ABSTRACT

This chapter reviews the behavior of a crosslinked elastomer in an engineered design, randomly or continuously loaded (as opposed to regular cyclic loading). Comparable real world service would be energy absorption, sealing applications, or as a load bearing member. For a more complete understanding of the predictable response under load, the chemistry, physics, thermodynamics, and mechanics of elastomers are briefly reviewed in terms of material science. Chemistry is involved in developing the elastomer and crosslinking it to create a usable, three dimensional structure. Physics explains the fundamentals of the "rubbery" state. Simple thermodynamic concepts help explain the responses to temperature and the gas/liquid states. Mechanics is concerned primarily with Rheology applied to stress-strain history.

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March 8, 1983

PURPOSE

"More an art than a science" is a cliché no longer valid for designing with elastomers. The prodigious technical output by a relatively few scientists has built a knowledge base that is as valid as that for metals (or more so). The pioneering work of both individuals and groups (the Malaysian Rubber Producers' Research Association, among others) has reduced the "art" to a "science," giving elastomers a secure position in the engineering materials spectrum. This chapter is designed to serve as a checklist for the designer who is new to elastomers rather than as a complete description of complex properties. The references cited contain state-of-the-art information and should be referred to for serious design.

"The study of the science of materials has become in recent years an integral part of virtually all university courses in engineering. The physicist, the chemist, and the metallurgist may, rightly, claim that they study materials scientifically, but the reason for the emergence of the 'new' subject of materials science is that it encompasses all these disciplines"(1). Elastomers are less remarkable as an engineering material when reviewed in terms of materials science, as will be seen in this chapter. Understanding their unique characteristic of viscoelastic response is the key to understanding elastomers in general.

INTRODUCTION

Elastomers, increasingly utilized as engineering materials, are unique in the materials spectrum. Their ability to simultaneously store and dissipate energy via their characteristic large strain behavior having time dependence is called viscoelasticity. Designers normally familiar with the linear elastic stress properties of metals can become equally confident in designing with elastomers by studying this chapter and its references.

The general teaching approach will begin with a simplified elastomer micro theory based on a mechanical analog for much of the molecular nature of an elastomer. The basic chemistry, physics, thermodynamics, and Continuum mechanics will be briefly reviewed to provide a basis for explaining the elastomeric state and the properties resulting from it. From this basis, the "language of rubber" will be converted into engineering terms suitable for design purposes. Finally, some simple engineering designs using the unique properties of elastomers will be developed.

CHEMISTRY OF ELASTOMERS

Vollmert(2) notes that a long-chain molecule is the primary structure of any polymeric material (Figure 1). The secondary (micro) structure is dictated by the actual molecular architecture, which in turn influences the development of the tertiary (macro) structure. The typical elastomer has a random coil microphase and the spaghetti structure macrophase. The random (lack of order) aspect of the chain is created by inherent molecular assymmetry (as opposed to the symmetry of polyethylene) (e.g., in diene monomers) or by the presence on basic substituted ethylene's of bulky branch groups such as benzene rings (SBR), methyl groups (EPDM), or cyano groups (NBR) that prevent growth of a symmetrical polymer chain. Long-chain molecules occur commonly in nature and are synthetically produced by polymerization (Figure 2).

The two broad classes of polymerization(3) are defined as chain addition polymerization (addition; Figure 2a) and functional group polymerization (condensation; Figure 2b). Addition polymers are created from one or more monomers, and their polymeric sequences are identical to the monomers. Condensation polymers result when two or more difunctional molecules (not necessarily monomers) combine to create a long-chain molecule. This may or may not be accompanied by by-products such as water, or CO_2, which have to be removed.

To be useful as an elastomer, the chain typically must have at least 700 to 800 covalently bonded monomer units; 1000 units or more are required to develop adequate physical properties and 2000 to 3000 units for maximum ultimate properties (Figure 3). A two-dimensional view of an isolated random chain is presented in Figure 4 in terms of the "random walk concept."

The end-to-end separation distance is a function of the number of monomer units (molecular weight) and ranges from 5 to 10% of the fully stretched length. Considering a random chain three-dimensionally (Cartesian coordinate system; Figure 5), Shen(4) notes that the vectorial distance is defined via a Gaussian error function. Understandably, chain entanglements are formed, Figure 6(5), the actual number being a function of molecular weight, size, and architecture(6). Crosslinking (vulcanization) of two adjacent chains creates a predictable three-dimensional structure (Figure 6). The relations between crosslink density and physical properties have been neatly summarized by Coran(7) (Figure 7). Quantification of the effects of physical entanglements has defied classical solutions to date, but high molecular weight elastomers have generally been found to have properties normally predicted by a crosslink density twice as high as the known value.

PHYSICS OF ELASTOMERS

The basic primary structure of any elastomer is a long series of one or more types of monomer units covalently (chemically) bonded together creating a macromolecule. Considering the number of units in the chain, the actual size is small compared with typical common particles, as detailed by VerStrate(8) in Table I; so small that a typical elastomer contains 10^{26} chain molecules per cubic meter(9). The covalent bond consists of two shared electrons traveling in a relatively symmetrical orbit when the atoms are identical (i.e., carbon atoms in the polymer backbone). Dissimilar branch atoms such as hydrogen covalently bonded to the carbon backbone (e.g., n-alkanes, Table II) have unsymmetrical electron orbital clouds because of size differences. This electrical imbalance creates a net positive cumulative effect (dispersion forces) changing the physical state from gaseous to liquid to solid. Electronegative atoms (those on the right-hand side of the periodic chart) have a strong electron withdrawing effect, deshielding the adjacent proton and making it partially positive. These atoms become even more electronegative when bonded to carbon atoms, causing polar bonds, so that the molecules become polar molecules, with or without permanent dipoles. This is the basis of oil-resistant elastomers, since the polar aspect of the molecule now tends to repel nonpolar fluids such as hydrocarbons.

Intermolecular and Intramolecular Forces

The covalent (intramolecular) bonds are chemical; the intermolecular forces are physical. J.D. van der Waals originally noted (in 1873) the structural similarity between gases and liquids (see Table II, for example). Subsequent work by Lennard-Jones and others not only defined individual intermolecular forces but developed the formulas necessary to calculate their strengths (Table III)(10). The potential energy vs. distance curve for all these forces is similar; Figure 8 illustrates that for the weakest force, dispersion. There is no molecular interaction at infinite distance. As the distance decreases, the electron clouds distort, causing an attractive force (Curve b). At approximately one molecular diameter, the electron clouds begin to overlap, causing a repulsive force (Curve a). Curve c represents the sum of the attractive forces (b) and the repulsive forces (a). The distance r_o and the depth of the potential energy well (E) are functions of the type of intermolecular force (Table III). Intermolecular bonding energy(11) ranges from 17 to 214 kJmol^{-1} (dispersion to hydrogen-bonding forces). Dispersion forces, the weakest of all intermolecular attractions, are common to all molecules, creating the familiar gas, liquid, and solid states in the n-alkanes series (Table II). Dispersion forces are the only type of intermolecular force in hydrocarbon elastomers (NR, BR, SBR, IIR, EPDM). The polar elastomers (those having fluorine, chlorine, oxygen, or nitrogen atoms) develop a substantial percentage of their physical strength from the various other intermolecular attractions. The dipole type interactions are both highly directional and short range. These characteristics contribute to the rapid decrease of physical strength of polar elastomers, particularly polyurethanes at relatively moderate temperatures.

<u>Elasticity</u>

Although the intermolecular potential energy stabilizes the elastomeric network, it plays little or no part in the elastic properties of polymers. "It is now well established that the stress in a deformed rubber originates within the chains of the network. Interchain interactions contribute negligibly to the stress"(12). "The essential requirement for a substance to be rubbery is that it consist of long flexible chainlike molecules. The molecules themselves must therefore have a 'backbone' of many noncolinear (angles other than 180°) single valence bonds, about which rapid rotation is possible, as a result of thermal agitation" (13a). These two unequivocal statements by Flory and Gent are basic to the study of elasticity and rubber.

