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WANG, MAN-SHENG

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# A RHEOLOGICAL STUDY OF ELASTOMERS

The University of Oklahoma

PH.D.

1979

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## THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

A RHEOLOGICAL STUDY OF ELASTOMERS

## A DISSERTATION

## SUBMITTED TO THE GRADUATE FACULTY

# in partial fulfillment of the requirements for the

## degree of

## DOCTOR OF PHILOSOPHY

BY

1

## MAN-SHENG WANG

## Norman, Oklahoma

A RHEOLOGICAL STUDY OF ELASTOMERS

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DISSERTATION COMMITTEE

#### ABSTRACT

Creep results at room temperature during uniaxial, unconfined compressive loading of vulcanized and unvulcanized natural rubber and styrene-butadiene copolymer are presented. A combined equation of the power law and the sine hyperbolic function that relates strain  $\varepsilon$  with time t

 $\varepsilon(t) = m' \sinh(\frac{\sigma}{\sigma_m}) t^n$ 

was derived from the basic creep data. Here  $\sigma$  is true stress, and m', n, and  $\sigma_m$  are material constants. This empirical relationship will be interpolative and extrapolative with some accuracy.

Creep rate can be obtained by means of differentiation of the original creep data. The plot of creep rate versus time can be used to understand the change of creep stages for the rubbers studied.

Although rubbers are not perfectly elastic solids, they exhibit high recovery after the loading is removed. Rebound tests for unvulcanized rubbers and their vulcanizates are reported.

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Stress-strain tests have traditionally been the most popular and universally used of all mechanical tests. However, the stress-strain curve can be obtained indirectly from the strain-time curves at constant times. The strain after 20 seconds is referred to as the 20-second "elastic" strain. The isochronous stress-strain curves constructed in this study are based on this point in time. The initial tangent modulus of elasticity (Young's modulus) of the two materials (vulcanizates of natural and synthetic rubber) were obtained by measuring the slope of the curve of stress versus 20-second elastic strain at zero stress. The Mullins softening effect observed in the tensile tests of rubbers was checked during the compressive tests.

Another expression of creep results — the plot of compliance (J) versus time (t) has been proposed. These curves have the advantage of demonstrating the viscoelastic characteristics of rubbers easily and can be employed to estimate the heat generated during deformation, if necessary.

The swelling of vulcanized rubbers in two organic solvents, paraffinic hydrocarbon (kerosene,  $C_{14}H_{30}$ ) and one belonging to the aromatic family (benzene,  $C_{6}H_{6}$ ), were investigated. Creep and rebound tests of those swollen rubbers were conducted and the results were compared with the ordinary samples.

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Finally, the static phenomena of rubbers under compressive deformation were discussed. The apparent Young's moduli of rubbers were calculated and compared with the Young's moduli.

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#### CHAPTER I

#### INTRODUCTION

Typical questions important to design engineers are the strength and toughness of material. Elastomers (Appendix A) exhibit some interesting, unique, and useful mechanical properties. The Young's modulus of an elastomer is much smaller than that of a hard solid. This low value of Young's modulus contributes to the high extensibility and forcible quick retraction of elastomers. No other materials, metallic or non-metallic, are capable of extending to strains as high as 600-700 percent reversibly.

The high elastic behaviors of elastomers are \* attributed to the following characteristics (76):

- The molecules must be very long and flexible, and a quasi-free rotation is assumed to exist around most of the bonded-together, neighboring chain atoms.
- (2) The molecules must be attached together by either permanent chemical bonds or linkage or by temporary

numbers in the parenthesis refer to the references at the end.

physical entanglements; either form of attachment is termed a crosslink (Appendix B).

(3) Apart from these cross-links, these molecules must be free to move readily past one another; i.e., the intermolecular attractions which exist between all molecules must be small.

The wide-spread use of rubber components in structures and machines makes it highly desirable to obtain an exact knowledge of the mechanical behavior, so that rational and efficient usage is possible. The use of elastomers is determined primarily by their mechanical properties rather than by their chemical behavior. The relationship between the mechanical behavior and the chemical structure of elastomers is an important factor for the synthetic polymer chemists to improve the quality and make elastomers with any desired properties.

Plastics, rubbers, and other structural materials will continue to deform with time when subjected to a constant stress at room temperature. They also exhibit the same behavior at high temperatures if the duration of loading is long. The time-dependent portion of the strain produced by application of constant stress is referred to as creep. Creep tests can be carried out in tension, compression, shear, or multiaxial-stress conditions. Since compression uses of elastomers far exceed

in number the shear and tension uses for industrial application, a knowledge of the creep properties of elastomers in compression is a prerequisite to predict the creep of elastomers in bending, torsion, other combinations of stress, buckling; etc.

Considering that a typical low-molecular-weight substance dissolve readily in suitable solvent to a sharply defined maximum concentration, vulcanizates of rubber swell and imbibe liquid without being dispersed. In general, vulcanized rubber is much more resistant than the unvulcanized one in organic solvents, and the swollen state becomes the final system for the former, whereas the unvu'canized rubber will gradually lose its form and become ultimately dispersed in true solvents. It is immaterial to a technologist whether the hose tube is swollen to a considerable degree by an active solvent, provided that the mechanical properties of the tube are not changed to any significant amount by the solvent. Therefore, swelling measurements in the rubber laboratory should always include measurements of changes in mechanical properties.

#### CHAPTER II

### THEORETICAL BACKGROUND AND LITERATURE SURVEY

The investigation of deformation in relation to the stresses by which they are accompanied is the subject of rheology.

Strain,  $\varepsilon$ , is a displacement defined as a relative change of a length and is homogeneous if the displacement varies linearily to reference coordinates (22). Stress,  $\sigma$ , is the acting force per unit area and may be thought of as being composed of normal (tensile and compressive) and tangential (shearing) components.

Hooke's law (Eq.(II.1)) is one of the simplest constitutive equations, which relates the uniaxial stress,  $\sigma$  to the strain  $\varepsilon$  for deformation of an ideal, elastic isotropic solid.

$$\sigma = E\varepsilon$$
 (II.1)

where E is Young's modulus.

The reciprocal of Young's modulus is called tensile or compressive compliance (1); it is denoted by the symbol J. In most theoretical work it is assumed that the compliance is independent of load.

# II.A. PARTICULAR STRESS-STRAIN RELATIONS FOR RUBBER-LIKE SUBSTANCES

In the state of pure homogeneous strain, there are three principal stresses ( $\sigma_{tx}$ ,  $\sigma_{ty}$ ,  $\sigma_{tz}$ ) acting in the directions parallel to the principal axes of strain on planes corresponding to the faces of the rectangular blocks. The principal stresses ( $\sigma_{tx}$ ,  $\sigma_{ty}$ ,  $\sigma_{tz}$ ) which are defined as the normal forces per unit strained area are true stresses, and are different from those so called nominal stresses ( $\sigma_{px}$ ,  $\sigma_{ny}$ ,  $\sigma_{nz}$ ) which are defined as the forces per unit unstrained area. The magnitude of principal stresses can be expressed in terms of the corresponding principal extension ratios  $\lambda_1$ ,  $\lambda_2$ , and  $\lambda_3$  (Appendix C).

Consider a body which is a unit cube before deformation. The force  $\sigma_{nx}$  acts on an area  $\lambda_2 \lambda_3$  measured in the strained state; therefore, the corresponding true stress is

$$\sigma_{tx} = \frac{\sigma_{nx}}{\lambda_2 \lambda_3} = \lambda_1 \sigma_{nx}$$

Also

$$\sigma_{ty} = \frac{\sigma_{ny}}{\lambda_1 \lambda_3} = \lambda_2 \sigma_{ny}$$
 (II.2)

$$\sigma_{tz} = \frac{\sigma_{nz}}{\lambda_{1}\lambda_{2}} = \lambda_{3} \sigma_{nz}$$

The strain energy function may be written (92)

$$W_{s} = \frac{1}{2G} \left( \lambda_{1}^{2} + \lambda_{2}^{2} + \frac{1}{\lambda_{3}^{2}} - 3 \right)$$
$$= \frac{G}{2} \left( \lambda_{1}^{2} + \lambda_{2}^{2} + \frac{1}{\lambda_{1}^{2}} \lambda_{2}^{2} - 3 \right) \quad (II.3)$$

where C is the shear modulus of the sample.

For simplicity, a two-dimensional case when only two forces  $\sigma_{nx}$  and  $\sigma_{ny}$  are applied (i.e.,  $\sigma_{nz} = \sigma_{tz} = 0$ ) is discussed. If the extension ratio in the direction x is  $d\lambda_1$  while  $\lambda_2$  is kept constant, the only work done by the applied force is that done by the force  $\sigma_{nx}$ 

$$dW_{s} = \sigma_{nx} d\lambda_{1}$$
 (II.4)



From Eq. (II.3) we get

$$dW_{s} = \left(\frac{\partial W_{s}}{\partial \lambda_{1}}\right) d\lambda_{1}$$
$$= G/2 \left(2\lambda_{1} - 2/\lambda_{2}^{2} \lambda_{1}^{3}\right) d\lambda_{1}$$
$$= G(\lambda_{1} - 1/\lambda_{1}^{3} \lambda_{2}^{2}) d\lambda_{1} \qquad (II.5)$$

From Eq.(II.4) and Eq. (II.5)

$$\sigma_{nx} = G(\lambda_1 - 1/\lambda_1^3 \lambda_2^2)$$
 (II.6)

The corresponding true stress  $\sigma_{tx}$  is then

 $\sigma_{tx} = \lambda_{1} \sigma_{nx}$   $= G(\lambda_{1}^{2} - 1/\lambda_{1}^{2} \lambda_{2}^{2})$   $= G(\lambda_{1}^{2} - \lambda_{3}^{2}) \qquad (II.7)$ 

A similar result is obtained for  $\sigma_{tv}$ 

$$\sigma_{ty} = G(\lambda_2^2 - \lambda_2^2)$$
 (II.8)

$$\sigma_{tz} = 0 \tag{II.9}$$

For the general case when  $\sigma_{tz}$  is not zero, the solution can be obtained by superimposing on a negative hydrostatic pressure -P to the above stress system. Then

$$\sigma_{tx} = C(\lambda_1^2 - \lambda_3^2) + P$$

$$\sigma_{ty} = G(\lambda_2^2 - \lambda_3^2) + P$$

$$\sigma_{tz} = P$$
(II.10)

For a simple extension corresponding to an extension ratio  $\lambda_1$ , we have  $\sigma_{ty} = \sigma_{tz} = 0$ , and use of the fact that  $\lambda_1 \lambda_2 \lambda_3 = 1$  will imply

$$\lambda_2^2 = \lambda_3^2 = 1/\lambda_2$$

Substituting into the first of Eq. (II.10), one obtains

$$\sigma_{tx} = G(\lambda_1^2 - 1/\lambda_1)$$
 (II.11)

and then

$$\sigma_{nx} = G(\lambda_1 - 1/\lambda_1^2) \qquad (II.12)$$

Suppose that one dimension of the rubber specimen, which for simplicity may be taken to be a cube with unit edge length, is increased in the ratio  $\lambda$ , while the other two dimensions (e.g., y,z directions) are reduced proportionally. From the incompressible condition (i.e., constancy of volume)

$$\lambda_1 = \lambda$$
  $\lambda_2 = \lambda_3 = \frac{1}{\sqrt{\lambda}}$ 

where  $\lambda_1$ ,  $\lambda_2$ , and  $\lambda_3$  are the deformed edge lengths.



Figure II-2 (a) Unstrained State (b) Simple Compression.

The corresponding strain energy is therefore

$$W_{\rm s} = 1/2 \ {\rm G}(\lambda^2 + 2/\lambda - 3)$$
 (II.13)

If  $\sigma_{nx}$  is the magnitude of the only acting force per unit cross-sectional area measured in the unstrained state in the direction of compression, the work done in increasing the length by an amount dx is

$$dW_{s} = \sigma_{nx} dx = G(\lambda - 1/\lambda^{2})$$
 (II.14)

Here  $\sigma_{nx}$  is negative due to compression. The true stress  $\sigma_{tx} = \lambda \sigma_{nx} = G_1 \lambda^2 - 1/\lambda$  is the same as derived from the general stress-strain relation.

#### II.B. CREEP

The resulting slow increase in deformation under constant stress is called creep. In general, the greater the load, the greater is the deformation and creep rate (de/dt).

In most creep tests, there is a measurable, partial recovery when the load is removed, which indicates that the creep must have both a viscous and an elastic component. Therefore a four-element model was used to describe the creep phenomena of materials. This model (Maxwell-Kelvin Model) is composed of a spring and a dashpot in series and another spring and dashpot in parallel.

II. B.1. Model (35)

In a creep test, a load is applied to a specimen, and its length is measured as a function of time. In addition to the initial strain due to the elastic characteristics, the deformation will increase with time for a viscoelastic material. The four-element model which describes the creep behavior of elastic material under tensile forces is shown in Figure II-3.



