate for many present day applications." This statement by Thor Smith¹ in 1962 is just as true in 1980, pointing out that the polymer industry, if not mature, is certainly on a broad plateau. The intention of this paper is to present to the engineering oriented individual a review of this technology in which books are compressed into paragraphs. My apologies are given to the serious students of polymer chemistry.

INTRODUCTION

Rubber and plastics, technically called polymers, are a predictable class of engineering materials produced by an industry employing over half of the country's chemists and chemical engineers. The building blocks are simple chemical units, combined by polymerization to create a long chain molecule. The final product can have physical properties ranging from a tough solid to the familiar elastic band.

POLYMER STRUCTURE AND SIZE

A flexible, long chain molecule is the basis of polymer chemistry. Nielsen², in a recent address noted there are three general categories of polymers:

1. Rubbery - materials with the glass transition temperature, T_g , below room temperature.
2. Rigid - crystalline materials with the glass-transition temperature above room temperature i.e., polystyrene, polycarbonate, polymethyl-methacrylate.
3. Partially crystalline - glass-transition temperature above or below room temperature= e.g., polyethylene, polypropylene, nylon, PTFE.

The process of vulcanization (cross linking) converts the individual polymeric chains into a three-dimensional network structure. High molecular weight polymers have a higher amount of molecular entanglements (understandable in view of Figure 1) created by molecular intertwining. Additional permanent entanglements (Figure 1) are created by crosslinking and these entanglements are almost equivalent to crosslinks.

The number of entanglements (or molecular weight between entanglements- M_c) is a function of the chain symmetry. Ethylene-propylene rubber has about 100 chain backbone carbons (not structural units) between entanglements. Polystyrene, a bulky molecule has about 350 chain backbone carbons between crosslinks. Chain entanglements are a substantial contribution to improving such properties as tensile strength, elongation, and compression-set.

The theory of rubber elasticity states: "the retractive force resisting a deformation is proportional to the number of network-supporting polymer chains per unit volume of elastomer." A supporting chain is a segment of polymer backbone between junctures (crosslinks). Crosslink density affects all vulcanizate properties. Figure 2 represents an idealization on the effect of crosslink density (130mm x 10 is 13 angstroms (Å)), representing two typical polymer segments (natural rubber, neoprene, polybutadiene, and EPM). Atypical rubber would have a crosslink every fifty (50) structural units.

EFFECT OF TEMPERATURE ON THE
PROPERTIES OF ELASTOMERS

All uncrosslinked polymeric materials are rubbery at some temperature above their glass-transition temperature, as temperature is the mobile energy of atoms and molecules. As shown in Figure 3 (from Reference 3), amorphous and crystalline polymers respond differently when raised in temperature from a super-cooled state. Considering first the amorphous (rubbery) polymer, this plot of specific volume versus temperature shows a change in a slope at a particular temperature called the glass-transition temperature, T_g . This phenomenon is universal to all elastomers and occurs when the fraction of empty space (free volume) in a polymer is about .025 (2-1/2%). It is of great significance in defining polymeric physical property changes accurately up to 100°C over T_g by using the Williams, Landel, and Ferry equation. Crystalline polymers do not show this slope change, as the forces maintaining the crystalline state override the increase in molecular mobility. The crystalline domains finally melt as evidenced by a pronounced increase in volume with no temperature change. It is in this "indistinct region" that crystalline (plastic) materials have rubbery capabilities that might be utilized in designing.

Smith¹ in his basic work on ultimate tensile properties, used Figure 4 to prove the validity of his ultimate property data on a fluoroelastomer. Smith notes that, in general, superposition should be applicable to data obtained on amorphous elastomers.

In more recent work, Landel⁴, shows an interesting series of fluoroelastomer stress - strain curves (Figure 5) plotted logarithmically. The curves, progressively displaced upward as the temperature is decreased, are terminated at a point representing rupture. The family of curves represent a decreasing temperature run at one strain rate with the temperature normalized to Kelvin.

FAILURE CONCEPTS

Having built the polymer, added the necessary crosslinks, and related percent crystallinity to physical properties, we now study failure modes. Smith,^{5,6} in some landmark work, developed his concept of ultimate properties, a major contribution. Earlier, Williams, Landel, and Ferry, with their WLF equation, pointed out that all amorphous polymers, irrespective of their chemical structure, will exhibit similar viscoelastic behavior at equal temperature intervals (T-T_g) above their respective glass-transition temperatures. Smith has added to this concept by showing that the ultimate tensile properties of a non reinforced, amorphous, crosslinked elastomer can be characterized by a failure envelope which is independent of time (strain rate) and temperature.

Figure 6 (from Reference 1) schematically illustrates the general effect of strain rate and temperature on the tensile, stress-strain properties of amorphous elastomers. The lines originating from 0 represent stress-strain curves determined at various strain rates and temperatures. The envelope ABC connects the rupture points. The rupture point moves counterclockwise around the "failure envelope" as either the strain rate is increased or the test temperature is decreased.

OA represents classical stress-strain behavior. DE and DT represent stress relaxation and creep terminating in a equilibrium state. The dotted lines from G represent stress relaxation and creep terminating in a potential rupture mode.

The stress-strain curves represent the nonlinear viscoelastic response of an amorphous elastomer to an imposed strain; increasing directly proportional to time.

Smith's next approach was to run a series of non-reinforced (gum) vulcanized elastomers and plot the log of stress and strain at break as shown in Figure 7 (as opposed to the previous Figure 5 which was plotted as the log of stress versus strain).

The data points reflect 10 strain rates (from 0.02 to 20 inches per minute) for each of the nine temperatures noted. Again, the familiar parabolic curve is apparent. The data scatter in the low temperature area is understandable in light of the T_g curve (figure 3); the rubbery characteristic is becoming "blurred" in this temperature range due to micro crystallinity appearing.

Another major contribution by Smith¹ was the development of a method for analyzing curves such as Figure 8, to separate the time dependence of stress from its finite strain dependence. By plotting the log of stress versus the log of time at a fixed strain, it can be determined whether the elastomer is being tested at equilibrium (indicated when the slope of such a plot is 0). The value derived is called equilibrium modulus, E_e. A negative slope indicates viscous relaxation or Chemical degradation.