To illustrate, consider a single random chain (Figure 5); fill the open spaces surrounding this chain with numerous other random chains (Figure 1), each stabilized by configurational entropy dictated by the intermolecular attractions of adjacent elastomer chains (Figure 8); crosslink the matrix (as conceptualized in Figure 6); and apply a strain to the matrix. The entire mass deforms in an affine displacement (much as a deck of cards deforms when one card slides). The rapid rotation of noncolinear bonds is not a free rotation, however. Individual molecules each have intramolecular potential energy barriers created by varying electron densities. This is illustrated in Figure 9 by the curve for a simple molecule, ethane, for which the maximum energy barrier is at the eclipsed position. The physical restraints conferred by other polymer chains in cooperative conformations generally preclude rotation beyond this maximum.

When a strain is applied to a more complex molecule, example a diene monomer unit (natural rubber, neoprene, nitrile rubber), each individual diene monomer unit (Figure 10) has a high degree of potential mobility. There are two major torsional (rotational) modes (K_t), coupled with minor bending (K_b) and stretching modes (K_s). When an elastomer matrix is subjected to moderate strains, the deformation proceeds by a similar molecular rearrangement thru these torsional, bending and stretching modes. In a lightly strained mode, the deformed network typically has sufficient stored energy to almost return to its original undeformed state when the strain is released. A comparison between the high degree of molecular freedom for the diene monomer unit (Figure 10) and an aromatic monomer unit (Figure 11) is revealing. Polymers containing aromatic units in the backbone have limited movement available due to their geometry, leaving little hope for a true rubbery phase such as is available in aliphatic backbone polymers(25).

THERMODYNAMICS OF ELASTOMERS

Figure 12, a plot of retained stress versus temperature of a fixed length of rubber(14a) indicates a thermodynamic response. Thermodynamics, an integral part of physical chemistry, is the scientific discipline that deals with energy changes accompanying chemical and physical transformations. The three basic laws of thermodynamic experience have been humorously defined by Beerbower(15):

First (Rumford's conservation of energy):

"You can't win."

Second (Clausius' law of entropy):

"You can't even break even."

Third (Planck's vanishing point):

"You can't get out of the game."

Increasing crystallinity with decreasing temperature results in a reduced volume due to lower molecular activity. "We can't get out of the game" because thermodynamics comprises laws based on experience to which no exceptions have been found, nor are any likely to be found.

Gas, Liquid, and Solid States

The fundamental similarity of gas, liquid, and solid noted by van der Waals is illustrated by the n-alkane series (Table II). Van der Waals suggested that liquid was a dense gas and could thus be described by a modification of the equation of state for an ideal gas. The n-alkanes are in the gas, liquid, or solid phase, depending on the number of methylene sequences. Thermodynamics predicts that a transition from one phase to another can also be induced by a shift in temperature, pressure, density, or volume. This concept applies also to elastomers. Since they have gaseous precursors, they can be thought of as being essentially supercondensed gases.

GLASS TRANSITION TEMPERATURE, Tg

A plot of specific volume versus temperature for any elastomer always has a temperature point (or region) where the curve undergoes a discontinuity (Figure 13). This point, the glass transition temperature (Tg), depends not on thermodynamics but on physical conditions. For a given elastomer, it can be shifted by varying the cooling rate or by mechanical stressing. The random coil structure (Figure 1) is not sufficiently uniform to develop an orderly (crystalline) molecular architecture. The random chain aspect creates the rubbery state within a specific temperature range. The fraction of the random coil network volume that consists of unoccupied open spaces is called the fractional free volume (FFV) and is about 0.025% in the glassy state at Tg(16). At or below this fractional free volume value (at or below the glass transition temperature), the polymer chain is hindered in normal movement by inadequate space. The glass-like elastomer will be fractured by a small stress, since it cannot distribute the resulting strain to adjacent chains in the network. Increasing the temperature increases the fractional free volume. This, in turn, increases the molecular mobility and thus improves the resilience or rubbery nature. Note that the term "glassy" does not mean "crystalline" in this discussion.

Monomeric Friction Coefficient (ζ_0)

The ability of a short elastomer segment to move within the elastomer matrix depends on the monomeric friction coefficient (ζ_0). Translational chain movement occurs when an applied force (stress) creates a resulting displacement (strain). Consider an elastomer chain (Figure 5) in a bulk phase with numerous other elastomer chains adjacent to each other but not touching, as they are stabilized by intermolecular forces (Figure 8). The physical constraints stabilizing the elastomer matrix are entanglements and crosslinks (every fifty or so monomer units). At low extensions, these constraints do not seriously inhibit the potential rotating, bending, and stretching molecular motions indicated in Figure 10. The ability of the elastomer matrix to return to its original state on release of the external applied force, and the rate at which it does so, are governed by the monomeric friction component. This value, ζ_0, for different elastomers, ranges over three orders of magnitude (1000). Considering the mechanical nature of the response, it is apparent that elastomeric chain symmetry or lack thereof is a determining factor. Equally notable is the effect of plasticizers. Viscous (high molecular weight) plasticizers increase friction; low viscosity (low molecular weight) plasticizers have a lubricating effect and reduce monomeric friction.

MECHANICS OF ELASTOMERS (RHEOLOGY)

The elastomers discussed here have been categorized by Smith[17] as "single-phase non-crystallizable" and "crystallizable" (Table IV). This distinction is made because, in any elastomer, the strength is a function of molecular mobility phase, and the toughness is a function of molecular immobility phase. Multiphase elastomers, polyurethanes as an example, develop their strength from the microcrystalline, molecularly immobile urethane domains. The rubbery aspect is created by the amorphous, molecularly mobile, polyether or polyester segments.

Before proceeding with the mechanics of elastomers, the term "modulus" should be clarified. The rubber industry uses the term "modulus" when the correct term should be "tensile stress at a certain extension" (100%, 200%, 300%). Correctly used in engineering, the term "modulus" should mean (Table V):

Young's modulus(E) = tensile Stress(σ)/tensile Strain(ε),

Shear modulus(G) = shear Stress(σ_s)/shear Strain(ε_s).

The Stress-Strain Curve

A typical tensile test as performed in routine quality control is the simplest mechanical test to visualize. The test specimen is subjected to an increasing tensile stress, and the resulting change in length is plotted as a tensilgram (Figure 14). The stress(σ) is defined as the force per unit of original cross-sectional area and is measured in megapascals (MPa). The strain(ε) is defined as the fractional change in length $\Delta L/L_o$, where L_o is the original length and ΔL is the change in length.

Dynamic Mechanical Properties

Elastomeric components are unavoidably subject to mechanical force, or stress (σ) with a resulting strain (ε). Rheology is the branch of mechanics concerned with materials whose strain response to stress depends on their stress-strain history as well as on instantaneous states of stress, deformation, and deformation rate.

Consider an elastomeric component subject to a stress-strain cycle as detailed in Figure 15. The elastic stress, E' (tensile storage modulus), is in phase with the strain; it is the effect resulting from the rotational energy barriers (Figure 9). The viscous stress, E" (tensile loss modulus), is ninety degrees out of phase with the elastic stress, as viscous resistance depends on rate of deformation. This resistance is maximum when the strain is increasing most rapidly. The amplitude of the viscous stress cycle is related to the monomeric friction component (ζ_o). The total stress, E* (complex dynamic tensile modulus), has an amplitude, A_f, equivalent to $(A_1^2 + A_2^2)^{1/2}$ The displacement between total stress E* and elastic stress E' is the mechanical loss angle σ. Tan σ is the loss factor (A_2/A_1) and is an indication of the damping ability. Because of thermodynamics, the loss is returned as heat and is the source of heat build-up in a dynamically loaded component. Tan σ is greatly influenced by molecular architecture, crosslink type, and crosslink density. Plasticizers can be used with great effectiveness to increase or decrease tan σ.