Figure II-3. Maxwell-Kelvin Model.

Assume each spring to be Hookean; that means its deformation is proportional to the stress  $\sigma$  applied on it and inversely proportional to its modulus E. When a constant force is applied to a Hookean spring, the spring stretches immediately by an amount which does not change with time. Next, each dashpot is assumed to be filled with a Newtonian

liquid, so that its deformation is proportional to the time and stress applied on it and inversely proportional to the viscosity of the liquid in the dashpot. As a constant force is applied to such a dashpot, its deformation increases linearly with time.

When the total stress is applied to the spring  $E_1$ and dashpot  $n_3$ , the stress is shared by that parallel combination of spring  $E_2$  and dashpot  $n_2$  by amounts which vary with time. As the dashpot and spring of the parallel set stretch, more and more of the total stress is carried by the spring. Finally, all the stress is carried by  $E_2$  and none by  $n_2$ ; then the spring stretches no more. Considering the elongation behavior of the parallel spring and dashpot ( $E_2 \leq n_2$ ), the governing equation can be written:

$$\sigma = E_2 \varepsilon_2 + \eta_2 \frac{d\varepsilon_2}{dt}$$
(II.15)  
$$\frac{d\varepsilon_2}{dt} + \frac{E_2}{\eta_2} \varepsilon_2 = \frac{\sigma}{\eta_2}$$

Thus

$$\varepsilon_2 = \frac{\sigma}{E_2} + C \exp(-\frac{E_2}{\eta_2} t)$$
 (II.16)

where C is an integration constant. Initial condition:

when t = 0,  $\varepsilon_2 = 0$ . Thus,

$$C = -\frac{\sigma}{E_2}$$
(II.17)

and

$$\varepsilon_2 = \frac{\sigma}{E_2} [1 - \exp(-\frac{E_2}{\eta_2} t)]$$
 (II.18)

$$\epsilon_2 = \frac{\sigma}{E_2} [1 - \exp(-\frac{t}{\tau})]$$
 (II.19)

where  $\tau$ , the retardation time, is defined as  $\tau = \eta_2 / E_2$ .

The total deformation is equal to the sum of the deformation of the spring  $E_1$ , the dashpot  $n_3$ , and the parallel combination of  $E_2$  and  $n_2$ . The creep behavior of the Maxwell-Kelvin model is illustrated in Figure II-4 (70).



Figure II-4. Creep of a Four-element Model.

The total load was applied at zero time. Spring  $E_1$  stretches immediately by an amount  $\frac{\sigma}{E_1}$ , creep starts at a high rate but gradually tapers off to a constant positive rate due to dashpot  $n_3$ . If the load is removed at time  $t_1$ , the spring will snap back to its unstretched state. During the recovery time, the spring  $E_2$  gradually forces the plunger of dashpot  $n_2$  back to its original condition also. However, dashpot  $n_2$  does not retract to its original state as there is no force acting on it. This dashpot retains a deformation equal to  $\frac{\sigma t_1}{n_3}$ . The recovery curve obtained after the load is removed at time  $t_1$  is given by:

$$\varepsilon = \varepsilon_2 e^{-(t-t_1)/\tau} + \varepsilon_3$$
 (II.20)

where

$$\varepsilon_{2} = \frac{\sigma}{E_{2}} (1 - e^{-t_{1}/\tau})$$
$$\varepsilon_{3} = \frac{\sigma}{\eta_{3}} t_{1}$$

### II.B.2. Effect of Transition and Temperature on Creep

The creep property of a polymer is somewhat dependent upon temperature. At temperatures well below the glasstransition temperature  $T_g$ , certain segments of the polymer are frozen in fixed positions; then the polymer is rigid and brittle with a high modulus. Thus, the stress on it cannot be internally relieved, and very little creep will occur even after very long time (61). As the temperature is raised, a chain segment under stress will move so as to relieve the stress when possible. The stress removed from one segment is added to others, thus deforming them a little. These other chain segments in turn move so as to relieve the stress on themselves from time to time when given the opportunity. The result is a gradual change in the length of the test specimen with time (70). In the transition region, the creep properties become extremely temperature dependent. A given stress will cause a much greater deformation than the same load at much lower temperature, and the rate of creep  $d(\log \epsilon)/d(\log t)$  will go through a maximum near the glass-transition temperature for many polymers (36,52), especially those which have very high molecular weights. This type of motion is somewhat like viscous flow.

## II.B.3. Effect of Molecular Weight on Creep

At temperatures well below the glass-transition region, the creep behavior of an amorphous polymer does not depend upon molecular weight, which is to be expected as long as the molecular weight is above some minimum at which a good specimen can be prepared.

The creep becomes strongly dependent upon molecular weight in the glass-transition region. The reason for this dependence in uncrosslinked, amorphous materials is that the mechanical response of such materials is determined by their viscosity and elasticity resulting from chain entanglements. The melt viscosity of polymers is extremely depen-

dent upon molecular weight (21). When the polymer chains are so short that they do not become entangled with one arother, the viscosity is approximately proportional to the molecular weight. When the chains are so long that they become strongly entangled, it is very difficult to move one chain past another. Thus, the viscosity becomes very high and is proportional to the 3.4 or 3.5 power of the molecular weight (11,30,31,33,59,60).

Above the glass-transition temperature, amorphous, uncrossliked, high polymers behave as a viscous liquid or like rubber. Thus, the creep of such materials depends upon their molecular weight, too (64,82,94).

### 

In most uncrosslinked polymers the elastic part of creep comes from chain entanglements. When the molecular weight of a polymer increases, the number of entanglements increases too, so the elasticity and amount of recoverable creep increases. The fact that the relative amount of recovery after a short-time creep test is greater than after a long-time one indicates that the number of entanglements decreases on deforming the sample.

A small number of chemical crosslinks works like the physical entanglements. Only a very small degree of crosslinking is required to reduce greatly the creep. A high degree of crosslinking is the necessary condition of

becoming an ideal rubber (18,55,84). The prominent difference between the physical entanglement and chemical crosslink is the latter will not relax or become ineffective at high temperature. Thus, crosslinked elastomers show rubber-like elasticity for long time and even at high temperature after being deformed (68). The modulus in the rubbery region increases with the number of crosslinked points or as the characteristic molecular weight between crosslinks decreases (72,95).

Since widely spaced crosslinks have just a slight restriction on molecular motion, the glass-transition temperature  $T_g$  of such a polymer nears that of the uncrosslinked polymer. When the crosslink density becomes fairly high, molecular motion is restricted, and the  $T_g$ of the crosslinked polymer is increased (78).

Crosslinking has a very prominent effect on creep at temperatures above T<sub>g</sub>. Below the glass-transition temperature, so little chain motion occurs that crosslinking has very little effect on the modulus unless there exists a very high degree of crosslinking. If perfect network structures could be made, a large increase in modulus should theoretically occur at extremely high degrees of crosslinking such as in diamonds.

Farlie (24) measured both the rate of creep and the rate of stress relaxation of natural rubber as a function of the degree of crosslinking, and found that both rates decrease with crosslinking. Farlie's results, and those of Berry and Watson (7), also illustrate the

effect of either network morphology or the chemical nature of the crosslinking agent. Since the rates for sulfur vulcanizates at a given degree of crosslinking are two or three times as great as the rates found for peroxides as the vulcanizing agents, the sulfur linkage in sulfur vulcanizates may undergo an interchange reaction which relieves the stress.

### II.B.5. Effect of Crystallinity on Creep

In slightly crystalline polymers, the crystallites act just like crosslinks as a result of many segments being immobilized and firmly held together in the crystallites. Therefore, crystallinity decreases creep compliance, creep rate, and rate of stress relaxation (16,29,54,71,77,91).

Below T<sub>g</sub>, crystallinity has only a slight effect on the modulus because a glass has a modulus nearly as great as that of an organic crystal.

The modulus increases very rapidly with the degree of crystallinity. Up to about 15% crystallinity, a polymer behaves as crosslinked rubber (69). In the region around 20% crystallinity, the material becomes considerably more rigid than a rubber. Above 40% crystallinity much of the stress is carried by the crystalline phase rather than by the amorphous phase (16).

Crystallinity generally has little effect on  $T_{g'}$ but with some polymers, crystallized under certain conditions,  $T_{g}$  is raised (4,27). The increase appears to be
caused by either short amorphous chain segments between two crystallites or by stresses put on the amorphous chain segments as a result of the crystallization process (89).

The creep properties of crystalline polymers not only are very sensitive with temperature, but also in some cases at a given temperature, crystalline polymers creep more with time than crosslinked polymers or rigid amorphous polymers. This extensive creep may be due to recrystallization and the rotation of some crystallites in such a manner as to relieve the stress on them (34).

### II.B.6. Effect of Orientation on Creep

Creep is generally much less in the direction parallel to the uniaxial orientation than that in a direction perpendicular to the orientation for rigid polymers. Part of this decreased creep is due to the increased modulus in the direction parallel to the orientation chain. For example, many highly oriented fibers have a Young's modulus about an order of magnitude greater than that of unoriented polymer (17,51).

Orientation can change Poisson's ratio drastically (73). The Poisson's ratio in the direction parallel to the orientation direction is expected to be greater than that of the unoriented polymer. There is at least one exception, polyethylene (15,17).

II.C. POWER LAW FOR TIME INFLUENCE ON STRAIN

Findley (27) attempted to fit the creep of many plastic materials to analytic relationships similar to those suggested for metals (62). It was observed that the empirical power function of time (8)

$$\varepsilon = \varepsilon_0 + mt^n$$
 (II.21)

where  $\varepsilon_0$  and m are functions of stress for a given material. n is a material constant independent of stress, described tension creep of many different rigid plastics with good accuracy over a wide range of time.

Eyring (23,47,87) tried a molecular approach to predict non-linear viscoelastic behavior by considering the theory of thermally activated rate processes. This model is based upon the assumptions that:

- The deformation of the polymer involves the motion of chain molecules (chain sliding) or parts of a chain molecule (change in the conformation of the chain) over the potential-energy barrier.
- (2) The activation energy for the deformation process taking place does not change appreciably with temperature.
- (3) The physical and chemical properties of the materials are the same before and after deformation.

The situation is illustrated in Figure II-5.



Direction of flow and applied stress

Figure II-5. The Eyring Model for Creep.

According to the rate process theory, there exists a dynamic equilibrium when no stress is applied, i.e., the frequency of jumps will be equal in all directions and no net flow will occur; then the chain segments are moving with frequency v over the potential barrier in each direction.

$$v = v_0 \exp(-\Delta E/RT)$$
 (II.22)

where  $v_0$  is called the frequency factor which involves the fundamental vibration frequency and the entropy contribution to the frequency.

 $\Delta E$  is the activation energy.

R is the gas constant.

T is the absolute temperature.

If, however, a stress is applied, the energy barrier for a jump in the direction of the stress is decreased and the energy barrier for a jump in the opposite direction is increased correspondingly. Suppose that the applied stress can produce linear shift  $\beta\sigma$  of the energy barrier symmetrically, then we have a flow

$$v_{f} = v_{o} \exp \left[-(\Delta E - \beta \sigma)/RT\right]$$
 (II.23)

in the forward direction (i.e., the direction of application of the stress) as well as another flow

$$v_{r} = v_{o} \exp \left[-(\Delta E + \beta \sigma)/RT\right]$$
 (II.24)

in the backward direction, resulting in a net flow v',

$$v' = v_{f} - v_{r}$$
$$= v_{o} \exp(-\Delta E/RT) \{\exp(\beta\sigma/RT) - \exp(-\beta\sigma/RT)\}$$
$$= 2v_{o} \exp(-\Delta E/RT) \sinh\phi\sigma \qquad (II.25)$$

where  $\phi = \beta/RT$ .

in the forward direction.

Findley (26) and Goldstein (46) used this hyperbolic function satisfactorily to describe the stress dependence of m in Eq. (II.21) for moderate values of  $\sigma$ . A similar hyperbolic sine function with different constants

also describes the stress dependence of the time-dependent term  $\varepsilon_0$  in Eq. (II.21) for moderate stresses. Thus Eq. (II.21) may be written as follows:

$$\varepsilon = \varepsilon_0' \sinh \frac{\sigma}{\sigma_0} + (m' \sinh \frac{\sigma}{\sigma_m}) t^n$$
 (II.26)

where  $\varepsilon_0'$ ,  $\sigma_0$ , m', n,  $\sigma_m$  are constants which may vary with temperature. Findley's empirical equations are very helpful to the design engineer for constant-stress loading conditions as they predict the creep for a given material, given the constants  $\varepsilon_0$ , m, and n or  $\varepsilon_0'$ , m', n,  $\sigma_0$  and  $\sigma_m$ .