Smith now points out, "Failure envelopes for elastomers which have different values of the equilibrium modulus can be compared by constructing plots of

$$\text{LOG } (\lambda_b (X) \sigma_b/E) \text{ versus } \epsilon_b$$

as shown in figure 8." (The log of extension ratio at break times stress at break divided by equilibrium modulus plotted against log of strain at break.)

The fluoroelastomer curve data is taken from Figure 7, and the silicone, butyl, and natural rubber data is from Smith's basic article. Smith again points out that for elongation up to 150% (log 1.50 ≈ 0.18), there is excellent correlation, indicating there is little difference in the ultimate properties of elastomers, with the exception of effects resulting from crystallization indicated by the natural rubber curve. The difference in the two butyl formulations is due to the degree and type of crosslink in each.

STRESS AND STRAIN

The physical properties are predicted by polymeric structure, the crystalline polymers requiring more constants than the amorphous elastomers. In classical theory of elasticity for elastic solids, stress is proportional to strain in small deformations but independent of the rate of strain. Polymers, being nonlinear, viscoelastic materials have a behavior intermediate between an elastic solid and an ideal fluid. We are considering polymers in their amorphous (non crystalline) phase in this discussion and therefore, only have to consider three elementary types of strain in which the stress is related to external forces:

- a. Simple tension
- b. Simple Shear
- c. Hydrostatic compression

a. Tension, the mechanical behavior defined as Young's modulus E , the ratio of tensile stress to tensile strain.

b. Shear, rigidity or shear modulus G , is defined as the ratio of shear stress to shear strain.

c. Hydrostatic compression, or bulk modulus B , is defined as the ratio of hydrostatic pressure to volume change per unit volume.

Figure 9 illustrates not only the nonlinear behavior, but the differences in elastic deformability for amorphous polymers (rubber), crystalline polymers (plastics) and metals.

SHEAR MODULUS AND CRYSTALLINITY

Shear modulus, G , a value ranging from 1/3 to 1/4 of Young's modulus, E , is considered a measure of stiffness. In a recent discussion Nielson², illustrated shear modulus as a function of percent polymer crystallinity. The predicted line was based on the logarithmic rules of mixtures, and the curved (actual) line is based on actual values of over 100 polymers having varying present crystallinity. A value of 10^{10} dynes/cm² for 100% crystallinity (10^{10} dynes/cm² = 145,000 psi) is approximately equivalent to 1/3 the Young's modulus of 3.5×10^3 MPa (500,000 psi). Conversely, a typical low durometer rubber formulation, essentially amorphous, has a shear modulus of 53 psi which correlates with Nielsen's value of 3×10^6 dynes/cm² (44 psi). What Nielsen is saying is one of the main thrusts of this article--percent polymer crystallinity is a controlling factor of the physical strength of a non-crosslinked crystalline polymer.

Shear Modulus Versus Crystallinity - Figure 10 represents a plot of shear modulus versus temperature for four different non crosslinked polymers with inherent crystallinity ranging from 0 to 65%. The maximum value of 4×10^{10} dynes/cm² represent the low temperature glassy state. Increasing temperature moves the polymer into the leathery part of the shear modulus curve. The relatively level part of the curve is the rubbery plateau with shear modulus values dictated by % crystallinity. The precipitous drop-off in shear modulus is due to disappearance of the crystalline domains when their melting point is reached.

The Rubbery Plateau - The rubbery plateau of non-crosslinked polymers can be extended with higher molecular weight polymers. Figure 11, illustrating a typical amorphous non-crosslinked polymer, reflects the shear modulus values for low or non-crystalline polymers as noted in Figure 10. The increased molecular weight increases the time before onset of melting, due primarily to increased physical chain entanglements which act as pseudo-crosslinks.

Effect of Crosslinking - Contrary to non-crosslinked polymers which eventually flow due to melt disentanglement, crosslinking creates a stable three-dimensional structure. The rubbery modulus is maintained with relatively little change up to the point of thermal degradation. Nielsen again points this out in Figure 12, also illustrating shear modulus versus molecular weight between crosslinks. A typical nitrile elastomer crosslinked about every 50 polymeric structural units would have an M_c value of 8000 resulting in a shear modulus of 145 psi, and a Young's modulus of 450 psi - familiar numbers. The highest values might be representative of phenolics, polyimides, etc., and the mid-range values could be epoxies, polyphenylene sulfide or similar materials.

What is Fracture? - Gent⁷ comments, "Fracture is a highly localized and selective process--only a small number of those molecules making up a test piece or component actually undergo rupture, while the majority are not affected. For example, of the 10^{26} chain molecules per cubic meter in a typical elastomer, only one in 100 million (i.e., those crossing the fracture plane about 10^{18} per square meter) will be definitely broken. Moreover, these will not all break simultaneously, but will rupture successively as the fracture propagates across the specimen at a finite speed."

Fracture sites are inherent in all solids. For viscoelastic materials such as rubber, there is a stress amplification factor that causes local concentrations well in excess of the mean applied stress.

CHEMICAL DEGRADATION BY WATER

Chemical degradation of certain polymers can occur by a depolymerization mechanism referred to as hydrolysis (literally translated--"cleavage by water"). Hydrolysis can proceed very rapidly if the polymer is water soluble. Although both acids and bases catalyze the reaction, crystallinity often precludes the attack except at the surface.

The basic hydrolysis mechanism is the breaking of a polymer chain, the water molecule, dissociating into a hydrogen (-H) and a hydroxyl (-OH), with each group "capping" either side of the broken polymer chain. This creates a lower molecular weight species which sometimes goes back to the monomeric state.

Table 1 is modified from Schneberger's⁸ article. Carbon-carbon backbone polymers are very stable as a rule; however, polyacrylates thru the side groups strongly attract water.