Mechanical Properties Versus Temperature

Figure 16 is a generalized curve illustrating the change in shear modulus, G, with temperature shifts. The reduction in physical volume on cooling also increases the shear modulus rapidly, as indicated by Tg (Figures 13 and 16). The shear modulus is related not only to E (Table V) but also to hardness or durometer value (13b), as shown in Figure 17. Note that the so-called transition region is arbitrarily taken to be 100 MPa shear modulus (Figure 16). At 10 MPa shear modulus (Figure 17) the elastomer has a hardness of 95 durometer and has only minimal rubbery properties. The Tg can be shifted to higher or lower values by blending with other compatible elastomers or plasticizers. The shifted Tg is approximated with reasonable accuracy by the following relationship(18):

$$Tg = V_1 T_{g1} + V_2 T_{g2}$$

where T_{g1} and T_{g2} are the glass transition temperatures in degrees Kelvin (273.15 K = O^oC), and V_1 and V_2 are the volume fractions.

Williams-Landel-Ferry (WLF) Equation

The WLF equation can be used to predict, with considerable accuracy, the viscosity (shear modulus) of elastomers over the temperature range Tg to +100 C. This covers the entire range of shear modulus values in Figure 16. It is important to remember that oil-resistant (polar) and hydrofluorocarbon elastomers have high Tg values. Also, as mentioned above, a shift in Tg can be effected by pressure (16b) diminishing the fractional free volume (FFV) of the elastomer. Note the narrow range, only 2 to 5 C, between the transition region (G = 100 MPa) and Tg (G = 1000+ MPa). The WLF equation and its application are treated extensively in "Science and Technology of Rubber"(16).

Mechanics of a Deformable Solid

Formulations of medium (75 durometer) and lower hardness undergo minimum volume change under extension due to the higher ratio of elastomer to inert fillers. The ratio of normal strain to lateral strain is a constant for any given material and is called Poisson's ratio, ν. The actual value for elastomers, 0.4997, is for all practical purposes 0.5 (the upper limit). In classical mechanics, Poisson's ratio has the following relationships with other physical properties:

elastic (Young's) modulus, $E = 2(1 + \nu)G$;

shear (modulus of rigidity), $G = E/2(1 + \nu)$.

These elementary equations are further simplified since $\nu \cong 0.5$; thus, $E = 3G$. Lindley(19a) notes at the bottom of Table 3 that these ratios are logically applicable only to elastomers with minimal amounts of fillers.

Relaxation and Creep

Viscoelastic materials, since they are not truly elastic in terms of Hooke's Law, are subject to various types of relaxation. Figure 18 is a simplistic illustration, further defining the relaxation procedures described in Table VII(20). Assuming the equipment utilizing an elastomer is operating within the thermal stability range of the elastomer, Figure 19(14b) shows a legitimate approximation of serviceability, indicated by the curve labeled "good rubbers." Chemical changes on the backbone (chain scission) or crosslinks (cleavage) are indicated by the "reactive" rubber curve. "Although creep and stress relaxation are allied phenomena, there is no general relation between them"(21).

"Stress relaxation and creep are intimately related and one may be calculated from the other if stress-strain behavior of the rubber is known"(22a, 23). These two statements are from different chapters of the same book. Most experts agree that elastomeric components operating within conservative temperature limits have relaxation processes that are proportional to <u>logarithmic </u>time, but excessive temperatures cause relaxation processes that are proportional to <u>linear </u>time.

Compression Set

Compression set is a simple test that can be performed under constant stress (ASTM D395, Method A) or constant strain (ASTM D395, Method B). If the test is run at normal temperatures, it is measuring physical (primary) relaxation processes. At elevated temperatures, it is measuring chemical (secondary) relaxation processes. The results are difficult to correlate in terms of stress/strain relaxation. For example, reinforcing fillers, which have little effect on compression set, have pronounced effects (increasing the rates) on stress/strain relaxation(22b). The important difference to remember, particularly in seal design, is that stress relaxation gives an actual value indicating seal contact stress (the measure of sealing ability). Compression set, on the other hand, is an indication of recoverability after aging under 25% compression. The actual value reported is based on allowing the specimen to equilibrate in a relaxed mode for 30 minutes before taking the measurement of recovered height. This test does not give any indication of compressive stress available during the aging process. Compression set might be said to be related to stress relaxation in the same way that death is related to the process of dying.

DESIGNING WITH ELASTOMERS

Figure 20 shows rubber bonded or caused to adhere by some other means. Gent(13c) notes that "many rubber products are normally subjected to fairly small deformations, rarely exceeding 25% in extension or compression or 75% in simple shear."

Load Deformation: Shear

A common application of rubber in shock and vibration control causes shear. Lindley(24) states: "In shear, a rubber block with parallel loading surfaces bonded to metal has an essentially linear relation between the load(F) and deflection (x) up to about 80% strain. Shear stiffness, K_S, is given by:"

$$K_S = F/x = GA/t$$

where   G = shear modulus (Table VI)

A = cross-sectional area, and

t = thickness of rubber block.

Shear strain, $\varepsilon_S = x/t$;   Shear stress, $\sigma_S = F/A$.

Load Deformation: Compression

Consider rubber under compression (Figure 20). Rubber, because of its high bulk modulus (Table VI) and Poisson's ratio of 0.5, "barrels" when placed under compression. "At low strains, up to about 10%, linearity can be assumed for most design purposes, the compression stiffness, K_C, of a block being"(24):

$$K_C = F/x = E_C A/t$$

The compression modulus (E_C) is a function of Young's modulus (E), shape factor (S), and a numerical factor from Table VI (k):

$$E_C = E(1+ 2kS^2) \quad (19b).$$

The shape factor (S) is the ratio of loaded area to force-free area. For a solid having dimensions x, y, and z,

$$S = xy/2z(x + y).$$

The usefulness of the shape factor(s) is apparent from Figure 21. The effective modulus(E_C) can range above a value of 1000 (35 durometer). By utilizing shape factors, load bearing pads of rubber can be made to support substantial weight (compression) while allowing substantial lateral motion (shear). Lindley's works (19, 24) are key information sources and are available from the Malaysian Rubber Producers' Association at no charge.

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TABLE I

STRUCTURE CHARACTERIZATION OF ELASTOMERS

	Particle Diameter, microns(μ) (1mm)
	0.0001 0.001 0.01 0.1 1 10 100 1.000 10.000
Common Atmospheric Dispersoids	Smog Clouds & Fog Drizzle Rain
	Mist
Typical Particles and Gas Dispersoids	Carbon Black Zinc Oxide Fume Colloidal Silica Ground Talc Atmospheric Dust Viruses Bacteria
Filters	
Polymeric Structures	Segments Random Coil Maximum Extended Lengths Domains (Crystaline and Amorphous)
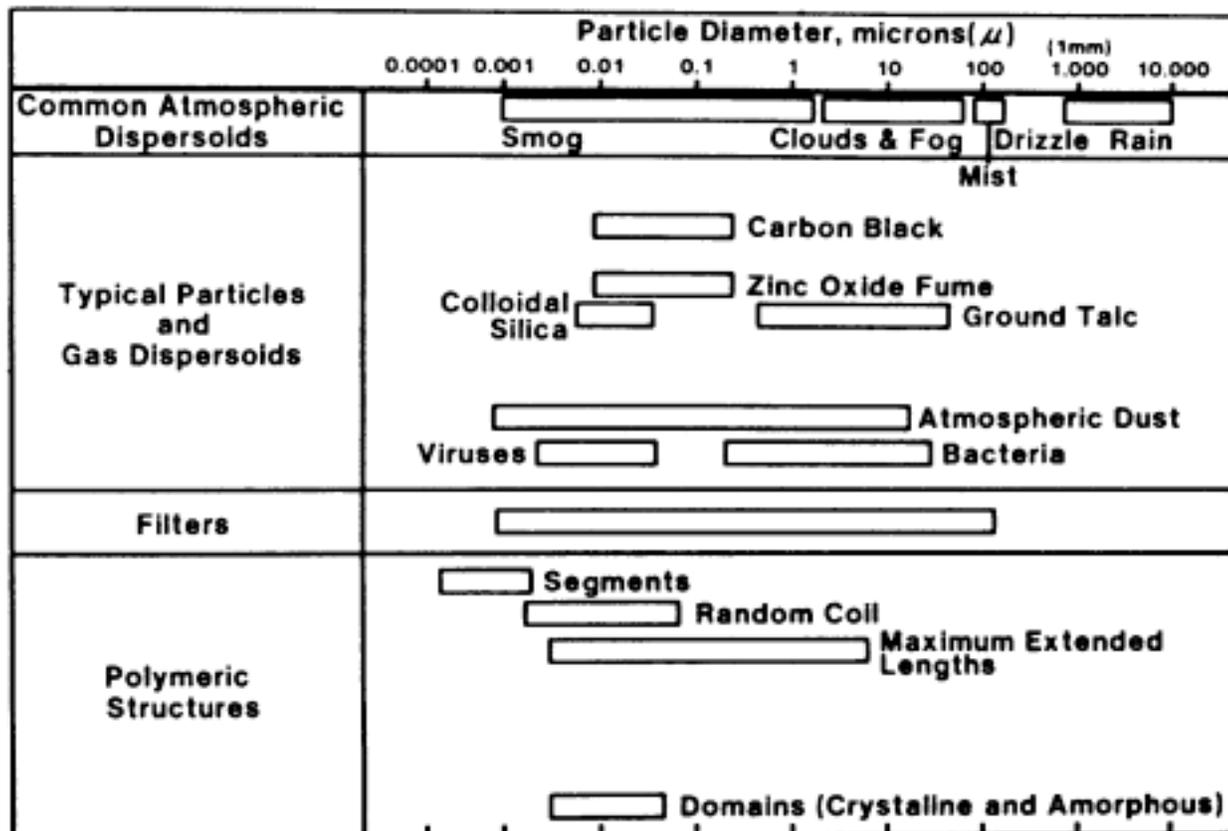
TABLE II