### II.D. SWELLING PHENOMENA OF RUBBERS

The behavior of rubber toward a solvent that absorbs large quantities of liquid without loss of shape or elastic property constitutes one of its most striking characteristics. In the process of swelling, the molecules of the swelling agent don't greatly affect the structure of the rubber but merely serve to increase its bulk property and prevent the tendency of crystallization (40,41).

Swelling, like dissolving, is concerned with the equilibrium between phases. Consider the simplest case in which one phase contains two components, while the other contains only one; the pure phase is the liquid. Although this situation is just reversed with those of the natural solution, the difference has no significance from the

thermodynamic standpoint. Thermodynamically, if the transfer process between two phases is performed at constant temperature and pressure, then the equilibrium between the phases corresponds to that condition in which it is not possible to obtain work from a transfer of mass between the phases. Thus the Gibbs free energy change must vanish at the equilibrium conditions, i.e.,

$$\Delta G = 0 \qquad (II.27)$$

at equilibrium (3).

For the particular case when the mixed phase is a high polymer plus low-molecular-weight solvent and the single phase is pure liquid, the Gibbs free energy of dilution  $\Delta G_1$  can be defined as the change in the Gibbs free energy of the solution due to the transfer of 1 mole of liquid (say component 1) from the pure phase to a very large quantity of the mixed phase. At equilibrium,  $\Delta G = 0$  under constant temperature and pressure. From the thermodynamic relationship, the quantity  $\Delta G_1$  can be expressed in terms of the heat of dilution  $\Delta H_1$  and the entropy of dilution  $\Delta S_1$ . Thus,

 $\Delta G_1 = \Delta H_1 - T\Delta S_1 \qquad (II.28)$ 

where  $\Delta H_1$  and  $\Delta S_1$  are the change in the enthalpy and entropy of the system per mole of liquid transferred from the pure phase to the mixed phase, respectively.

When the low-molecular-weight liquid has an appreciable vapor pressure and assuming that the vapor obeys the ideal gas law, then the molar Gibbs free energy of dilution is given by:

$$\Delta G_1 = RT \ln(P/P_0) \qquad (II.29)$$

where P is the vapor pressure of the liquid component in equilibrium with the swollen rubber at the temperature T.  $P_O$  is the saturation vapor pressure of the liquid at the temperature T.

The heat of dilution  $\Delta H_1$  and Gibbs free energy  $\Delta G_1$ can be determined experimentally; thus  $\Delta S_1$  is derived from Eq. (II.28). An alternative method of obtaining  $\Delta H_1$ is by measuring the heat of mixing calorimetrically. However, this method is very difficult to apply in the case of rubber solution due to the fact that the liquid absorption process is somewhat slow, but wherever it can be applied it provides a useful check on the data obtained from the vapor pressure measurements.

At equilibrium  $\Delta G_1 = 0$ , so RT  $\ln(P/P_0) = 0$  or  $P/P_0 = 1$ , which indicates that the equilibrium vapor pressure of the liquid in the mixed phase is equal to the vapor pressure of the pure liquid when equilibrium is established. Therefore, the equilibrium degree of swelling will be the same whether the polymer is in direct contact with the pure liquid, or whether it is indirect communication with the liquid by way of the saturated vapors.

The free energy of dilution may be obtained from any of the colligative properties which are thermodynamically related to the vapor pressure, in addition to measuring the vapor pressure directly (37,38,39). The osmotic pressure is the most important one. It is defined as the excess pressure necessary to apply to the mixed phase in order that it shall be in equilibrium with the pure liquid. The appropriate relation for osmotic pressure is

$$\pi = -(RT/V_1)\ln(P/P_0)$$
 (II.30)

where  $V_1$  is the molar volume of the pure liquid. or

$$\Delta G_1 = -\pi V_1 \tag{II.31}$$

The quantity  $\pi$  may also represent the swelling pressure (42). The difference between these two terms (osmotic pressure and swelling pressure) is that for an osmotic pressure measurement a semi-permeable membrane is required in order to separate the two phases (both are liquids), while in the measurement of swelling pressure (where the mixed phase is solid), the separating membrane becomes superfluous.

The vapor pressure of a solution may also be related to the freezing point (the depression of freezing point is another colligative property), by an approximate expression:

$$\ln(P/P_0) = (L_f/RT_f^2) \Delta T \qquad (II.32)$$

where  $\mathbf{L}_{\mathbf{f}}$  is the molar latent heat of fusion of the solvent.

- ${\tt T}_{\rm f}$  is the melting point of the solvent.
- $\Delta {\tt T}$  is the freezing-point depression produced by the solute.

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# CHAPTER III

MATERIALS, EQUIPMENT, AND EXPERIMENTAL PROCEDURES

TTT.A. MATERTALS

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(1) Solid Rubbers

VNR: Vulcanized Natural Rubber UnVNR: Unvulcanized Natural Rubber VSBR: Vulcanized SBR UnVSBR: Unvulcanized SBR

All the rubber samples were provided by B.F. Goodrich Rubber Co. (Akron, Ohio). The unvulcanized rubbers have the same chemical composition as those corresponding vulcanizates but have not undergone heat treatment. The chemical compositions by weight are:

 SBR(#1180)
 NR(#10963)

 Polymer
 46.57%
 Polymer
 44.64%

 Curing Agent
 6.11%
 Curing Agent
 4.22%

 Fillers
 37.12%
 Fillers
 40.74%

(2) <u>Organic Solvents</u> Kerosene  $(C_{14}H_{30})$  Density = 0.756 gm/c.c. Benzene  $(C_{6}H_{6})$  Density = 0.853 gm/c.c. (at 25°C)

III.B. EQUIPMENT:

Most measurement systems may be divided into three parts (49):

- (1) A detector-transducer stage which detects the physical variables and performs either a mechanical or an electrical transformation to convert the signal into a more usable form. In the general sense, a transducer is a device which transforms one physical effect into another. In most cases, however, the physical variable is transformed into an electrical signal because this type of signal is most easily measured.
- (2) Some intermediate stage which modifies the direct signal by amplification, filtering, or other operation so that a desired output is available.

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(3) A final or terminating stage which acts to indicate, record, or control the variable being measured.

Figure III-1 shows the schematic of the generalized measurement system.



Figure III-1. Schematic of the Generalized Measurement System.

HP<sup>\*</sup>Model 7DCDT is the detector-transducer employed in this study. Its operation theory, performance characteristics, and application are described in this section.

III.B.1. PRINCIPLES OF OPERATION:

A DCDT coil assembly consists of (1) a differential transformer coil, (2) a DC-excited solid state oscillator and a phase sensitive demodulator all in one small package (Figure III-2).



Figure III-2. Functional Diagram of DCDT

The oscillator converts the DC input power to AC which is used to excite the primary winding. The axial core

<sup>\*</sup>Hewlett Packard

position determines the amount of voltage induced in the secondary windings. Each of the two secondary circuits contains a secondary winding, a full-wave bridge, and an RC filter. These secondary circuits are connected in series so that the resultant output is a DC voltage proportional to the core displacement from electric center. The electric center is the position of the core relative to the coil when the output is zero. It is located approximately at the middle point of the coil length. The polarity of the voltage is a function of the location of the core with respect to the electric center.

# III.B.2. PERFORMANCE CHARACTERISTICS:

Output amplitude and phase relationships at frequencies other than the specified frequency can be approximated from the following equations.

$$\Theta = \tan^{-1} \frac{f_o}{f_{-3db}}$$
$$A_r = \frac{1}{\sqrt{1 + (\frac{f_o}{f_{-3db}})^2}}$$

where  $\Theta$  = phase angle between displacement and electric output.  $A_r$  = amplitude ratio.  $f_{\Theta}$  = displacement frequency.

 $f_{-3db}$  = displacement frequency where the DCDT output is down 3db.

If less ripple is desired, additional external filtering may be added, but a consequent loss of frequency response should be expected. If, on the other hand, better frequency response is desired, DCDTs with a network having shorter time constants can be supplied on special order. Then, if the ripple is excessive, the user can add an external network with sharper cut-off characteristics than those ordinarily supplied as an integral part of the transducer.

The resolution capacity of DCDTs is theoretically infinite, being limited only by the read-out device. Normal excitation is 6VDC, 20 milliamps for the 7DCDT series. The excitation voltage range for 7DCDT is 5 to 7 VDC.

The scale factor is a function of the amplitude of the excitation voltage. The percentage change in scale factor as a function of the excitation voltage will not exceed the percentage change of the excitation voltage.

### III.B.3. APPLICATION CONSIDERATIONS

The power consumption of HP Model 7DCDT is approximately 120 milliwatts. This model must not be subjected to temperature greater than 140°F.

When selecting DCDT series, the maximum peak-topeak displacement to be measured, the operating temperature range, and the full-scale sensitivity of the associated electronic equipment should be considered.

III.C. EXPERIMENTAL PROCEDURES

In an insulated cabinet, there are six loading stations. Figure III-3 illustrates one of the stations. The creep tests were performed under unconfined, uniaxial compression. The room temperature was controlled by an air conditioner and maintained nearly constant (78°F) within  $\pm 2°F$ .

External stress was applied to the specimen by weights on the pan suspended on a wire that passes over the pulley on the loading block. It is necessary to add weight at regular strain intervals to compensate for the increase of cross-sectional area caused by deformation, which is an approximate way to keep true stress constant. Calculation of the weight to be added at each interval is based upon the assumption that rubber is incompressible.

Axial deformation was measured to better than 10<sup>-4</sup> in. by a linear displacement transducer (HP Model 7DCDT). The output of each transducer was monitored continuously on a recorder. An iron-constantan thermocouple mounted on each station monitored the temperature near each sample.

Prior to the time when the actual creep tests were executed, each sample was kept in the cabinet for about two days, which allowed sufficient time for the sample to reach equilibrium at the test temperature.

All samples were "seated" to keep uniaxial compression as definite as possible. The seating load was



Figure III-3. View of One Creep Station.

- B: Loading Block
- S: Sample
- H: Sample Holder
- TD: Transducer
  - P: Pulley

usually equal to the test load and was applied for 10 seconds and released. Very small deformation for vulcanizates of rubbers during seating has a negligible effect on the subsequent response of the sample. Immediately after seating of the test specimen, the test load was applied.

## CHAPTER IV

#### EXPERIMENTAL RESULTS AND DISCUSSIONS

IV.A. CREEP DATA:

The basic data obtained during this investigation were the creep curves (true stress, strain, time) for unconfined, uniaxial compression at constant temperature. Figures IV-1 through -4 show typical creep curves for the vulcanized and unvulcanized NR, SBR, respectively. For creep tests of metals, rather long-time periods are necessary to observe the deformation behavior (sometimes longer than several years). However, since rubbers always reach large deformations in short time, short-time observations are adequate. Figures IV-5 through -12 give the creep data in extended time units (minute and second). Appendix F supplies all the numerical values upon which these curves were based.

These creep curves can be expressed as polynomial functions by means of regression analysis (Appendix G). Tables IV-1 through -4 give those coefficients of polynomials for various kinds of rubbers, stresses and time units. Although these polynomials fit the experimental data accurately, they are tedious to use because a poly-









80 70 60 1000 psi TOTAL STRAIN (%) 50 600 psi 500 psi 40 400 psi 30 300 psi 200 psi 20 150 psi 10 100 psi 0 8 10 6 2 4 TIME (MIN) Figure IV-5. Representative Creep Curves for VNR(#10963) at 78°F.









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80 70 60 TOTAL STRAIN (%) 50 1000 psi -800 psi -40 500 psi • 400 psi 30 300 psi-250 psi • 20 200 psi • 150 psi -100 psi-10 0 60 50 30 TIME (SEC) 40 20 10 Representative Creep Curves for VSBR Figure IV-11.

(#1180) at 78°F.