PHYSICAL CHANGES - STRESS RELAXATION

When a crosslinked elastomer is held at a constant deformation (strain), the stress decreases as a function of time, as the polymeric network reaches equilibrium. Assuming no chemical effect, the rate is approximately linear with the logarithm of time. As Figure 13 illustrates, in a "reactive" situation (chemical attack), the reaction proceeds at a very rapid rate, with a noticeable change within twenty-four hours.

Figure 14 is an idealized model - illustrating the difference between creep and stress relaxation, and Table 2 is a summary of major differences between the two viscoelastic processes.

REINFORCED

In our previous discussions of high temperature rupture, we talked only of non-reinforced elastomers. Several elastomers have the ability to form microcrystalline domains on being stressed, in decreasing order, common ones might be natural rubber, neoprene, polybutadiene, butyl and some EPDM. The ability to strain-crystallize gives enhanced tear strength up to certain rates and temperatures. Beyond this point, strength is dependent on viscous characteristics T-Tg, and molecular structure. Figure 15 illustrates fracture energy as function of temperature and tear rate of natural rubber.

The addition of reinforcing fine particle fillers gives remarkable improvements in tear and tensile strength of amorphous elastomers such as SBR, NBR, etc. The reinforcing effect is again restricted to a specific range of rates of tearing and test temperatures, as illustrated by Figure 16, an SBR formulation reinforced with carbon black. These illustrations of a crystallizing and amorphous elastomer point out why the high temperature tensile rupture studies were performed on non-reinforced elastomers. There is an improvement in physical strength at elevated temperature by reinforcing fillers but not nearly as dramatic as noted at lower temperatures.

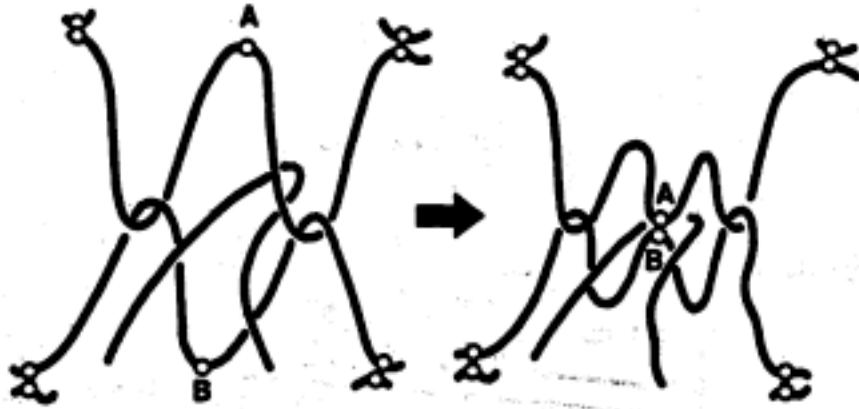
HYDROSTATIC

In the previous discussion of "Stress and Strain," we mentioned hydrostatic compression (bulk Modulus B). There has been considerable interest in this effect because

usage of polymers in submarines, well logging, and underwater cables. Mears et.al.⁹ has done considerable investigation. The referenced article reports the effects of pressures up to 100,000 psi on polyethylene and polypropylene under tensile and compressive loadings. As expected, the effects are predictable, depending on the secondary molecular structure. Polyethylene tends to deform more by shear end necking due to its folded chain secondary structure. Polypropylene (Figure 17) fails by fracture tearing across the cross-section, again predictable from its spiral chain secondary structure. In all cases, the modulus increases, although other properties respond in different ways. Vroom and Westover¹⁰ have set up seven major classifications of polymers according to their responses to increasing hydrostatic pressure.

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Generation of effective entanglements during crosslinking.