n-ALKANE (C_nH_{2n+2}) HOMOLOGOUS SERIES

Chemical Formula	Common Name	Molecular Weight	Physical State	B.P./M.P. °C
CH_4	Methane	16	Gas	-161.5/-183
C_2H_6	Ethane	30	Gas	-88.6/-172
C_3H_8	Propane	44	Gas	-42.1/-188
C_4H_{10}	Butane	58	Gas	-0.5/-135
C_5H_{12}	Pentane	74	Liquid	36.1/-130
$C_{12}H_{26}$	Kerosene	170	Liquid	216.0/- 10
$C_{18}H_{38}$	Paraffin	254	Solid-soft	303.0/ 28
$C_{50}H_{102}$	Hard Waxes	702	Solid-brittle	/ 92
$C_{100}H_{202}$	LMW Polyethylene	1402	Solid-hard	/ 115
$C_{1000}H_{2002}$	MMW Polyethylene	14002	Solid-tough	/ 138

TABLE III

BOND INTERACTIONS,

INTRAMOLECULAR (PRIMARY) AND INTERMOLECULAR (SECONDARY)

Type of Interaction	Strength	Distance Function	Model
Covalent	Very strong	Complex function	Quantum mechanical
Ionic	Very strong	$1/r$, range-long	$E = \dfrac{Z^+ Z^-}{r}$
Ion-dipole	Strong	$1/r^2$, range-short	$E = \dfrac{Z^+ \mu}{r^2}$
Dipole-dipole	Mod. strong	$1/r^3$, range-short	$E = \dfrac{-2\mu_1 \mu_2}{r^3}$
Ion-induced dipole	Weak	$1/r^4$, range-very short	$E = \dfrac{-Z^2 a}{2r^4}$
Dipole-induced dipole	Very weak	$1/r^6$, range-ex. short	$E = -\dfrac{\mu^2 a}{r^6}$
London dispersion	Very weak	$1/r^6$, range-ex. short	$E = \dfrac{-2\bar{\mu} a}{r^6}$

TABLE IV

STRENGTH OF ELASTOMERS

Elastomer type	Source of strength
Single-phase non-crystallizable	Viscoelastic processes
	Molecular network
	Orientation of chains
Filled, non-crystallizable	Increased energy dissipation
	Deflection and bifurcation of microcracks
	Cavitation
Crystallizable	Formation and deformation of crystalline domains
Block copolymers	Plastic domains

TABLE V

MECHANICAL PROPERTIES OF ISOTROPIC MATERIALS

$$E(\text{Young's modulus}) = \frac{\text{tensile stress } (\sigma)}{\text{tensile strain } (\varepsilon)}$$

$$G(\text{Shear modulus}) = \frac{\text{shear stress } (\sigma_s)}{\text{shear strain } (\varepsilon_s)}$$

$$\nu(\text{Poisson's ratio}) = \frac{\Delta D/D_0}{\Delta L/L_0}$$

$$E = 2G(1 + \nu) \qquad \text{or} \qquad G = \frac{E}{2(1 + \nu)}$$

TABLE VI

HARDNESS AND ELASTIC MODULI*

Hardness IRHD 2	Young's Modulus E MPa	Shear Modulus G MPa	k	Bulk Modulus E MPa
30	0.92	0.30	0.93	1000
35	1.18	0.37	0.89	1000
40	1.50	0.45	0.85	1000
45	1.80	0.54	0.80	1000
50	2.20	0.64	0.73	1030
55	3.25	0.81	0.64	1090
60	4.45	1.06	0.57	1150
65	5.85	1.37	0.54	1210
70	7.35	1.73	0.53	1270
75	9.40	2.22	0.52	1330

*Data Source: "Engineering Design with Natural Rubber"
Table 3, page 8 (MRPRA) 1978.

TABLE VII

"RELAXATION" PHENOMENA OF ELASTOMERS

Creep	Stress - Relaxation
• Increase in strain with time.	• Decay of stress with time.
• Under constant stress.	• Under constant strain.
• A physical reaction.	• Of a chemical nature.
• Characteristic of the viscous flow of all rubber-like material.	• Thru a breaking of primary chemical bonds.

PRIMARY   ∿ A-A-A-A-A-A-A-A-A-A-A-A-A ∿

                      | |

                      R_l R_l

Extended chain

Random coil	**Folded chain**	**Spiraled chain (helix)**

SECONDARY

Cell-structure of random coils	**Spaghetti-structure**	**Fringed micelle**

TERTIARY

Polymer crystal with folded chains	**Over-spiraling (super-helix)**

FIGURE 1. POLYMERIC STRUCTURES.

Addition (a)

Monomer   Monomer

+

↓

Polymer

Condensation (b)

Superfluous groups

Monomer   Monomer

+

↓

Polymer   + CO_2, H_2O etc.

FIGURE 2. POLYMERIZATION TECHNIQUES.

FIGURE 3. TENSILE STRENGTH VS. DEGREE OF POLYMERIZATION.
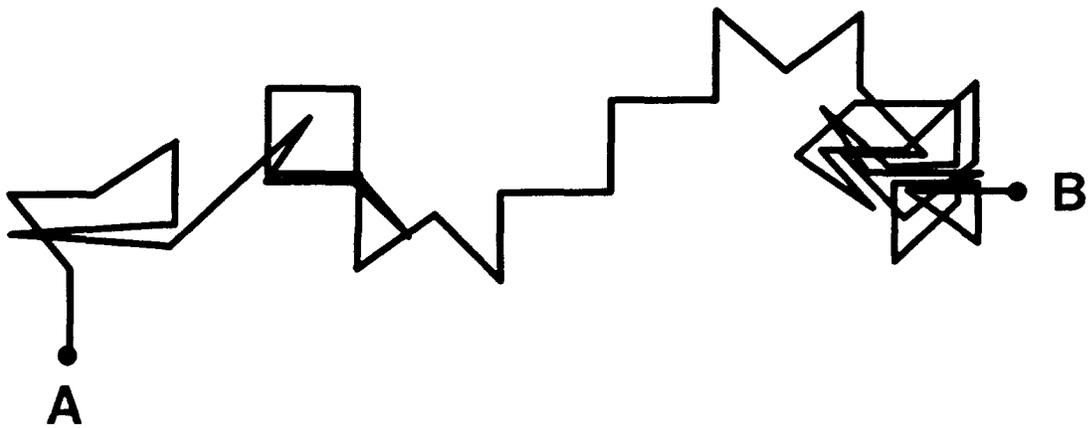
A-B Distance = 5-10% of A-B extended