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# Coefficients of Creep Polynomial Function for VNR

|               |   | 100 psi   | 200 psi   | 400 psi  | 600 psi  |
|---------------|---|---|---|--|--|
| HR<br>(0-100) | A<br>A<br>1<br>A<br>2<br>A<br>3<br>A<br>4<br>A<br>5<br>A<br>6                               | 0.494029x10 <sup>2</sup><br>0.844158<br>-0.487679x10 <sup>-1</sup><br>0.170486x10 <sup>-2</sup><br>-0.291528x10 <sup>-4</sup><br>0.187046x10 <sup>-6</sup><br>0.302202x10 <sup>-9</sup> | $0.604907 \times 10^{2}$<br>$0.109711 \times 10$<br>$-0.913004 \times 10^{-1}$<br>$0.355243 \times 10^{-2}$<br>$-0.624539 \times 10^{-4}$<br>$0.397511 \times 10^{-6}$<br>$0.748776 \times 10^{-9}$ | $0.647499 \times 10^{2}$<br>0.910203<br>$-0.622601 \times 10^{-1}$<br>$0.222804 \times 10^{-2}$<br>$-0.378219 \times 10^{-4}$<br>$0.239763 \times 10^{-6}$<br>$0.385789 \times 10^{-9}$  | $0.674504x10^{2}$ $0.125481x10$ $-0.109729$ $0.455264x10^{-2}$ $-0.833027x10^{-4}$ $0.537314x10^{-6}$ $0.116149x10^{-8}$   |
| MIN<br>(0-10) | A<br>A<br>A<br>A<br>A<br>A<br>A<br>A<br>A<br>A<br>A<br>A<br>A<br>A<br>A<br>A<br>A<br>A<br>A | $\begin{array}{r} 0.320707 \times 10^{2} \\ 0.104701 \times 10^{2} \\ -0.431203 \times 10 \\ 0.991705 \\ -0.116008 \\ 0.457721 \times 10^{-2} \\ 0.243567 \times 10^{-3} \end{array}$   | $\begin{array}{r} 0.445155 \times 10^{2} \\ 0.587008 \times 10 \\ -0.233749 \times 10 \\ 0.513789 \\ -0.551076 \times 10^{-1} \\ 0.187676 \times 10^{-2} \\ 0.102376 \times 10^{-3} \end{array}$    | 0.53 <sup>2</sup> 7 <sup>4</sup> 3x10 <sup>2</sup><br>0.103951x10 <sup>2</sup><br>-0.67~118x10<br>0.209489x10<br>-0.293937<br>0.125158x10 <sup>-1</sup><br>0.805923x10 <sup>-3</sup>     | $0.575529 \times 10^{2}$ $0.572055 \times 10$ $-0.255698 \times 10$ $0.678482$ $-0.891670 \times 10^{-1}$ $0.377909 \times 10^{-2}$ $0.220215 \times 10^{-3}$            |
| SEC<br>(0-60) | A <sub>0</sub><br>A1<br>A2<br>A3<br>A4<br>A5<br>A6  | $0.254607 \times 10^{2}$ $0.236445 \times 10$ $-0.355204$ $0.312467 \times 10^{-1}$ $-0.119512 \times 10^{-2}$ $0.111120 \times 10^{-4}$ $0.244888 \times 10^{-6}$                      | $0.431974x10^{2}$ $0.136548x10$ $-0.934966x10^{-1}$ $0.329895x10^{-2}$ $-0.558024x10^{-4}$ $0.353508x10^{-5}$ $0.000000$  | $0.517822 \times 10^{2}$<br>0.717753<br>$0.507626 \times 10^{-2}$<br>$-0.529948 \times 10^{-2}$<br>$0.281619 \times 10^{-3}$<br>$-0.343824 \times 10^{-5}$<br>$-0.487649 \times 10^{-7}$ | $0.531518 \times 10^{2}$<br>0.162665 \times 10<br>-0.308106<br>0.308653 \times 10^{-1}<br>-0.125312 \times 10^{-2}<br>0.124822 \times 10^{-4}<br>0.248109 \times 10^{-6} |

| Table | IV-2 |
|-------|------|
|-------|------|

Coefficients of Creep Polynomial Function for UnVNR

#### 600 psi 100 psi 200 psi 400 psi 0.227466x10<sup>2</sup> 0.373760x10<sup>2</sup> $0.530307 \times 10^2$ 0.945507x10 A 0.586412 0.441327 0.341756 0.398988 A 1 $-0.431279 \times 10^{-1}$ -0.147434x10<sup>-1</sup> $-0.183444x1c^{-1}$ $-0.309514 \times 10^{-1}$ A2 A3 A4 $0.167332 \times 10^{-2}$ 0.644728x10<sup>-3</sup> $0.267690 \times 10^{-3}$ $0.130433 \times 10^{-2}$ HR -0.110991x10<sup>-4</sup> $-0.246292 \times 10^{-4}$ $-0.299395 \times 10^{-4}$ -0.245015x10<sup>-5</sup> (0-100)0.193565x10<sup>-6</sup> $0.866795 \times 10^{-8}$ $0.162238 \times 10^{-6}$ $0.710075 \times 10^{-7}$ A 5 $0.368144 \times 10^{-9}$ $0.366810 \times 10^{-9}$ $0.114207 \times 10^{-9}$ 0.000000 A<sub>6</sub> 0.348903x10<sup>2</sup> $0.192857 \times 10^2$ $0.510317 \times 10^2$ 0.697215x10 A 0.299695x10 0.410658x10 -0.154628 0.196739x10 A 1 -0.284841x10 0.111104x10 -0.650815 <sup>A</sup>2 -0.189995x10 0.885878 -0.498841 0.107208 <sup>А</sup>з 0.572332 MIN $0.810515 \times 10^{-1}$ -0.783037x10<sup>-2</sup> -0.789912x10<sup>-1</sup> A<sub>4</sub> -0.123655 (0-10) $0.525114 \times 10^{-2}$ $0.336388 \times 10^{-2}$ $-0.368075 \times 10^{-2}$ $0.123940 \times 10^{-3}$ A \_5 $-0.251827 \times 10^{-3}$ <sup>A</sup>6 $0.336545 \times 10^{-3}$ $0.687812 \times 10^{-5}$ $0.209870 \times 10^{-3}$ $0.168905 \times 10^2$ $0.338924 \times 10^2$ $0.367633 \times 10^2$ 0.550497x10 Ao 0.407238 0.670274 0.321394x10 0.563941x10 A 1 $-0.261487 \times 10^{-1}$ -0.639356x10<sup>-1</sup> -0.543883 -0.110270x10 A2 $0.325582 \times 10^{-2}$ $0.873749 \times 10^{-3}$ $0.493809 \times 10^{-1}$ 0.104002 <sup>А</sup>з А<sub>4</sub> SEC $-0.141045 \times 10^{-4}$ $-0.861680 \times 10^{-4}$ $-0.190207 \times 10^{-2}$ $-0.403736 \times 10^{-2}$ (0-60)0.177599x10<sup>-4</sup> 0.111792x10<sup>-5</sup> 0.378655x10<sup>-4</sup> $0.862401 \times 10^{-7}$ A<sub>5</sub> $0.387932 \times 10^{-6}$ $-0.560605 \times 10^{-8}$ $0.819422 \times 10^{-6}$ 0.000000 A<sub>6</sub>

# Table IV-3

# Coefficients of Creep Polynomial Function for VSBR

|         | •              | 100 psi                    | 200 psi                            | 500 psi                    | 1000 psi                   |
|---------|----------------|----------------------------|------------------------------------|----------------------------|----------------------------|
|         | A              | 0.120071x10 <sup>2</sup>   | 0.196650x10 <sup>2</sup>           | 0.421019x10 <sup>2</sup>   | 0.522344x10 <sup>2</sup>   |
|         | A,             | 0.654399                   | 0.122430x10                        | 0.747133                   | 0.351041                   |
|         | A <sub>2</sub> | -0.643041x10 <sup>-1</sup> | -0.930741x10 <sup>-1</sup>         | $-0.510513 \times 10^{-1}$ | $0.162788 \times 10^{-1}$  |
| HR      | A              | 0.289608x10 <sup>-2</sup>  | 0.387077 <b>x10<sup>-2</sup></b>   | $0.210170 \times 10^{-2}$  | $-0.178979 \times 10^{-2}$ |
| (0-100) | ر<br>۸,        | -0.553897x10 <sup>-4</sup> | -0.719174x10 <sup>-4</sup>         | $-0.396409 \times 10^{-4}$ | $0.450332 \times 10^{-4}$  |
|         | Ă              | 0.364282x10 <sup>-6</sup>  | 0.469869x10 <sup>-6</sup>          | $0.261455 \times 10^{-6}$  | $-0.322264 \times 10^{-6}$ |
|         | A <sub>6</sub> | 0.871473x10 <sup>-9</sup>  | 0.101 <i>5</i> 78x10 <sup>-8</sup> | 0.602235x10 <sup>-9</sup>  | -0.119223x10 <sup>-8</sup> |
|         | A              | 0,859290x10                | 0.164579x10 <sup>2</sup>           | 0.417213x10 <sup>2</sup>   | 0.479810x10 <sup>2</sup>   |
|         | A <sub>1</sub> | 0.224754x10                | 0.189278x10                        | 0.215658x10                | 0.981611                   |
|         | A              | -0.112094x10               | -0.961858                          | -0.140325x10               | -0.214446                  |
|         | A              | 0.311478                   | 0.265813                           | 0.455457                   | 0.205548x10 <sup>-1</sup>  |
| MIN     | Α <sub>μ</sub> | -0.409009x10 <sup>-1</sup> | -0.375303x10 <sup>-1</sup>         | -0.669401x10 <sup>-1</sup> | -0.711199x10 <sup>-3</sup> |
| (0-10)  | A              | 0.164154x10 <sup>-2</sup>  | $0.257344 \times 10^{-2}$          | 0.298908x10 <sup>-2</sup>  | 0.000000                   |
|         | A<br>6         | $0.107481 \times 10^{-3}$  | $-0.680544 \times 10^{-4}$         | 0.192230x10 <sup>-3</sup>  | 0.000000                   |
|         | A              | 0.689064x10                | 0.151829x10 <sup>2</sup>           | 0.298995x10 <sup>2</sup>   | 0.451464x10 <sup>2</sup>   |
|         | A,             | 0.737180                   | 0.430864                           | 0.416830x10                | 0.169368x10                |
|         | A              | -0.140373                  | -0.447537x10 <sup>-1</sup>         | -0.958829                  | -0.374410                  |
| SEC     | A <sub>3</sub> | $0.130467 \times 10^{-1}$  | $0.219433 \times 10^{-2}$          | 0.947123x10 <sup>-1</sup>  | 0.356744x10 <sup>-1</sup>  |
| (0-60)  | A              | -0.502609x10 <sup>-3</sup> | $-0.465507 \times 10^{-4}$         | -0.372949x10 <sup>-2</sup> | -0.137177x10 <sup>-2</sup> |
|         | A              | 0.466858x10 <sup>-5</sup>  | 0.342980x10 <sup>-6</sup>          | $0.354443 \times 10^{-4}$  | 0.126237x10 <sup>-4</sup>  |
|         | A <sub>6</sub> | 0.102595x10 <sup>-6</sup>  | 0.000000                           | 0.751243x10 <sup>-6</sup>  | 0.280023x10 <sup>-6</sup>  |

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Table IV-4

|                        |   | Coefficients of Creep Polynomial Function for UnVSBR   |  |   |  |  |
|------------------------|---|--|--|---|--|--|
|                        |   | 100 psi  | 200 psi  | 400 psi   | 500 psi  |  |
| HR<br>(0-100)          | A<br>A<br>1<br>A<br>2<br>A<br>3<br>A<br>4<br>A<br>5<br>A<br>6 | $0.510340 \times 10^{2}$<br>$0.214306 \times 10^{1}$<br>-0.184543<br>$0.758411 \times 10^{-2}$<br>$-0.138580 \times 10^{-3}$<br>$0.897499 \times 10^{-6}$<br>$0.188725 \times 10^{-8}$ | $0.636792 \times 10^{2}$ $0.959989$ $-0.403250 \times 10^{-1}$ $0.111538 \times 10^{-2}$ $-0.173375 \times 10^{-4}$ $0.113270 \times 10^{-6}$ $0.611987 \times 10^{-10}$                       | $0.729815 \times 10^{2}$<br>$0.117530 \times 10^{1}$<br>$-0.586258 \times 10^{-1}$<br>$0.180275 \times 10^{-2}$<br>$-0.293713 \times 10^{-4}$<br>$0.187182 \times 10^{-6}$<br>$0.286306 \times 10^{-9}$ | $0.784294x10^{2}$<br>$0.114155x10^{1}$<br>$-0.735757x10^{-1}$<br>$0.263747x10^{-2}$<br>$-0.454227x10^{-4}$<br>$0.289636x10^{-6}$<br>$0.515763x10^{-9}$                             |  |
| MIN<br>(0-10)          | A<br>A<br>1<br>A<br>2<br>A<br>3<br>A<br>4<br>5<br>A<br>6      | $0.142125 \times 10^{2}$ $0.278002 \times 10^{2}$ $-0.151584 \times 10^{2}$ $0.434651 \times 10$ $-0.589423$ $0.248465 \times 10^{-1}$ $0.156703 \times 10^{-2}$                       | $0.397749 \times 10^{2}$ $0.543429 \times 10$ $0.389027 \times 10$ $-0.224361 \times 10$ $0.386891$ $-0.180557 \times 10^{-1}$ $-0.127020 \times 10^{-2}$                                      | 0.550376x10 <sup>2</sup><br>0.107086x10 <sup>2</sup><br>-0.470948x10<br>0.116214x10<br>-0.145258<br>0.599617x10 <sup>-2</sup><br>0.340847x10 <sup>-3</sup>  | $0.619055 \times 10^{2}$ $0.120296 \times 10^{2}$ $-0.555500 \times 10$ $0.137965 \times 10$ $-0.170061$ $0.677923 \times 10^{-2}$ $0.407516 \times 10^{-3}$                       |  |
| SEC<br>(0 <b>-6</b> 0) | A<br>A<br>1<br>A<br>2<br>A<br>3<br>A<br>4<br>A<br>5<br>A<br>4 | 0.508812x10<br>0.359890x10<br>-0.530804<br>$0.454383x10^{-1}$<br>$-0.166809x10^{-2}$<br>$0.144657x10^{-4}$<br>$0.349533x10^{-6}$   | $0.208430 \times 10^{2}$<br>$0.630511 \times 10$<br>$-0.126744 \times 10$<br>$0.124186 \times 10^{-1}$<br>$-0.490655 \times 10^{-2}$<br>$0.469073 \times 10^{-4}$<br>$0.987409 \times 10^{-6}$ | $0.408117 \times 10^{2}$ $0.448460 \times 10$ $-0.878975$ $0.860509 \times 10^{-1}$ $-0.340579 \times 10^{-2}$ $0.326541 \times 10^{-4}$ $0.684520 \times 10^{-6}$                                      | $0.479829 \times 10^{2}$<br>$0.455364 \times 10$<br>-0.805752<br>$0.718464 \times 10^{-1}$<br>$-0.267109 \times 10^{-2}$<br>$0.234472 \times 10^{-4}$<br>$0.555718 \times 10^{-6}$ |  |

nomial function can represent a creep curve for a specified stress in only a certain relatively (small time interval.