Figure 1

Crosslink Density vs. Physical State

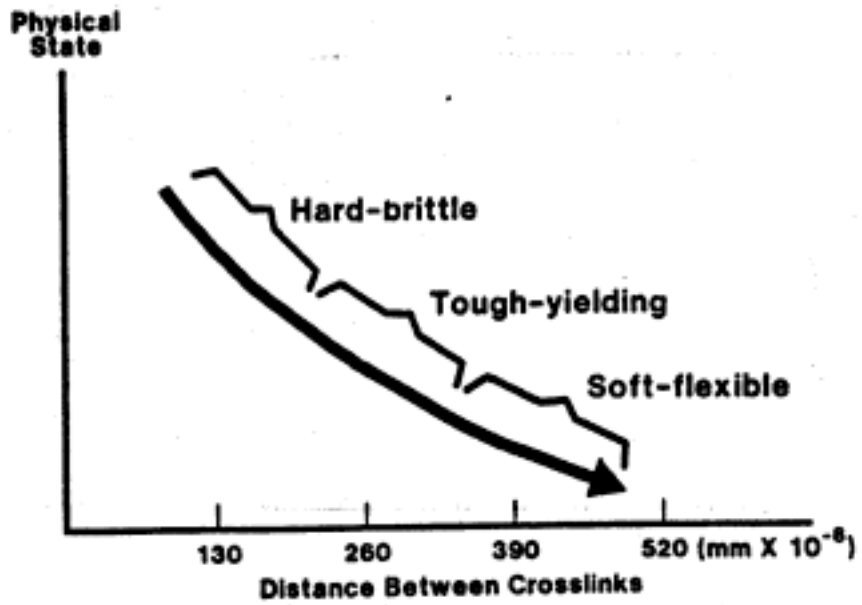


Figure 2

Amorphous & Crystalline Polymers

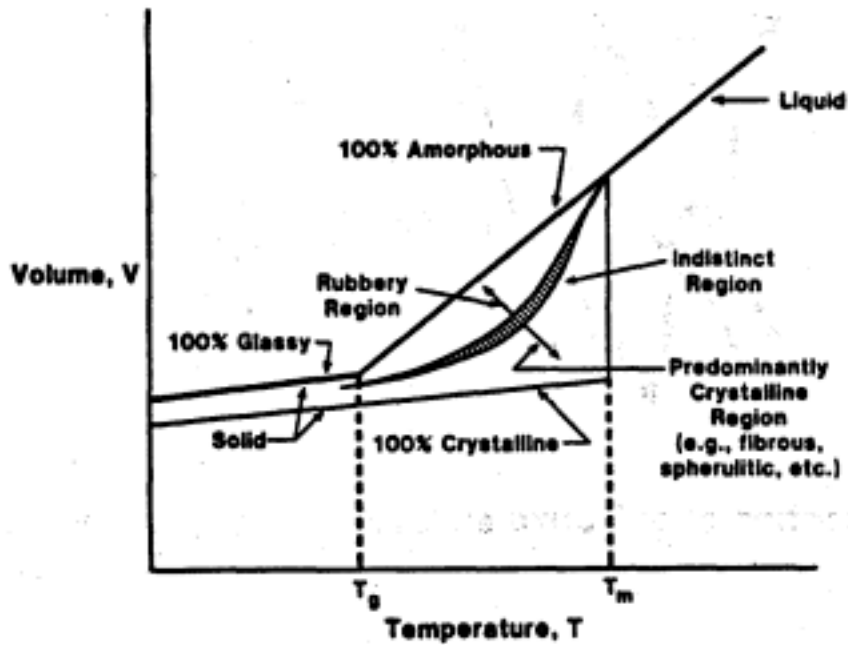


Figure 3

Fluoroelastomer

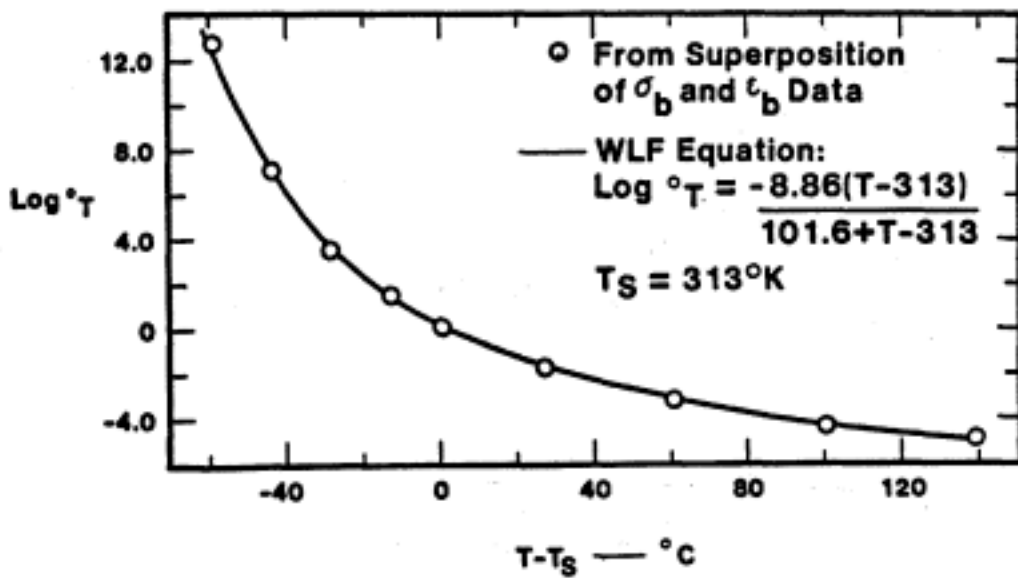


Figure 4

Stress-Strain Curves, Plotted Logarithmically, For a Fluoroelastomer

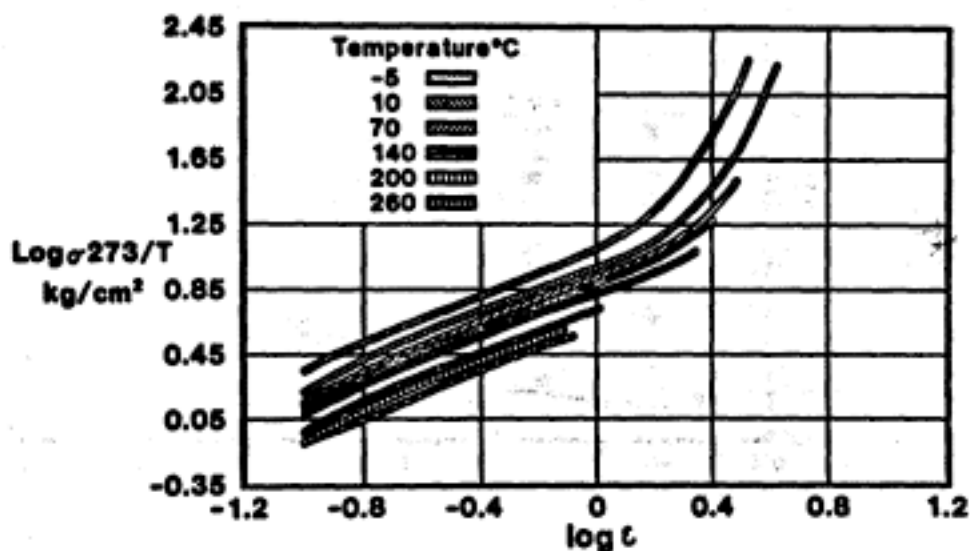


Figure 5

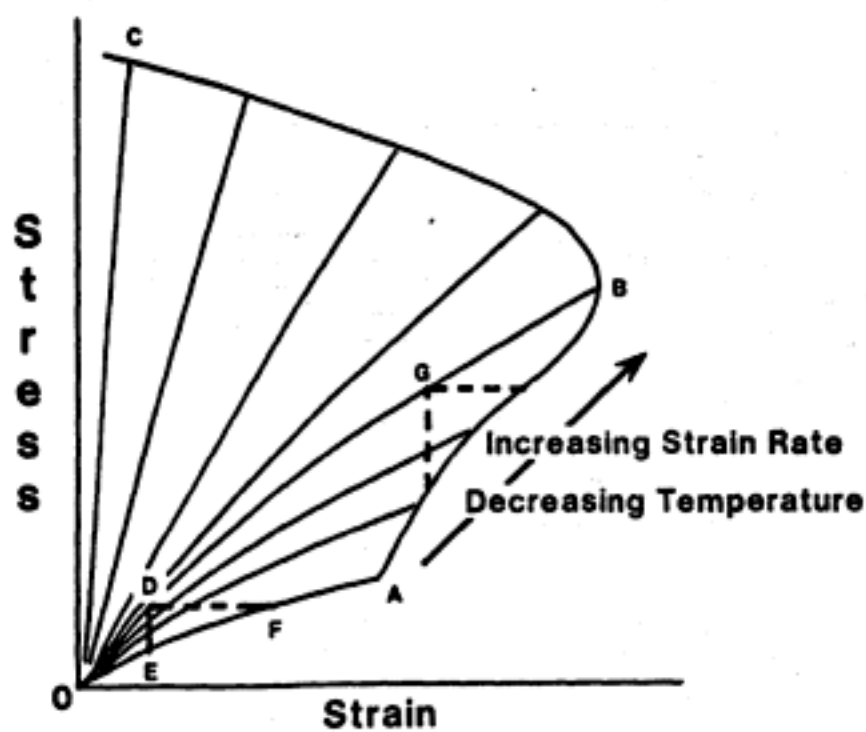


Figure 6. Effect of Strain Rate and Temperature on the Tensile, Stress-Strain Properties of Amorphous Elastomers