FIGURE 4. RANDOM WALK, 1000 STEPS.
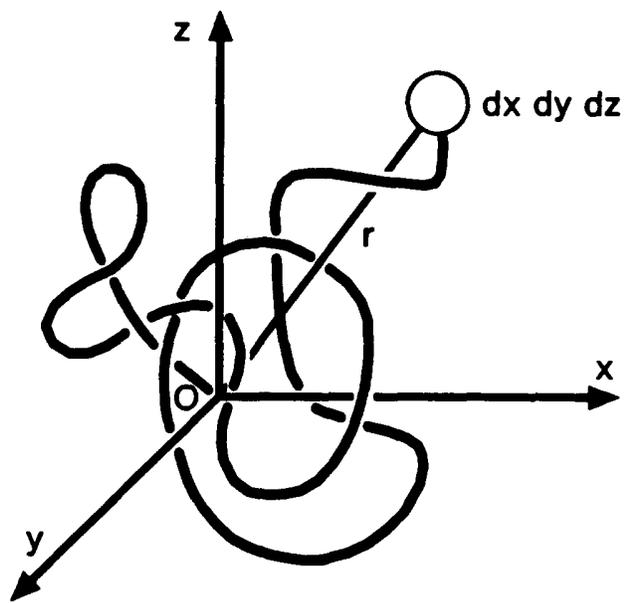
FIGURE 5. RANDOM CHAIN IN CARTESIAN COORDINATE SYSTEM.
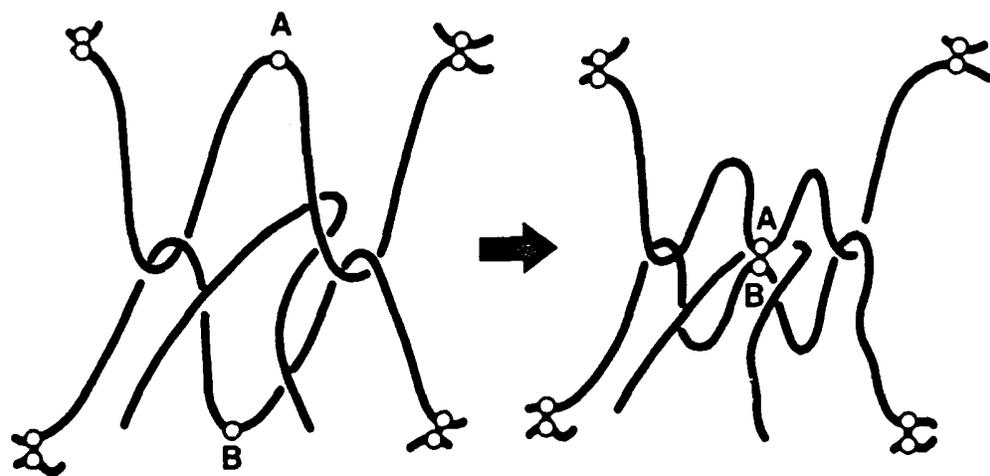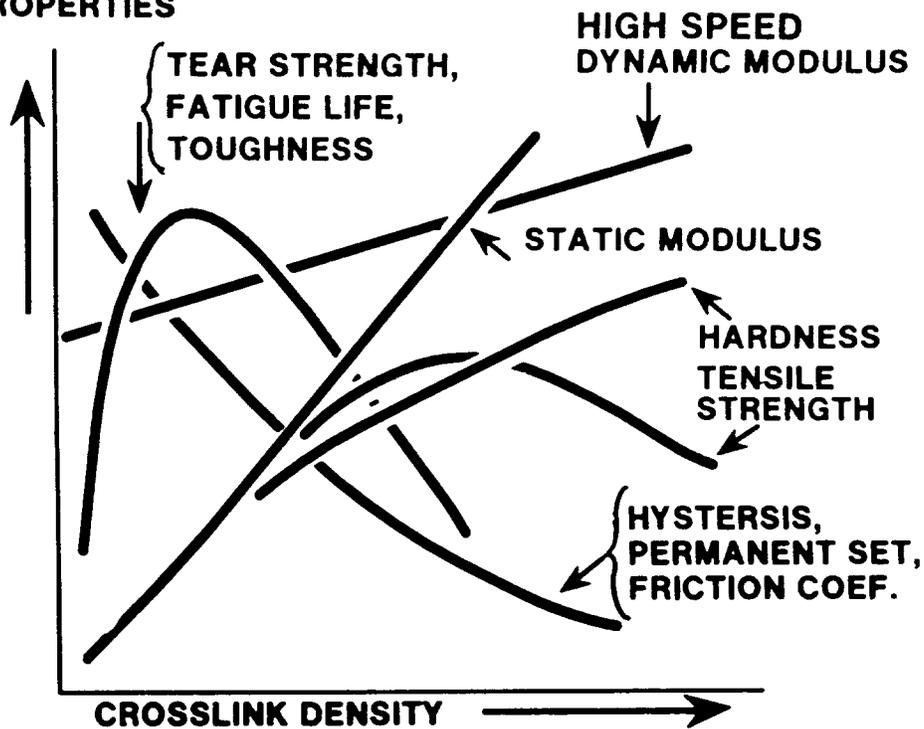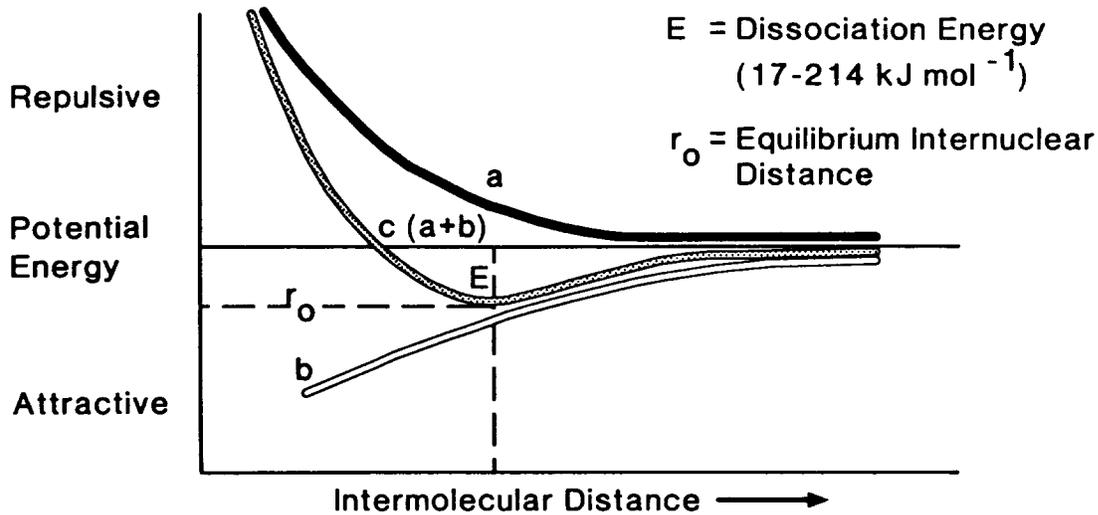
FIGURE 7.