The general power-law equation combined with a hyperbolic sine function for stress dependence

$$\varepsilon(t) = \varepsilon_0' \sinh \frac{\sigma}{\sigma_0} + m' \sinh \frac{\sigma}{\sigma_m} t^n$$
 (II.26)

will allow empirical equations to be developed which represent creep behavior to an acceptable accuracy for longer time periods.

In order to describe the experimental data by Eq. (II.26), it is necessary to evaluate the constants n,  $\varepsilon_{o}$ ,  $\sigma_{o}$ , m', and  $\sigma_{m}$  from the experimental data. Rearranging Eq. (II.21) and taking the logarithm of both sides yields

$$\log(\varepsilon - \varepsilon_{o}) = \log m + n\log t$$
 (IV.1)

Eq.(IV.1) represents a straight line with log ( $\varepsilon - \varepsilon_0$ ) as ordinate and log t as abscissa. Thus, if the data can be represented by Eq. (IV-1), the value of  $\varepsilon_0$  may be determined by trial such that a plot of log( $\varepsilon - \varepsilon_0$ ) versus log t yields a straight line as nearly as possible. The ordinate of this straight line at t=1 gives the value of m while n is the slope of the line. The resulting plots of log  $\varepsilon$  versus log t are shown in Figures IV-13, -14, -15, and -16 for vulcanized and unvulcanized NR, SBR, respectively. The constants  $\sigma_m$  and  $\sigma_0$  in Eq. (II.26) are those values of  $\sigma_m$ and  $\sigma_0$  such that a plot of m versus sinh  $\frac{\sigma}{\sigma_m}$  and  $\varepsilon_0$  versus






VSBR(#1180) at 78° F.



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sinh  $\frac{\sigma}{\sigma_0}$  yields straight lines as shown in Figures IV-17 and -18. Values of  $\varepsilon_0$  and m were obtained from the slopes of these lines. The results are listed as follows:

For VNR:  $\varepsilon(t) = 292.7 \sinh \frac{\sigma}{3000} \cdot t^{0.0307}$  (IV.2) (#10963)

For VSBR:  $\epsilon(t) = 254.4 \sinh \frac{\sigma}{2800} \cdot t^{0.0650}$  (IV.3) (#1180)

Note  $\varepsilon_0$  is neglected in this case. In fact,  $\varepsilon_0$ is only a correction term needed to make a plot of log  $(\varepsilon - \varepsilon_0)$  versus log t a quasi-straight line. Although  $\varepsilon_0$ has the physical meaning of "instant elastic deformation" (the value of  $\varepsilon$  at t=0), sometimes the  $\varepsilon_0$  values obtained are unreasonable. For example, O'Conner and Findley (74) got a negative value of  $\varepsilon_0$  for polyethylene. It probably results from the fact that the creep equation employed is an empirical relationship and thus cannot provide the best description of the creep properties of all materials. If only long-term creep is considered (e.g. hours are used on time scale and only points in excess of, say, 0.1 hour considered) such a correction term  $\varepsilon_0$  is not necessary.

Since the empirical equation  $\varepsilon(t) = S(t) \sinh \frac{\sigma}{\sigma_m}$ consists of two parts which were obtained by means of trial processes, both will contribute to the possibility of introducing errors. For the vulcanized NR, n=0.0307 is the average of five n values: 0.0314, 0.0309, 0.0307, 0.0303, and 0.0301 that correspond to the five adopted





stresses 150, 200, 300, 400 and 500 psi in that order The average value of n for these five stresses corresponds most closely to the value of n for a stress of 300 psi. Likewise since the straight line (Figure IV-17) for  $\sigma_m = 3000$ passes (m = 28.86, sinh  $\frac{\sigma}{\sigma_{\rm m}}$  = 0.097) which is close to the desired point (m = 28.86, sinh  $\frac{\sigma}{\sigma_m}$  = sinh  $\frac{300}{3000}$  = 0.10), it gives the best agreement between the experimental and calculated data (errors below 5% in the period from 1 second to 100 hours). On the other hand, this empirical powerlaw equation may not be good for  $\sigma_{+}$  = 500 psi. The addition of the two errors due to trials makes it attain 34% inaccuracy (at 90 hours). Tables IV-5 and -6 furnish the comparison results between the experimental creep data and the calculated values from Eq. (IV-2). The same comments are applicable to SBR. The creep data of 100 psi (n=0.0670), 150 psi (n=0.0665), 200 psi (n=0.0645), 300 psi (n=0.0636) and 400 psi (n=0.0633) were employed to obtain Eq. (IV-3). The average value of n is 0.0650. Tables IV-7 and -8 give the results of comparison.

The variation of humidity and temperature always influences the creep results (104). The humidity was neglected during this investigation due to the hydrophobic characteristics of NR and SBR. These two kinds of elastomers even have fair resistance to steam (19).

An increase in temperature always accelerates the molecular and segmental motion, bringing the system more rapidly to equilibrium and accelerating all types of visco-

.

Comparison between the Experimental Creep Data of VNR (All strains are in units of %)

and the Calculated Values from Eq.(IV-2)

|    | True Stress |                                    |                          |       |                  |      |  |
|----|-------------|------------------------------------|--------------------------|-------|------------------|------|--|
| T  | ime         | 100 psi                            | <u>150 ps</u>            | i     | 200 psi          | •    |  |
| 1  | sec.        | 8.52 _43.43#<br>(5.94)*            | 12.91<br>(13.08)         | 1.30  | 17.03<br>(17.61) | 3.29 |  |
| 2  | sec.        | 8.70 -26.82<br>(6.86)              | 13.18<br>(13.67)         | 3.58  | 17.40<br>(17.86) | 2.58 |  |
| 5  | sec.        | 8.95 -26.77<br>(7.06)              | 13.56<br>(14.95)         | 9.30  | 17.90<br>19.24)  | 6.96 |  |
| 10 | sec.        | 9.14 -15.40<br>(7.92)              | <b>13.</b> 85<br>(15.19) | 8.82  | 18.28<br>(19.75) | 7.44 |  |
| 20 | sec.        | 9.34 -17.04<br>(7.98)              | 14.15<br>(15.36)         | 7.88  | 18.68<br>(20.12) | 7.16 |  |
| 30 | sec.        | 9.46 -17.66<br>(8.04)              | 14.33<br>(15.71)         | 8.78  | 18.91<br>(20.38) | 7.21 |  |
| 40 | sec.        | 9.54 -15.78<br>(8.24)              | 14.45<br>(15.89)         | 9.06  | 19.08<br>(20.50) | 6.93 |  |
| 50 | sec.        | 9.60 -15.52<br>(8.31)              | 14.55<br>()              |       | 19.21<br>(20.88) | 8.00 |  |
| 1  | min.        | 9.66 -15.27<br>(8.38)              | 14.64<br>(16.12)         | 9.18  | 19.32<br>(21.13) | 8.57 |  |
| 2  | min.        | 9.87 -13.32<br>(8.71)              | 14.95<br>(16.41)         | 8.90  | 19.73<br>(21.38) | 7.72 |  |
| 3  | min.        | 9.99 -11.37<br>(8.97)              | 15.14<br>(16.47)         | 8.08  | 19.98<br>(21.45) | 6.85 |  |
| 4  | min.        | 10.08 -10.77<br>(9.10)             | 15.27<br>(16.65)         | 9.04  | 20.16<br>(21.45) | 6.01 |  |
| 5  | min.        | 10.15 -10.69<br>(9.17)             | 15.38<br>(17.06)         | 9.85  | 20.30<br>(21.57) | 5.89 |  |
| 6  | min.        | 10.20 -10.51<br>(9.23)             | 15.46<br>(17.17)         | 9.96  | 20.41<br>(21.64) | 5.68 |  |
| 8  | min.        | 10.30 -10.75<br>(9.30)             | 15.60<br>(17.41)         | 10.40 | 20.59<br>(21.70) | 4.11 |  |
| 10 | min.        | 10.37 -11.50<br>(9.30)             | 15.71<br>(17.46)         | 10.02 | 20.73<br>(21.76) | 4.73 |  |
| 1  | hr.         | 10.95 - 5.69<br>(10.36)            | 16.60<br>(18.45)         | 10.03 | 21.90<br>(23.07) | 5.07 |  |
| 2  | hr.         | 11.19 - 1.63<br>(11.01)            | 16.95<br>(18.71)         | 9.41  | 22.38<br>(23.77) | 5.85 |  |
| 3  | hr.         | 11.33 - 1.07<br>(11.21)            | 17.16<br>(18.96)         | 9.49  | 22.66<br>(24.28) | 6.67 |  |
| 5  | hr.         | <b>11.51</b> 0.09 ( <b>11.5</b> 2) | 17.44<br>(19.40)         | 10.10 | 23.02<br>(24.80) | 6.94 |  |

\* The value in parenthesis is the experimental data # The error percentage

(Continued)

True Stress

|     | ime | 100 ps           | <u>si</u> | <u>150 ps</u>    | si    | 200 ps                      | i     |
|-----|-----|------------------|-----------|------------------|-------|-----------------------------|-------|
| 10  | hr. | 11.76<br>(12.27) | 4.16      | 17.81            | 11.13 | 23.51<br>(25.80)            | 8 87  |
| 15  | hr. | 11.90<br>(13.06) | 8.88      | 18.03<br>(20.20) | 10.74 | 23.81<br>(26.39)            | 9.62  |
| 20  | hr. | 12.01<br>(13.55) | 11.36     | 18.19<br>(20.20) | 9.95  | 24.02                       | 10.00 |
| 25  | hr. | 12.09<br>(13.72) | 11.88     | 18.32<br>(20.74) | 11.67 | 24.18<br>(26.84)            | 9.91  |
| 30  | hr. | 12.16<br>(13.54) | 10.19     | 18.42<br>(20.98) | 12.20 | 24.32<br>(26.84)            | 9.39  |
| 35  | hr. | 12.22<br>(13.99) | 12.65     | 18.51<br>(21.48) | 13.83 | 24.43                       | 9.18  |
| 40  | hr. | 12.27<br>(13.14) | 6.62      | 18.58<br>(22.06) | 15.78 | 24,53                       | 8.91  |
| 45  | hr. | 12.31<br>(13.44) | 8.41      | 18.65<br>(22.45) | 16.93 | 24.62<br>(27.16)            | 9.35  |
| 50  | hr. | 12.35<br>(13.77) | 10.31     | 18.71<br>(22.55) | 17.03 | 24.70                       | 9.85  |
| 55  | hr. | 12.39<br>(13.71) | 9.63      | 18.77 (22.55)    | 16.76 | 24.78                       | 9.63  |
| 60  | hr. | 12.42<br>(13.80) | 10.00     | 18.82<br>(22.64) | 16.87 | 24.84                       | 9.64  |
| 65  | hr. | 12.45<br>(13.82) | 9.91      | 18.86<br>(22.64) | 16.70 | 24.90                       | 9.62  |
| 70  | hr. | 12.48<br>(13.85) | 9.89      | 18.91<br>(22.41) | 15.62 | 25.96                       | 9.79  |
| 75  | hr. | 12.50<br>(13.40) | 6.72      | 18.95            | 14.52 | (27.07)<br>25.01<br>(27.74) | 9.84  |
| 80  | hr. | 12.53<br>(14.29) | 12.32     | 18.98            | 14.00 | (27.06)                     | 10.31 |
| 85  | hr. | 12.55<br>(14.30) | 12.24     | 19.02<br>(22.13) | 14.05 | 25.11                       | 10.19 |
| 90  | hr. | 12.58<br>(14.35) | 12.33     | 19.05            | 14.54 | 25.15                       | 10.34 |
| 95  | hr. | 12.60<br>(14.47) | 12.92     | 19.09<br>(22.44) | 14.93 | 25.20                       | 10.61 |
| 100 | hr. | 12.62<br>(14.72) | 14.27     | 19.11<br>(22.46) | 14.92 | (25.23<br>(28.33)           | 10.94 |