Fluoroelastomer Failure Envelope

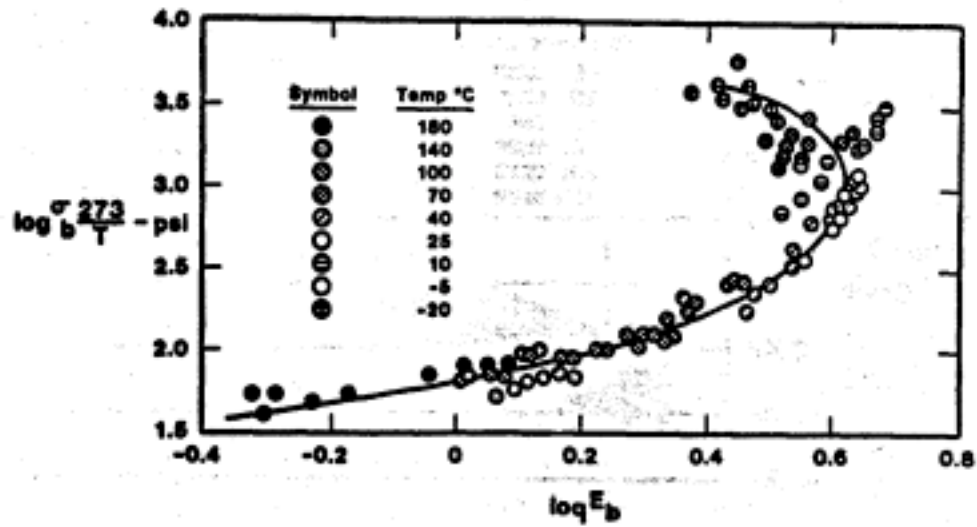


Figure 7

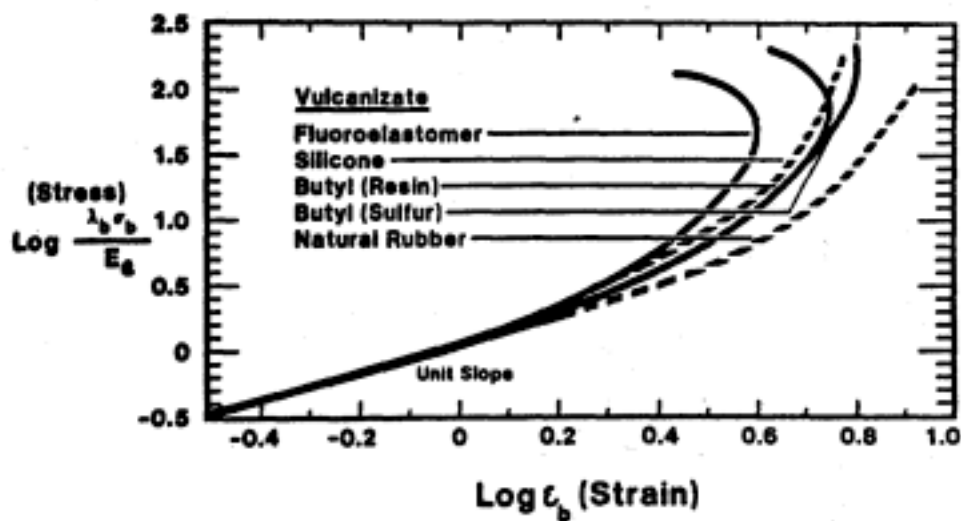


Figure 8. The Log of Stress and Strain at Break For Non-Reinforced Elastomers

Young's Modulus Comparison

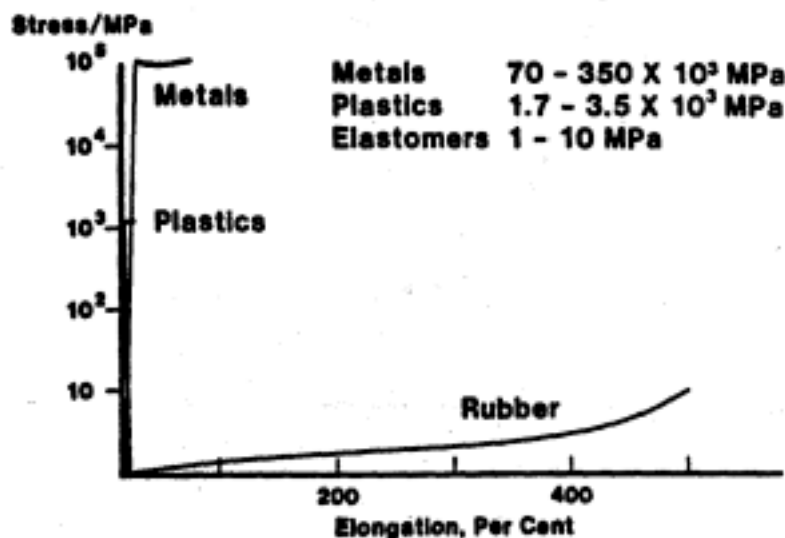
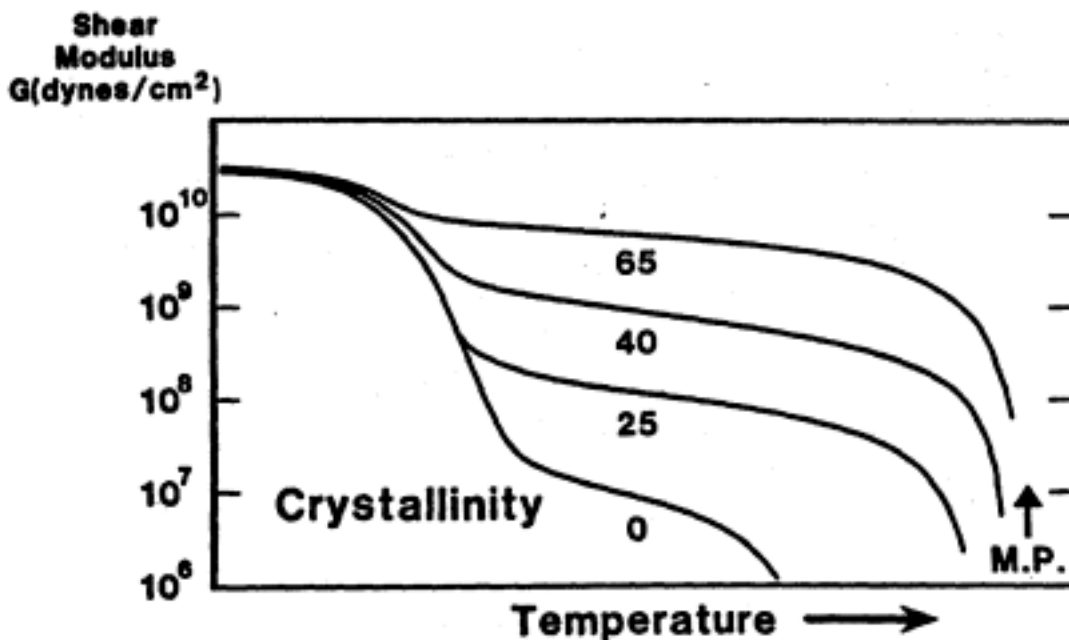


Figure 9



Note: Elastomers Normally Under 30%

Figure 10. Shear Modulus Versus Temperature For Different Crystallinities

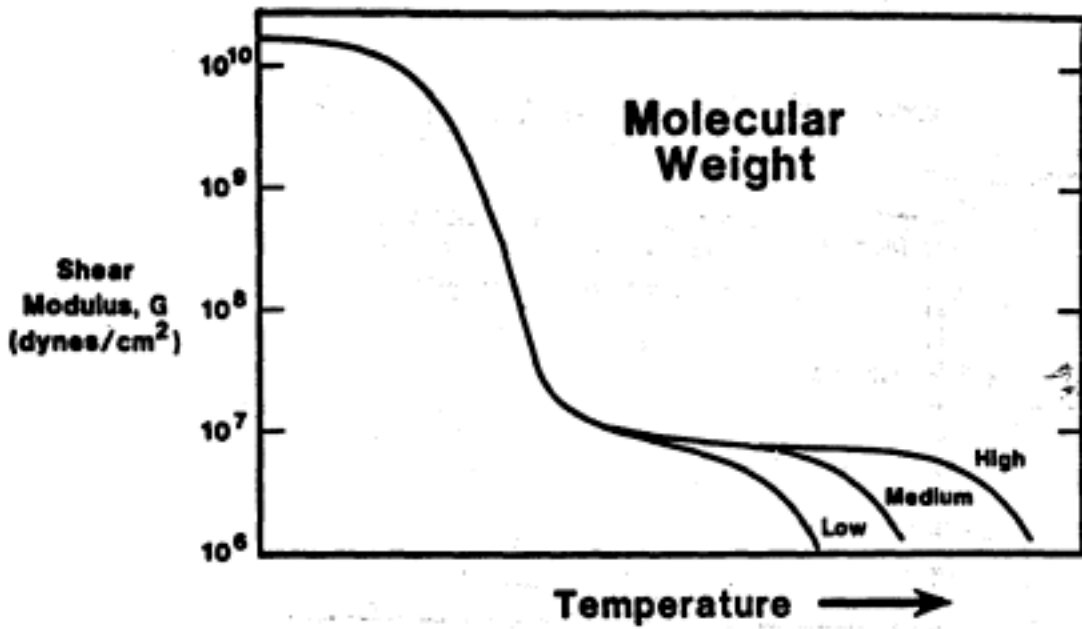


Figure 11. The Rubbery Plateau of Non-Crosslinked Polymers As a Function of Molecular Weight