FIGURE 8. INTERMOLECULAR POTENTIAL ENERGY.
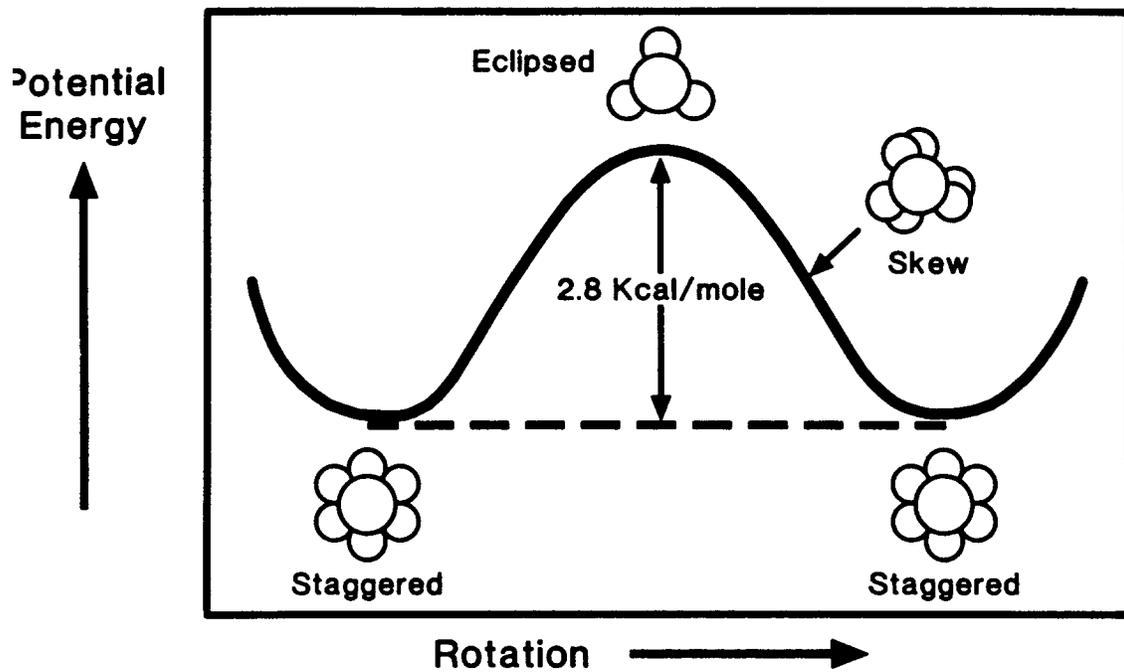
FIGURE 9. ROTATIONAL ENERGY BARRIERS.
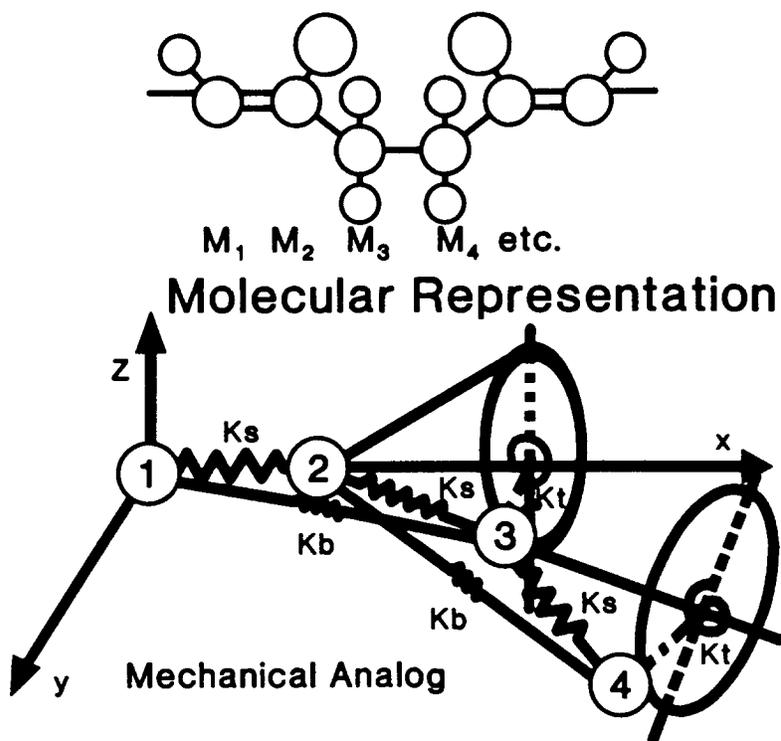
FIGURE 10. POLYISOPRENE SEGMENT.
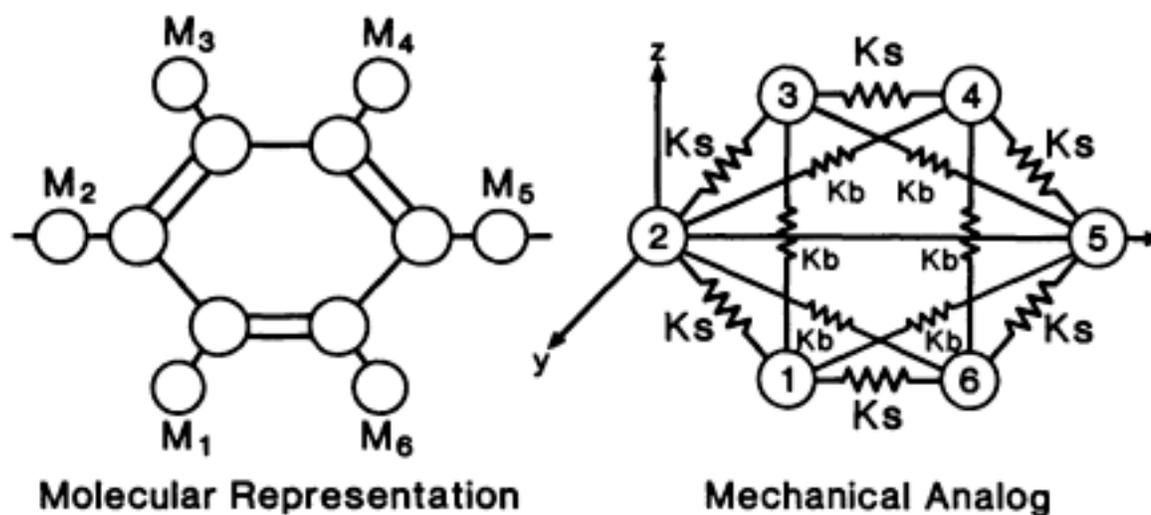
FIGURE 11. AROMATIC CHAIN ELEMENT.
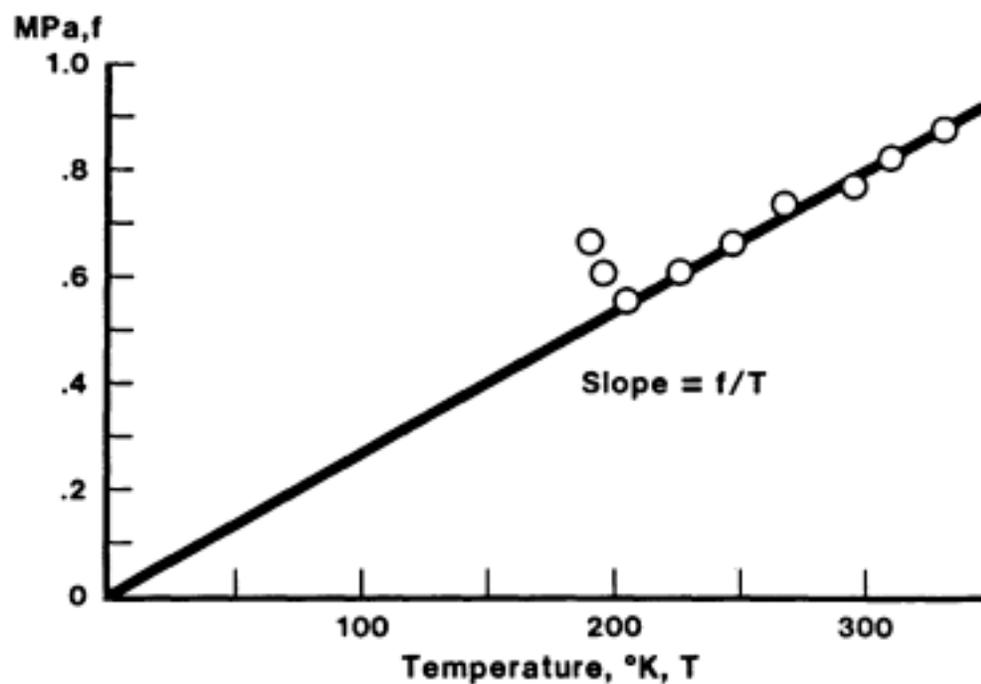