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Comparison between the Experimental Creep Data of VNR (All strains are in units of %) and the Calculated Values from Eq.(IV-2)

|    |             |                         | True Stress                     |                         |
|----|-------------|-------------------------|---------------------------------|-------------------------|
|    | <u>lime</u> | <u>300 psi</u>          | <u>400 psi</u>                  | 500 psi                 |
|    |             |                         |                                 |                         |
| 1  | sec.        | 25.81<br>(26.33) 1.97   | 34.33<br>(31.41) - 9.30         | 43.22<br>(34.98) -23.56 |
| 2  | sec.        | 26.37<br>(26.85) 1.79   | 35.07<br>(31.64) -10.84         | 44.15 (35.70) -23.67    |
| 5  | sec.        | 27.12<br>(27.17) 0.18   | 36.07<br>(31.49) -14.54         | 45.41<br>(38.50) -17.95 |
| 10 | sec.        | 27.70<br>(27.30) - 1.46 | 36.85<br>(34.71) - 6.16         | 46.39<br>(40.35) -14.97 |
| 20 | sec.        | 28.30<br>(28.40) 0.35   | 37.64<br>(35.63) - 5.64         | 47.38<br>(41.42) -14.39 |
| 30 | sec.        | 28.65<br>(28.53) - 0.42 | 38 <b>.11</b><br>(35.69) - 6.78 | 47.98<br>(41.54) -15.50 |
| 40 | sec.        | 28.91<br>(28.60) - 1.01 | 38.45<br>(35.69) - 7.73         | 48.40<br>(41.92) -15.46 |
| 50 | sec.        | 29.11<br>(28.73) - 1.32 | 38.71<br>(35.80) - 8.13         | 48.74<br>(42.04) -15.94 |
| 1  | min.        | 29.27<br>(28.86) - 1.42 | 38.93<br>(35.98) - 8.20         | 49.01<br>(42.12) -16.36 |
| 2  | min.        | 29.90<br>(29.31) - 2.01 | 39.77<br>(36.09) -10.28         | 50.06<br>(42.36) -18.18 |
| 3  | min.        | 30.27<br>(29.38) - 3.03 | 40.26<br>(36.32) -10.85         | 50.69<br>(42.57) -19.07 |
| 4  | min.        | 30.54<br>(29.77) - 2.59 | 40.62<br>(36.49) -11.32         | 51.14<br>(42.81) -19.46 |
| 5  | min.        | 30.75<br>(29.83) - 3.08 | 40.90<br>(36.67) -11.54         | 51.49<br>(43.04) -19.63 |
| 6  | min.        | 30.92<br>(29.90) - 3.41 | 41.13<br>(36.72) -12.01         | 51.78<br>(43.15) -20.00 |
| 8  | min.        | 31.20<br>(29.96) - 4.14 | 41.50<br>(36.78) -12.83         | 52.24<br>(43.38) -20.42 |
| 10 | min.        | 31.41<br>(30.02) - 4.63 | 41.78<br>(36.90) -13.22         | 52.60<br>(43.50) -20.92 |
| 1  | nr.         | 33.19<br>(31.70) - 4.70 | 44.14<br>(37.70) -17.08         | 55.57<br>(43.58) -27.51 |
| 2  | nr.         | 33.90<br>(33.64) - 0.77 | 45.09<br>(38.81) -16.18         | 56.77<br>(43.62) -30.15 |
| 3  | nr.         | 34.33<br>(33.94) - 1.15 | 45.66<br>(38.84) -17.56         | 57.48<br>(43.82) -31.17 |
| 5  | hr.         | 34.87<br>(34.10) - 2.26 | 46.38<br>(39.08) -18.68         | 58.39<br>(43.95) -32.86 |

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(Continued)

|           | True Stress |                         |                                  |                          |  |  |
|-----------|-------------|-------------------------|----------------------------------|--------------------------|--|--|
| <u>_T</u> | ime         | <u>300 psi</u>          | 400 psi                          | 500 psi                  |  |  |
| 10        | hr.         | 35.62 - 3.94<br>(34.27) | 47.38<br>(39.69) -19.38          | 59.64<br>(44.60) -33.72  |  |  |
| 15        | hr.         | 36.07 - 3.41<br>(34.88) | 47.97<br>(40.28) -19.09          | 60.39<br>(45.41) - 32.99 |  |  |
| 20        | hr.         | 36.39 - 3.23<br>(35.25) | 48.40 -19.68<br>(40.44)          | 60.93<br>(46.04) -32.34  |  |  |
| 25        | hr.         | 36.64 - 2.92<br>(35.60) | 48.73 -20.32<br>(40.50)          | 61.34<br>(46.46) -32.03  |  |  |
| 30        | hr.         | 36.84                   | 49.00 -20.48<br>(40.67)          | 61.69                    |  |  |
| 35        | hr.         | 37.02 - 3.78<br>(35.67) | 49.23 -20.51<br>(40.85)          | 61.98<br>(46.64) -32.89  |  |  |
| 40        | hr.         | 37.17 - 3.89<br>(35.78) | 49.44 -19.68<br>(41.31)          | 62.24<br>(46.74) -33.16  |  |  |
| 45        | hr.         | 37.30 - 3.64<br>(35.99) | 49.62 -18.59<br>(41.84)          | 62.46<br>(47.01) -32.86  |  |  |
| 50        | hr.         | 37.42 - 3.71<br>(36.08) | 49.78 -18.02<br>(42.18)          | 62.66<br>(47.24) -32.64  |  |  |
| 55        | hr.         | 37.54                   | 49.92 - <b>1</b> 8.24<br>(42.22) | 62.85                    |  |  |
| 60        | hr.         | 37.64 - 3.44<br>(36.39) | 50.06 -18.54<br>(42.23)          | 63.02<br>(47.24) -33.40  |  |  |
| 65        | hr.         | 37.73 - 3.34<br>(36.51) | 50.18 -18.60<br>(42.31)          | 63.17<br>(47.26) -33.66  |  |  |
| 70        | hr.         | 37.81 - 3.00<br>(36.71) | 50.29 -18.86<br>(42.31)          | 63.32<br>(47.31) -33.84  |  |  |
| 75        | hr.         | 37.89 - 2.82<br>(36.85) | 50.40 -19.77<br>(42.08)          | 63.45                    |  |  |
| 80        | hr.         | 37.97 - 2.68<br>(36.98) | 50.50 -20.70<br>(41.84)          | 63.58<br>(47.69) -33.32  |  |  |
| 85        | hr.         | 38.04 - 2.84<br>(36.99) | 50.59 -21.17<br>(41.75)          | 63.69<br>(47.75) -33.38  |  |  |
| 90        | hr.         | 38.11 - 2.69<br>(37.11) | 50.68 -21.16<br>(41.83)          | 63.81<br>(47.78) - 34.18 |  |  |
| 95        | hr.         | 38.17 - 2.47<br>(37.25) | 50.77 -21.11<br>(41.92)          | 63.91<br>(47.84) -33.59  |  |  |
| 100       | hr.         | 38.23 - 2.52<br>(37.29) | 50.85 -20.84<br>(42.08)          | 64.01<br>(48.01) -33.33  |  |  |

66 Table IV-7

Comparison between the Experimental Creep Data of VSBR (All strains are in units of %)

and the Calculated\_Values from Eq.(IV-3)

|    |      | <b></b>                          |        | True Stress  | · · · · · · · · · · · · · · · · · · ·                    |
|----|------|----------------------------------|--------|--|--|
|    | lime | 100 psi                          |        | <u>150_nsi</u>   | 200 psi  |
| 1  | sec. | 6.96                             | 9.91#  | 10.45<br>(12.00) 12.92                                     | 13.94 9.66   |
| 2  | sec. | (7.0 <u>5)</u><br>7.28<br>(7.92) | 8.08   | 10.93<br>(13.06) 16.31                                     | 14.58<br>(15.66) 6.90                                    |
| 5  | sec. | 7.73<br>(8.44)                   | 8.41   | $ \begin{array}{c} 11.60 \\ (13.19) \\ 12.05 \end{array} $ | 15.47<br>(15.00) - 0.31                                  |
| 10 | sec. | 8.08<br>(8.71)                   | 7.23   | 12.13<br>(13.19) 8.04                                      | 16.18<br>(16.80) 3.69                                    |
| 20 | sec. | 8.46<br>(9.10)                   | 7.03   | 12.69<br>(13.32) 4.73                                      | 16.93<br>(17.14) 1.23                                    |
| 30 | sec. | 8.68<br>(9.25)                   | 6.16   | 13.03<br>(13.59) 4.12                                      | 17.38<br>()  |
| 40 | sec. | 8.84<br>(9.37)                   | 5.66   | 13.28<br>(13.59) 2.28                                      | 17.71<br>(17.37) 1.96                                    |
| 50 | sec. | 8.97<br>(9.44)                   | 4.98   | 13.47<br>(13.68) 1.54                                      | 17.96<br>(17.37)3.40                                     |
| 1  | min. | 9.08<br>(9.50)                   | 4.42   | 13.63<br>(13.72) 0.66                                      | $ \begin{array}{r} 18.18 \\ (17.37) - 4.66 \end{array} $ |
| 2  | min. | 9.50<br>(10.55)                  | 9.95   | 14.26<br>(13.98) - 2.00                                    | 19.02<br>(17.94) - 6.02                                  |
| 3  | min. | 9.75<br>(10.82)                  | 9.09   | 14.64<br>(14.25) - 2.74                                    | (19.52) - 6.78   |
| 4  | min. | 9.94<br>(10.95)                  | 9.02   | 14.92<br>(14.51) - 2.83                                    | 19.89<br>(18.40) - 8.10                                  |
| 5  | min. | 10.08<br>(10.95)                 | 7.94   | 15.13<br>(14.51) - 4.27                                    | 20.18<br>(18.51) - 9.02                                  |
| 6  | min. | 10.20<br>(10.95)                 | 6.85   | 15.31<br>(14.51) - 5.51                                    | 20.42<br>(18.63) - 9.61                                  |
| 8  | min. | 10.40<br>(10.95)                 | 5.02   | 15.60<br>(14.64) - 6.56                                    | 20.81<br>(18.86) -10.34                                  |
| 10 | min. | 10.55<br>(11.61)                 | 9.13   | 15.83<br>(14.78) - 7.10                                    | 21.11<br>(19.08) -10.64                                  |
| 1  | hr.  | 11.85<br>(11.81)                 | - 0.34 | 17.79<br>(19.66) 9.51                                      | 23.73<br>(21.29) -11.46                                  |
| 2  | hr.  | 12.40<br>()                      |        | 18.61<br>()  | 24.82<br>(24.82) 0.00                                    |
| 3  | hr.  | 12.73<br>(12.47)                 | - 2.08 | 19.11<br>()  | 25.49<br>(24.90) - 2.37                                  |
| 5  | hr.  | 13.26 .<br>(12.62)               | - 4.28 | 19.75<br>(22.82) 13.45                                     | 26.35<br>(24.99) - 5.44                                  |

\* The value in Parenthesis is the experimental data # The error percentage

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(Continued)