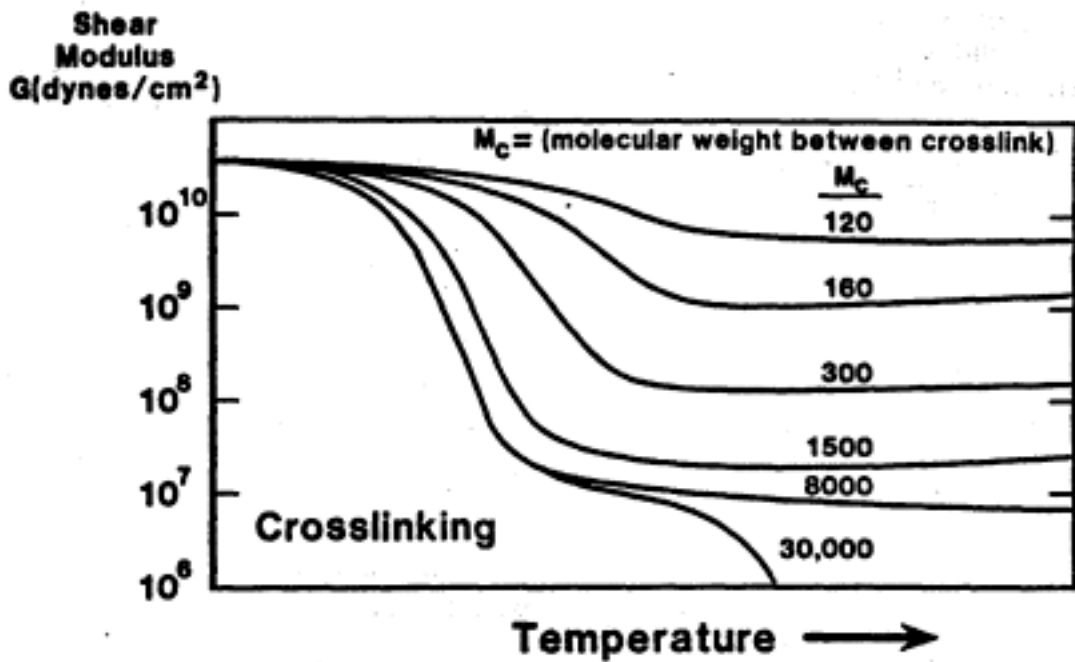


Figure 12. Shear Modulus Versus Temperature for Various Molecular Weights and Crosslinking