FIGURE 12. STRESS VS. TEMPERATURE AT FIXED LENGTH.
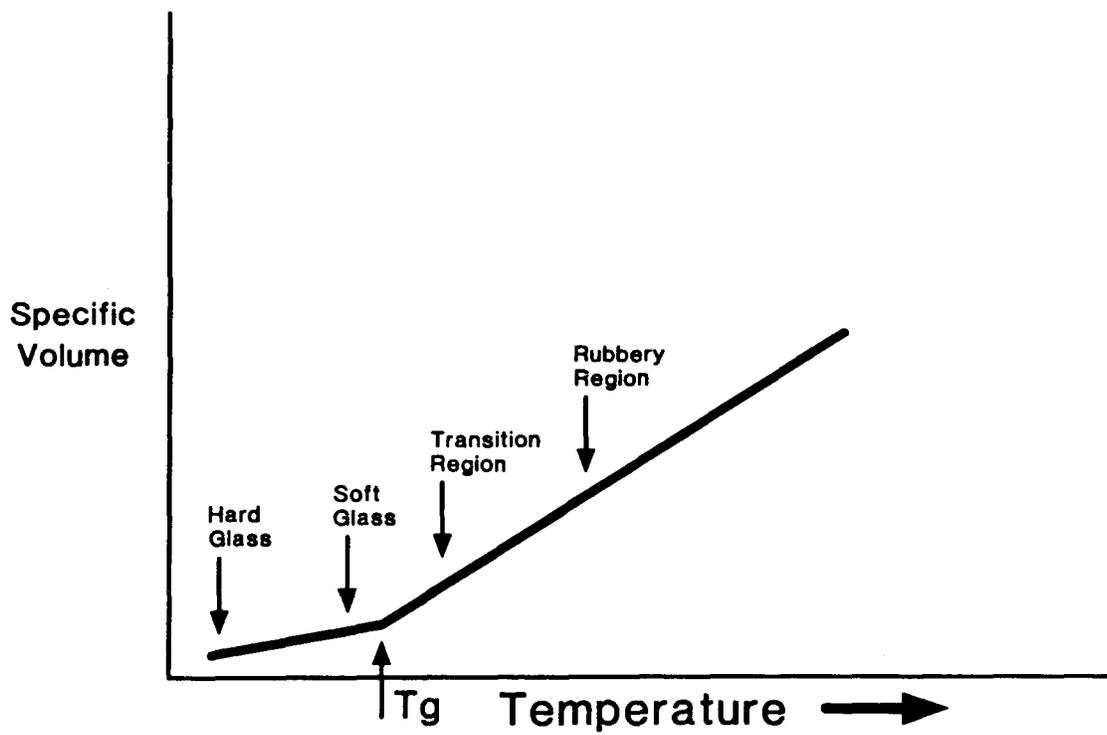
FIGURE 13. SPECIFIC VOLUME VS. TEMPERATURE.
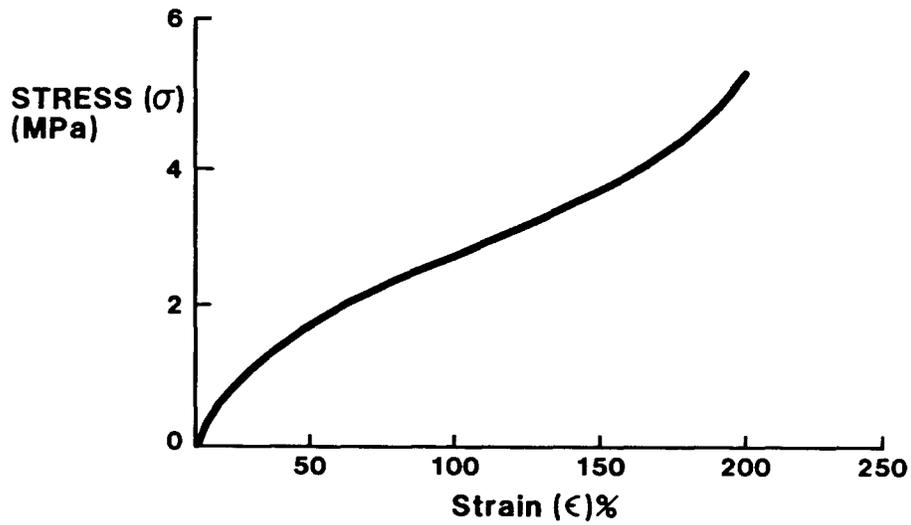
FIGURE 14. TYPICAL STRESS-STRAIN CURVE (70 DUROMETER SBR).
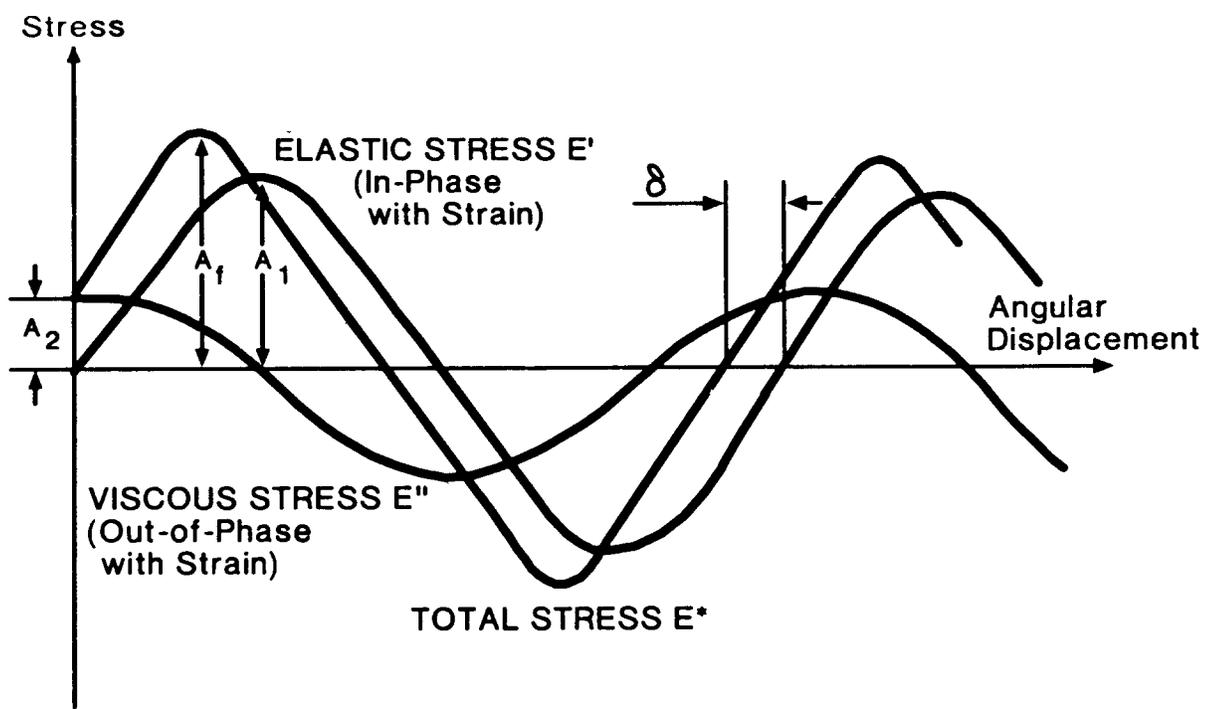
FIGURE 15.   STRESS VS. SINUSOIDAL STRAIN.
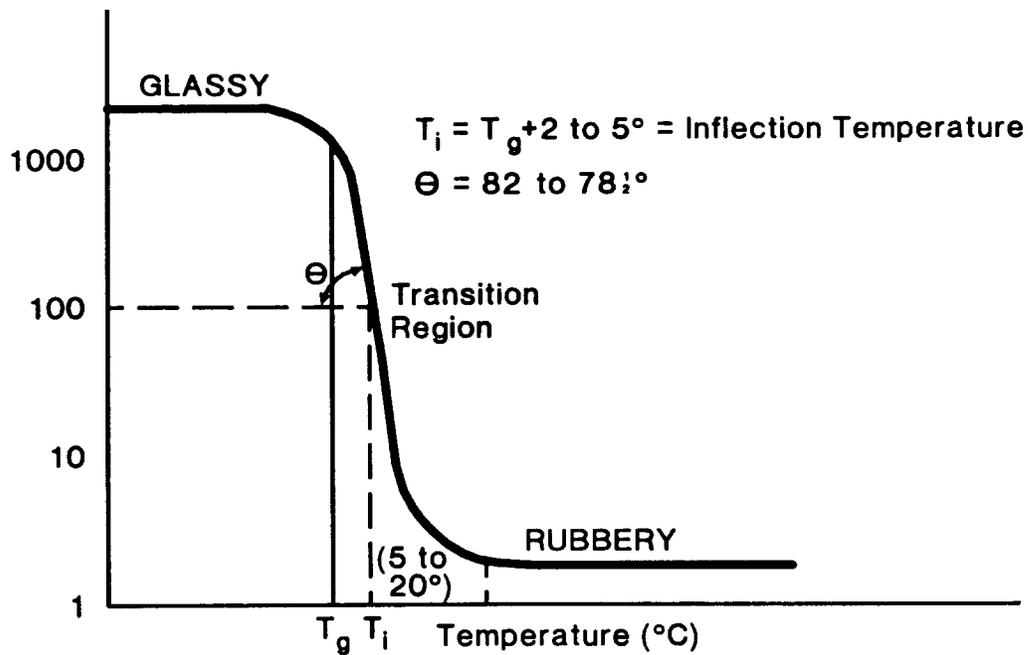