True Stress

| <u> </u>                | me  | 100 ps:          | <u>i</u> | 150 ps:                   | i_    | 200 ps           | si_    |
|-------------------------|-----|------------------|----------|---------------------------|-------|------------------|--------|
| 10                      | hr. | 13.76<br>(12.76) | - 7.84   | 20.66<br>(24.27)          | 14.87 | 27.56<br>(25.23) | - 9.24 |
| 15                      | hr. | 14.13<br>(15.62) | 9.54     | 21.21<br>(24.87)          | 14.72 | 28.29<br>(26.06) | - 8.56 |
| 20                      | hr. | 14.40<br>(15.90) | 9.43     | 21.61<br>(25.46)          | 15.12 | 28.82<br>(26.56) | - 8.51 |
| 25                      | hr. | 14.60<br>(16.16) | 9.65     | 21.92<br>(25.86)          | 15.24 | 29.24<br>(26.87) | - 8.82 |
| 30                      | hr. | 14.78<br>(16.38) | 9.16     | 2 <b>2.1</b> 9<br>(25.92) | 14.39 | 29.59<br>(28.38) | - 4.26 |
| 35                      | hr. | 14.93<br>(16.58) | 9.95     | 22.41<br>(25.99)          | 13.77 | 29.89<br>(29.03) | - 2.96 |
| 40                      | hr. | 15.06<br>(16.56) | 10.68    | 22.60<br>(26.12)          | 13.48 | 30.15<br>(29.52) | - 2.13 |
| 45                      | hr. | 15.17<br>(17.18) | 11.70    | 22.78<br>(26.25)          | 13.22 | 30.38<br>(29.93) | - 1.50 |
| 50                      | hr. | 15.28<br>(17.45) | 12.44    | 22.94<br>(26.38)          | 13.04 | 30.59<br>(30.55) | - 0.13 |
| 55                      | hr. | 15.37<br>(17.78) | 13.55    | 23.08<br>(26.25)          | 12.08 | 30.78<br>(30.75) | - 0.09 |
| 60                      | hr. | 15.46<br>(18.13) | 14.73    | 23.21<br>(26.52)          | 12.48 | 30.96<br>(31.10) | 0.45   |
| 65                      | hr. | 15.54<br>(18.63) | 16.59    | 23.33<br>(26.65)          | 12.46 | 31.12<br>(31.53) | 1.30   |
| <b>7</b> 0 <sup>`</sup> | hr. | 15.62<br>(18.67) | 16.34    | 23.44<br>(26.98)          | 13.12 | 31.27<br>(31.95) | 2.13   |
| 75                      | hr. | 15.69<br>(18.88) | 16.90    | 23.55<br>(27.11)          | 13.13 | 31.41<br>(32.13) | 2.24   |
| 80                      | hr. | 15.75<br>(19.17) | 17.84    | 23.65<br>(27.11)          | 12.76 | 31.54<br>(32.34) | 2.47   |
| 85                      | hr. | 15.82<br>(19.42) | 18.54    | 23.74<br>(27.84)          | 14.73 | 31.66<br>(32.47) | 2.49   |
| 90                      | hr. | 15.87<br>(19.55) | 18.82    | 23.83<br>()               |       | 31.78<br>(32.67) | 2.72   |
| 95                      | hr. | 15.93<br>(19.67) | 19.01    | 23.91<br>(27.51)          | 13.09 | 31.89<br>(32.81) | 2.80   |
| 100                     | hr. | 15.98<br>(19.80) | 19.29    | 23.99<br>(27.31)          | 12.16 | 32.00<br>(32.97) | 2.94   |

| Table | • тv_8                      |
|-------|-----------------------------|
| TANTE | 5 <b>T</b> A <del>n</del> o |

Comparison between the Experimental Creep Data of VSBR (All strains are in units of %) and the Calculated Values from Eq.(IV-3) True Stress

| ſ  | rime  | 250             | 200              |                               |
|----|-------|-----------------|------------------|-------------------------------|
| _  |       | SJO DS1         | <u>300 psi</u>   | <u>400 psi</u>                |
|    |       |                 |                  |                               |
| 1  | sec.  | 17.43 0.41      | 20.91 8 03       | 27.93                         |
|    |       | (19.24) 9.41    | (22.96) 0.95     | (27.93) 0.00                  |
| 2  | sec.  | 18.23           | 21.88            | 29.22                         |
|    |       | (20.50) $9.89$  | (23.19) 5.65     | (28.65) - 1.99                |
| 5  | sec.  | 19.35           | 23.22            | 31 01                         |
|    |       | (21.26) $8.98$  | (23.67) 1.90     | $(28 \ 01) - 7.26$            |
| 10 | sec.  | 20.24           | 24 20            |                               |
|    | •     | (21.38) 5.33    | (26.94) 9.84     | (31, 02) - 1.63               |
| 20 | sec.  | 21 17           | 25 /11           | (J1.9%)                       |
|    | 5001  | (21,76) 2.71    | (27, 67) 8.17    | 33.94                         |
| 30 | 600   | 04 ph           |                  | (32.30)                       |
| 0  | Sec.  | (22.14) 1.81    | 20.09            | 34.84                         |
| 10 |       |                 |                  | (32.85) - 0.00                |
| 40 | sec.  | 22.15           | 26.58            | 35.50                         |
|    |       | (22.14)         | (27.92)          | (33.18) - 0.99                |
| 50 | sec.  | 22.47           | 26.97            | 36.02                         |
|    |       | (++)            | ()               | (33.30) - 8.17                |
| 1  | min.  | 22.74           | 27.29            | 36.45                         |
|    |       | (22.64) - 0.44  | (28.05) 2.71     | (33.41) - 9.10                |
| 2  | min.  | 23.79           | 28.55            | 38 13                         |
|    |       | (22.89) - 3.93  | (28.80) 0.88     | (33.64) - 13.34               |
| 3  | min.  | 24.42           | 29.31            | 30 15                         |
|    |       | (23.40) - 4.36  | (28.93) - 1.31   | ()                            |
| 4  | min.  | 24.88           | 29.86            | (======)                      |
|    |       | (23.65) - 5.20  | (29.18) - 2.33   | (34, 24) -16.60               |
| 5  | min   | 25 25           | 30.30            |                               |
| 2  |       | (23, 77) - 6.23 | (20, 1/2) - 2.96 | 40.47                         |
| 6  |       |                 |                  | (34.33) -7.70                 |
| Q  | mirr. | (22.55) - 6.90  | 30.66            | 40.95 18 00                   |
| 0  | •     | (23.90)         | (29.56)          | (34.44) -10.90                |
| 8  | min.  | 26.03           | 31.24 5.26       | 41.72                         |
|    |       | (24.02)         | (29.68)          | $(34.56)^{-20.72}$            |
| 10 | min.  | 26.41           | 31.70 6.80       | 42.33                         |
|    | •     | (25.16) - 4.97  | (29.68) 0.80     | (34.79) - 21.67               |
| 1  | hr.   | 29.68           | 35.61            | 47.56                         |
|    |       | (31.70) 0.80    | (32.45) - 9.74   | (38.23) - 24.40               |
| 2  | hr.   | 31.04           | 37.25            | 10 76                         |
|    |       | (34.34) 9.61    | (36.72) - 1.44   | (39.26) -26.74                |
| 3  | hr.   | 31.87           | 38.25            | CJ/1207                       |
| -  |       | (35.03) 9.02    | (36.75) - 4.08   | (30,85) -28.18                |
| 5  | hr.   | 32.95           | 30 54            |                               |
| -  | -     | (36.10) 8.72    | (36.80) - 7.44   | 52.81<br>( $\mu_0$ 82) -29.37 |
|    |       | •               |                  |                               |

(Continued)

True Stress

| <u> </u> | ime | 250 psi                  |      | <u>300 psi</u>                | 400 psi                             |
|----------|-----|--------------------------|------|-------------------------------|-------------------------------------|
| 10       | hr. | 34.47<br>(37.61)         | 8.35 | 41.36<br>(36.94) -11.96       | 55.24<br>(42.15) -31.06             |
| 15       | hr. | 35.38<br>(38.68)         | 8.53 | 42.46<br>(37.24) -14.02       | (+2.15)<br>56.72<br>(42.72) -32.71  |
| 20       | hr. | 36.05<br>(39.31)         | 8.29 | 43.26<br>(38.01) -13.81       | 57.79<br>(42.95) -34.09             |
| 25       | hr. | <b>36.5</b> 8<br>(39.75) | 7.97 | 43.90<br>()                   | 58.63<br>(43.21) -35.69             |
| 30       | hr. | 37.02<br>(39.81)         | 7.01 | 44.42<br>(38.69) -14.81       | 59.33<br>(43.51) -36.36             |
| 35       | hr. | 37.39<br>(40.12)         | 6.80 | 44.87<br>(40.11) -11.87       | 59.93<br>(µ3.85) -36.67             |
| 40       | hr. | 37.71<br>(40.31)         | 6.45 | 45.26<br>(40.78) -11.10       | 60.45<br>(44.00) -37.10             |
| 45       | hr. | 38.00<br>(40.50)         | 6.17 | 45.61<br>(41.16) -10.81       | 60.92<br>(141.20) -37.83            |
| 50       | hr. | 38.26<br>(41.13)         | 6.98 | 45.92<br>(41.40) -10.92       | 61.33<br>(14,20) -38.44             |
| 55       | hr. | 38.50<br>(41.51)         | 7.25 | 46.21<br>(41.58) -11.14       | 61.72<br>(http://www.co.vec.ast.70) |
| 60       | hr. | 38.72<br>(41.70)         | 7.15 | 46.47                         | 62.07<br>(hk 72) -38.77             |
| 65       | hr. | 38.92<br>(41.95)         | 7.22 | 46.71<br>(42.02) -11.26       | 62.39<br>(44.73) -38.95             |
| 70       | hr. | 39.11<br>(42.14)         | 7.19 | 46.94<br>(42.20) -11.23       | 62.69<br>(44.90) -39.40             |
| 75       | hr. | 39,29<br>(42,39)         | 7.31 | 47.15                         | (44.97) = -39.44                    |
| 80       | hr. | 39.45                    | 7.48 | 47.34                         | (45.17) - 59.41<br>63.24            |
| 85       | hr. | 39.61                    | 7.11 | (42.79) 10.09<br>47.53 -10.43 | (45.38) - 39.30<br>63.49            |
| 90       | hr. | 39.76                    |      | (43.04) 10.79<br>47.71 -10.24 | (45.56) - 39.35<br>63.72            |
| 95       | hr. | 39.89                    | 6.99 | 47.88                         | (45.59) - 39.77<br>63.95            |
| 100      | hr. | 40.03                    | 6.82 | (43.52) -10.02                | (45.54) -40.43<br>64.16             |
|          |     | (42.90)                  |      | (43.74) - 9.05                | (45.58) -40.76                      |

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elastic processes (103). Since the creep test covers several decades on the logarithmic time scale, it is not practicable to determine the entire creep curve at a single temperature by a constant-stress test. The socalled time-temperature superpositon principle, WLF equation (99), states that a creep master curve represents hypothetical behavior at one temperature which can be obtained from several curves (possibly 10 or more) at different temperatures, each for a much shorter interval on the log t scale and which can be translated parallel to the log t scale, so that segments from different curves join to form a continuous master curve (32,67).

A convenient way of formulating this effect of temperature is in terms of the ratio  $a_T$  of the response time of a specified reaction  $\theta$  at temperature T to another value  $\theta_g$  at its glass transition temperature. For many cases, including most nonpolar amorphous polymers,  $a_T$ does not vary with  $\theta$ , so that changes in temperature shift the distribution of response times, representing all possible molecular responses of the system, to smaller or greater values of  $\theta$  but do not otherwise alter it. The quantity  $a_T$  is called a shift factor. Mathematically, the WLF equation can be expressed as follows:

$$\log a_{T} = -\frac{A(T - T_{g})}{B + (T - T_{g})}$$
(IV.4)

where A and B are material constant in units of degrees.

Some values of  $T_g$ , A, and B for rubbers are listed in Table IV-9.

### IV.B. CREEP RATE

The strain-rate curves provide a useful tool for determining the limit of primary and secondary creep and the onset of the tertiary creep (Figure IV-19.a). Primary creep ends when the creep rate becomes constant or increases in the case of high stresses. The region of constant creep rate is secondary creep and the tertiary creep begins at the upturn in the creep rate-time curves (Figure IV-19.b). Generally, the change of strain rate with time and the effect of stress on the creep rate sometimes provide useful information for analyzing and modeling the mechanical behavior of materials.



Showing the Corresponding Creep Rate Versus Time.

Values of  $T_g$ , A and B of Eq.(IV-4) for Rubbers

| Material   | Tg( <sup>O</sup> K) | A(deg) | B(deg) |
|--|---------------------|--------|--------|
| Hevea Rubber   | 200                 | 16.8   | 53.8   |
| Poly-1,4-butadiene*                                  | 172                 | 11.2   | 60.5   |
| Poly-1,2-butadiene                                   | 261                 | 12.7   | 35.5   |
| SBR  | 210                 | 20.3   | 25.6   |
| Butyl Rubber   | 205                 | 16.8   | 108.6  |
| Ethylene-propylene<br>(16:84 by volume)<br>Copolymer | 242                 | 13.1   | 40.7   |
| Ethylene-propylene<br>(56:44 by volume)<br>Copolymer | 216                 | 13.1   | 40.7   |
| Polyurethane   | 238                 | 15.6   | 32.6   |

\* cis:trans:vinyl = 43:50:7

Mathematically, the creep rate function could be obtained from the original creep function, if it is available (e.g., a polynomial of degree six)

$$\varepsilon(t) = \sum_{i=0}^{6} A_{i}t^{i} \qquad (IV-5)$$

By differentiating Eq. (IV-5) with respect to time t, the creep rate function would be:

$$\dot{\epsilon}(t) = \sum_{i=1}^{6} iA_{i}t^{i-1} \qquad (IV-6)$$

However, because of the sensitivity of this polynomial to scatter in the data, particularly upon differentiating (which gave anomalous results), this analytical approach was abandoned. Another alternative investigated was the three- and five-point Lagrangian interpolation. For the purposes intended here, however, the curves of Figures IV-1 through IV-4 were differentiated graphically. Because of the scatter in the original data on strain as a function of time, the absolute values of the slopes determined graphically are questionable. For this reason only the lower and upper bounds of the strain rates as a function of time for stresses between 100 and 400 psi for unvulcanized rubbers and stresses between 100 and 1000 psi for vulcanized rubbers are shown in Figures IV-20 through IV-23. These figures illustrate that for both vulcanized and unvulcanized rubber, only primary and secondary (but not tertiary) creep occurs during the first 100 hours at stresses below 1000 psi, which indicates that the long chain of the rubber does not break during these compression tests.