Relaxation Characteristics

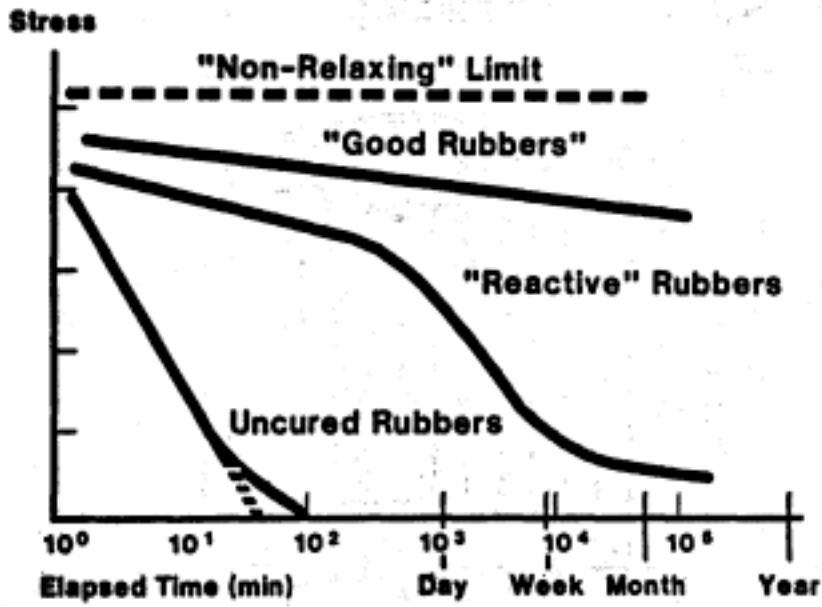


Figure 13

Relaxation Models

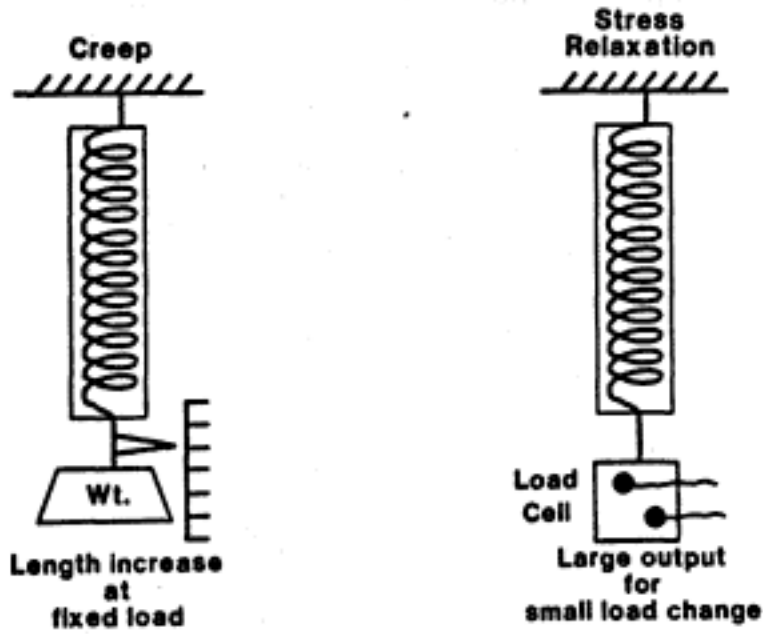


Figure 14

Fracture Energy-G Strain-Crystallizing Elastomer

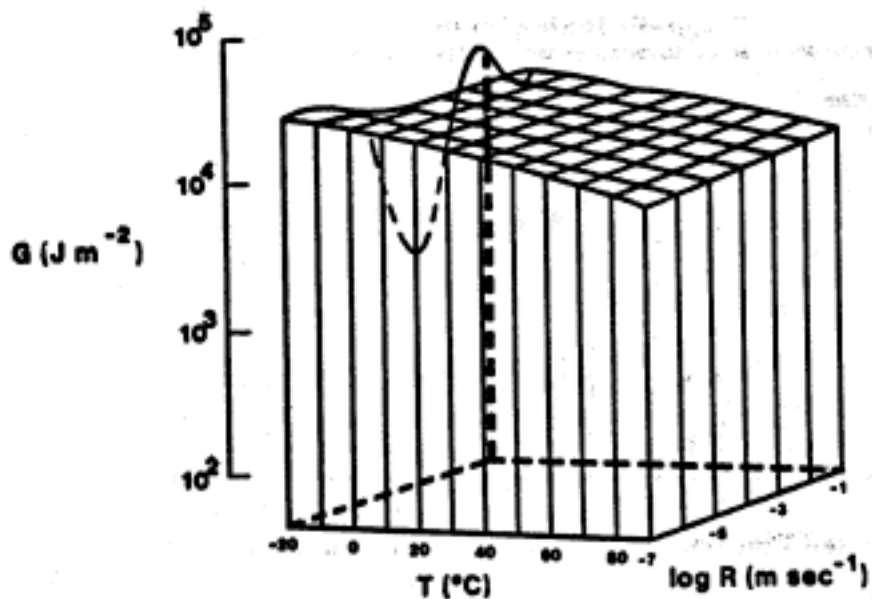


Figure 15

Fracture Energy-G Amorphous Elastomer-Reinforced

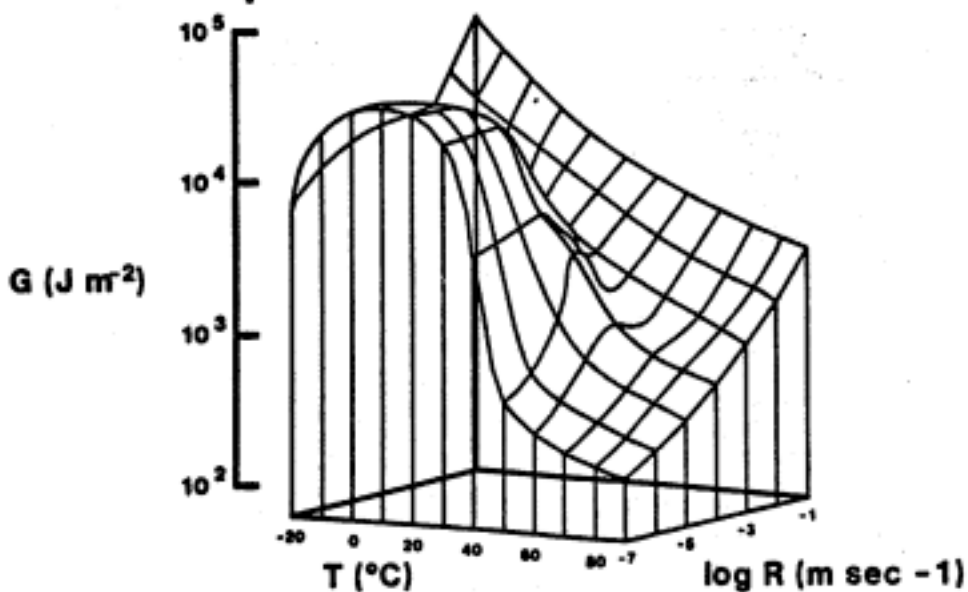


Figure 16

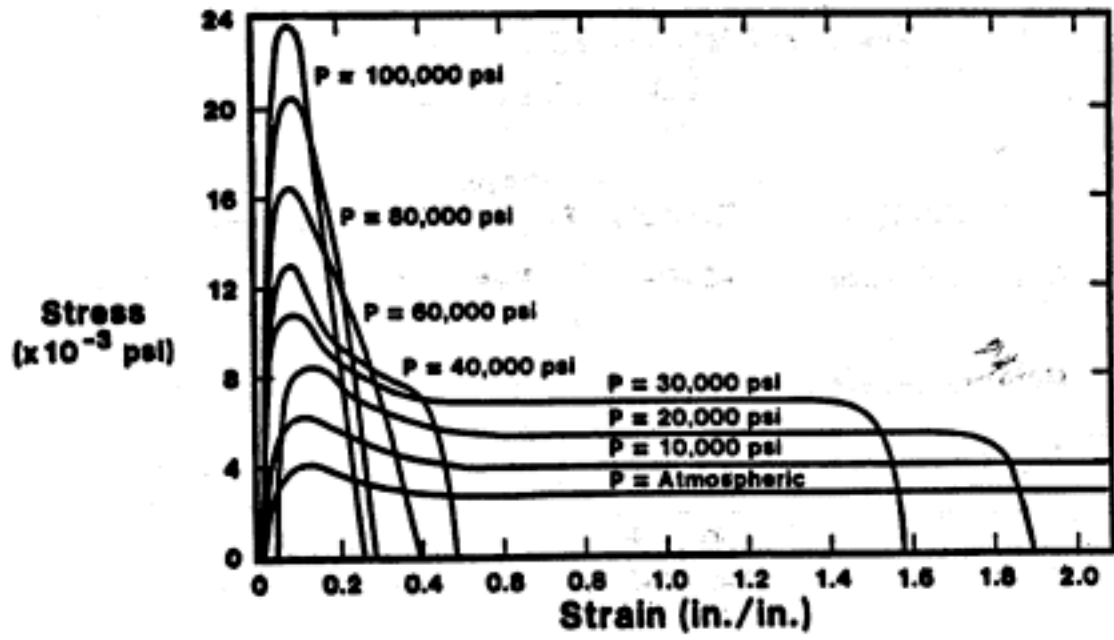


Figure 17. Stress-Strain Characteristics of Polyethylene As a Function of Hydrostatic Pressure

TABLE 1

Relative Resistance of Chemical Bonds to Hydrolysis

Bond	Formula	Water Resistant	Elastomer
Carbon-Carbon	-C-C-	Yes	Most Elastomeric Polymer Chains
Hydrogen-Carbon	-C-H	Yes	All Organic Elastomers
Ether	-C-O-C-	Yes	Urethanes, Epichlorohydrins
Ester	$\begin{array}{c} \text{O} \quad \text{H} \\ \parallel \quad \\ -\text{C}-\text{O}-\text{C}- \\ \\ \text{H} \end{array}$	No	Urethanes, Acrylates
Isocyanate	$\begin{array}{c} \text{H} \quad \text{O} \\ \quad \parallel \\ -\text{N}-\text{C}-\text{O}- \end{array}$	No	Urethanes

TABLE 2

"Relaxation" Phenomena of Elastomers

Creep

- Increase in strain with time.
- Under constant stress.
- A physical reaction.
- Characteristic of the viscous flow of all rubber-like material.

Stress - Relaxation

- Decay of stress with time.
- Under constant strain.
- Of a chemical nature.
- Thru a breaking of primary chemical bonds.