FIGURE 16.   SHEAR MODULUS VS. TEMPERATURE (IDEALIZED, CROSSLINKED 70 DUROMETER).
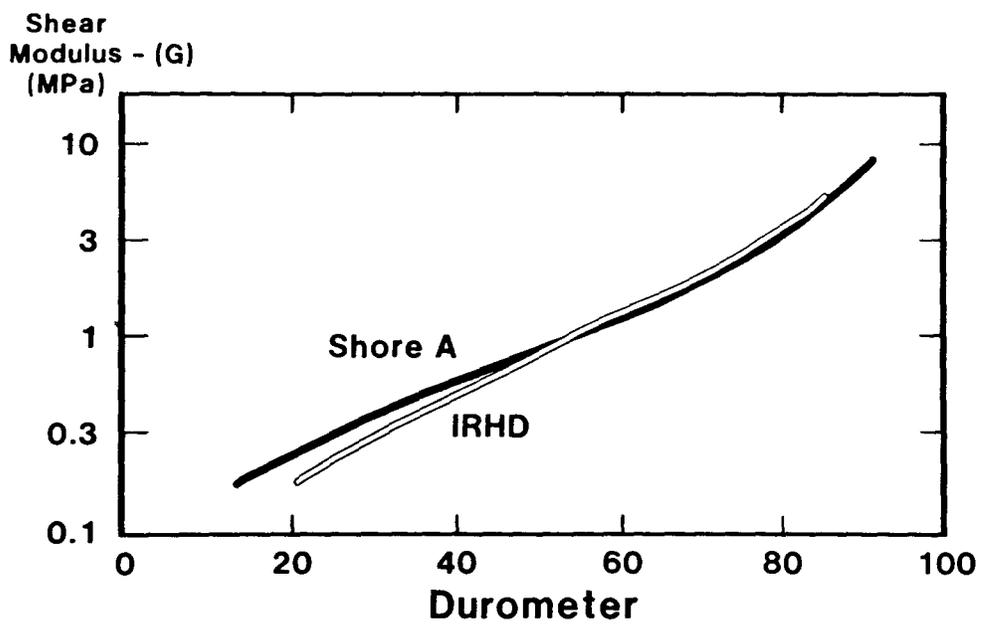
FIGURE 17.   SHEAR MODULUS VS. HARDNESS.
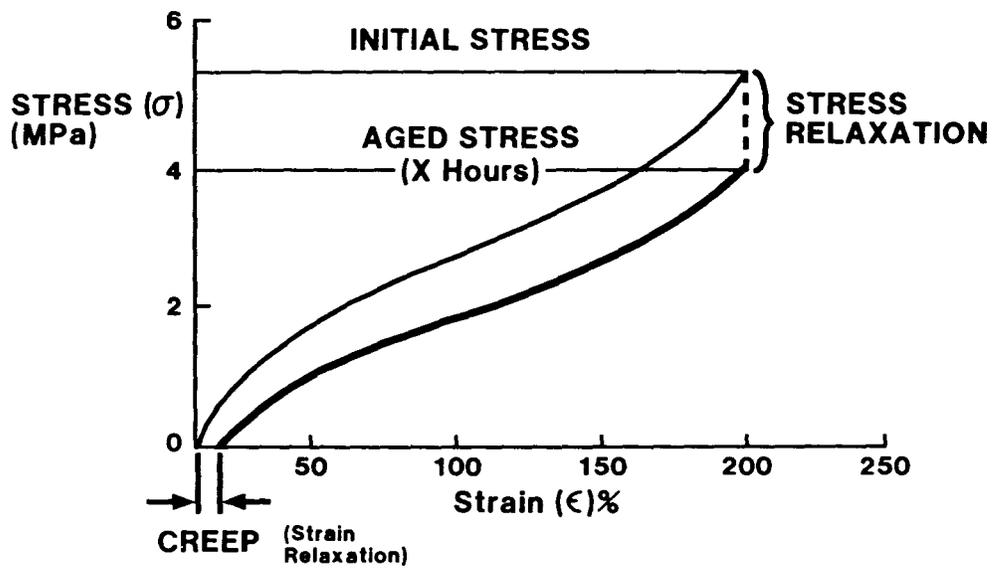
FIGURE 18.   RELAXATION PHENOMENA.
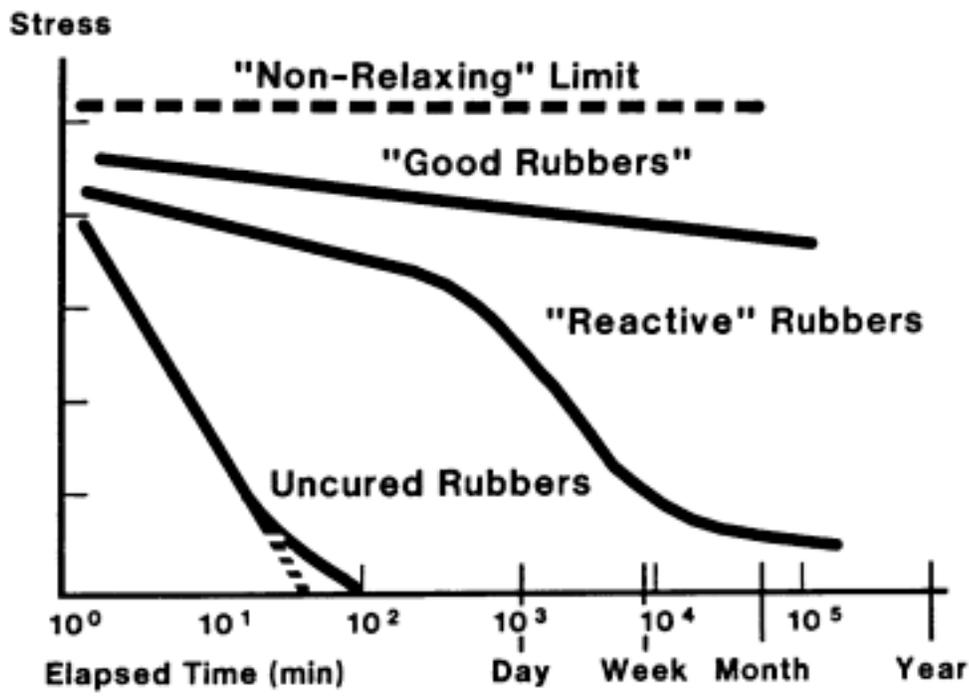
FIGURE 19. RELAXATION CHARACTERISTICS.

FIGURE 20.