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UnVNR(#10963) at  $78^{\circ}$ F.







Figure IV-23. Typical Creep Rate-Time Data for UnVSBR(#1180) at 78°F.

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### IV.C. CREEP RECOVERY AND REBOUND TEST

When an ideal elastic solid encounters external forces, it is deformed into a new equilibrium shape. On the removal of external forces, it reverts to its original form. The solid stores all the energy which it obtained from the work done by the forces during deformation. A metal piece with small deflection is an example. Although rubber exhibits highly elastic property, it is a non-ideal elastic solid because of its ease of attaining large deformation. Rubber has mechanical properties which are intermediate between those of an elastic solid and a viscous liquid. It is a viscoelastic solid.

The creep recovery of rubber is rapid at first but the recovery rate gradually decreases, although if the unloading time is substantially longer than the time under load, virtually complete recovery can occur. Figure IV-24 illustrates the recovery response.



Figure IV-24. Creep Recovery of VNR to Single-Step Loading.

For a viscoelastic solid, the total strain is the sum of three separate parts: the immediate elastic deformation  $\boldsymbol{\epsilon}_1,$  the delayed elastic deformation  $\boldsymbol{\epsilon}_2,$  and the viscous flow part  $\varepsilon_3$ . If the solid shows linear behavior, the magnitude of the strains  $\varepsilon_1$ ,  $\varepsilon_2$  and  $\varepsilon_3$  are exactly proportional to the magnitude of the applied stress. Linear amorphous polymers show a finite  $\varepsilon_3$  at temperatures above their glass transitions, but at lower temperatures their behavior is dominated by  $\epsilon^{}_1$  and  $\epsilon^{}_2$  (98).

The fractional recovery (FR) is defined as (93):

$$FR = \frac{\text{strain recovered}}{\text{maximum creep strain}} = \frac{\varepsilon_{c}(t_{1}) - \varepsilon_{r}(t)}{\varepsilon_{c}(t_{1})}$$
(IV-7)

where  $\boldsymbol{\epsilon}_{_{\mathbf{C}}}(\mathbf{t}_{_{\mathbf{1}}})$  is the creep at the time at which the load is removed.

 $\varepsilon_r$  (t) is the residual strain.

The values of fractional recovery of rubbers at different times of removing the load are listed in Table IV-10.

#### TABLE IV-10

|        | Fractional | Recover | y of Rub | ber   |          |
|--------|------------|---------|----------|-------|----------|
| Rubber | -<br>-     | lime of | Removing | the   | Load     |
|        |            | 20 Sec. | <u>1</u> | Min.  | <u> </u> |
| VNR    |            | 78.79%  | 8        | 1.488 | 5        |
| UnVNR  |            | 16.67%  | 1        | 4.408 | 5        |
| VSBR   | •          | 75.90%  | 7        | 8.00% | 5        |
| UnVSBR |            | 13.62%  |          | 9.369 | 5        |

The residual strain was measured at a time equal to the loading time.

In some applications, the load instead of being applied continuously will be applied intermittently for limited periods. In the period for which the load is removed, the test specimen will have an opportunity to recover. The extent to which this occurs will depend upon the ratio of the time under load to the time without load. The residual strain for a fixed ratio of the loaded to unloaded time will increase as the magnitude of the strain at the time of removal of the load increases. Rebound tests were conducted with intervals of 20 seconds and 1 minute for vulcanized and unvulcanized NR and SBR under a nominal stress of 200 psi. Figures IV-25 to -32 show the results. The comparison between the vulcanized and unvulcanized rubber for SER is shown in Figure IV-33.

# IV.D. ISOCHRONOUS STRESS-STRAIN PLOTS; ELASTIC MODULUS AND VISCOSITY OF RUBBERS

The basic creep plots in normal form ( $\varepsilon$  - t with  $\sigma$  as parameter) are not completely satisfactory in comparing the mechanical properties among several different materials, especially where different stress levels have been used for different materials.

The stress-strain plot indicates whether a material is brittle or ductile in nature. The area under a stressstrain curve is proportional to the energy absorbed in breaking the material (70). From a practical standpoint,



Figure IV-25. The Result of Rebound Test for VNR(#10963) at 80°F and 200 psi of Nominal Stress with a Loading Interval of 20 Seconds.



Figure IV-26. The Result of Rebound Test for VNR(#10963) at 80<sup>°</sup>F and 200 psi of Nominal Stress with a Loading Interval of 1 Minute.







Figure IV-28. The Result of Rebound Test for UnVNR(#10963) at 80<sup>0</sup>F and 200 psi of Nominal Stress with a Loading Interval of 1 Minute.



Figure IV-29. The Result of Rebound Test for VSBR(#1180) at 80<sup>°</sup>F and 200 psi of Nominal Stress with a Loading Interval of 20 Seconds.







of Nominal Stress with a Loading Interval of 20 Seconds.



of Nominal Stress with a Loading Interval of 1 Minute.



Figure IV-33. The Comparison of Rebound Testsfor VSBR and UnVSBR at 80°F and 200 psi of Nominal Stress with a Loading Interval of 20 Seconds.
such plots are very important. Generally, stress-strain measurements are made in tension by stretching the specimen until the specimen breaks. The method most often used to determine the change in length is measuring the separation of the jaws or clamps holding the specimen. Although this procedure is the simplest way of determining the elongation, it always leads to serious errors. For example, some slippage in the specimen grips leads to an apparent elongation greater than the true elongation. Second, the cross-sectional area will decrease during the stretching process, but near the clamps the test specimen is still retaining its original width and thickness. Also, the strain varies very severely along the length of the specimen when a neck forms. Thus, the whole specimen cannot stretch uniformly.

A much simpler method to obtain the stress-strain plot is to erect an ordinate on the basic creep curves at a specified time (cross plot) from which the strain values reached for each stress level examined can be obtained. One of the advantages of using the creep data to get the isochronous stress-strain plot, instead of measuring the stress and strain directly, is that the deficiency due to the change of cross-sectional area can be prevented.

The strain after 20 seconds will be referred to as the 20-second "elastic" strain. The stress-strain curve corresponding to the selected loading time (20 seconds) for vulcanized NR and SBR is illustrated in Figure IV-34 and Figure IV-35, respectively. Accordingly, Young's modulus of these two materials can be obtained by measuring





the slope of the curve at zero stress. The results are as follows:

E = 225/16% = 1406.2 psi (NR #10963)

E = 250/21.6% = 1157.4 psi (SBR #1180)

On the other hand, it was not possible to obtain Young's modulus for unvulcanized NR and SBR by this method since the data at low stress levels was quite incoherent (possibly due to the fact that the unvulcanized rubbers do not exhibit any elastic behavior, Figure IV-33). In fact, the stress-strain rate plot ( $\sigma$  vs  $\frac{d\varepsilon}{dt}$ ) suggests that the unvulcanized rubber behaves more like a viscous fluid than an elastic solid. Its rheological behavior is similar to that of a non-Newtonian fluid (Figures IV-36 and -37).

For a non-Newtonian fluid, the basic definition of viscosity used for Newtonian fluids is meaningless, because the value changes when the shear rate or the shear stress is changed. For this reason, n<sub>a</sub> is termed an "apparent viscosity"—the viscosity of non-Newtonian fluid at a given shear rate (65). The numerical value of unvulcanized NR and SBR at the instant of applying stress are:

 $n_a (\frac{d\varepsilon}{dt} \Rightarrow o) = 28.4 \text{ psi-sec} = 1.96 \times 10^6 \text{ poise}$  (for UnVNR)  $n_a (\frac{d\varepsilon}{dt} = o) = 35.7 \text{ psi-sec} = 2.46 \times 10^6 \text{ poise}$  (for UnVSBR)



UnVNR from Creep Data.



If a vulcanized rubber that contains reinforcing fillers (e.g. carbon black) is relaxed (or perhaps swollen in a solvent so as to facilitate complete recovery) after a tensile deformation, the new dried rubber will display a curious phenomenon when the same action is repeated (45,66). It may be described best by reference to the stress-strain curve shown in Figure IV-38.



Figure IV-38. A Typical Stress-Strain Curve for a Rubber Containing Reinforcing Fillers. (The rubber was first stretched from O through A to C, D. On the second stretching it followed curve OBCD.)

Obviously, the rubber has been softened by the first stretching process, although the curves do not differ much at small elongation.

Bueche (13) developed a molecular model for this Mullins softening effect. Rubber molecules with a distribution of chain lengths are regarded as fastened at both ends to filler particles; detachment occurs when the particles separate sufficiently to stretch the molecular chains to their full extension (Figure IV-39).



Figure IV-39. Typical Chains Attached to Two Adjacent Filler Particles.

On extension the short chains (a) break first as they are the first to reach full extension and then carry a stress much larger than average. Before breaking, nevertheless, these chains will hold an enormous load and will give rise to a high modulus. On the second stretch, however, these broken chains will not be holding any load; consequently, the modulus will be lower.

The previously compressed rubbers were relaxed naturally, and then were subjected to second creep tests. The isochronous stress-strain curves are shown in Figure IV-40 and Figure IV-41 for NR and SBR, respectively. The Mullins softening phenomena do not appear in these plots. Contrarily, the stress-strain curves are steeper than the previous ones, and the moduli of previously loaded samples





are greater than those of the original ones. This increase of modulus may be due to an increase in concentration of fillers within the rubber (Ref: Guth's equation:  $E = E_0(1 + 2.5C + 14.1C^2)$ where  $E_0$  is the Young's modulus of rubber without reinforcing fillers and C is the concentration of fillers)(6).

#### IV.E. CREEP COMPLIANCE

Sometimes the creep compliance (J) is plotted against time to represent creep behavior. The compliance is obtained by dividing the strain at any time by the stress on that specimen. The compliance gives an apparent reciprocal modulus which changes with time. For a perfectly elastic solid, J=1/E.

The plots of J(t) vs log t under different true stresses for rubbers are illustrated in Figures IV-42, -43, -44, and -45. It was found that the creep-compliance curves did not coincide for different levels of stress (48), especially for the unvulcanized rubbers. However, the compliance of the vulcanizates of NR and SBR at the shortest time of measurement is identical for some levels of stress. The latter fact indicates the existence of the elastic limit of the vulcanizates.

Figure IV-46 shows the creep curves of unvulcanized NR and its vulcanizate under the load of 100 psi. Figure IV-47 illustrates the comparison for SBR. Striking differences are apparent in the effect of vulcanization on natural or synthetic rubbers. The unvulcanized rubbers show viscous flow behavior at room temperature after an external load is applied and attain large permanent deformations. After









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× UnVSBR ▲ VSBR 60 48 Jx10<sup>4</sup> (psi<sup>-1</sup>) 30 18 6 0 L 10<sup>-1</sup> 10<sup>0</sup> 2 10<sup>1</sup> .2 10<sup>2</sup> 5 2 5 5 TIME (HR) Figure IV-47. Comparison of the J-Log t Curves between VSBR and UnVSBR

under 100 psi of True Stress at 78°F.

the vulcanization process, the primary molecules have been tied into a stable network in the vulcanizates which respond quickly under load and then remains at nearly constant deformation for a long time thereafter.

Rubber-like materials dissipate energy when subjected to rapid cyclic deformation causing evolution of heat. Consider a specimen of rubber subjected to a uniaxial oscillating stress represented by

$$\sigma = \sigma_{\max} \sin \omega t \qquad (IV.8)$$

The resulting oscillating strain is given by (Figure IV-48)



 $\varepsilon = \varepsilon_{\max} \sin (\omega t - \delta)$  (IV.9)

Figure IV-48. Sinusoidal Variation of Stress and Strain.

The energy loss in the material during a complete cycle can be evaluated from the following integral that includes Eq. (IV.8) and Eq. (IV.9) (56)

$$\Delta W = \int_{0}^{\frac{2\pi}{\omega}} \sigma \, \frac{d\varepsilon}{dt} \, dt \qquad (IV.10)$$

$$= \pi \sigma_{\max} \sigma_{\max} \sin \delta \qquad (IV.11)$$

$$= \pi E_2(\omega) \epsilon_{\max}^2$$
 (IV.12)

$$\tau = \pi J_2(\omega) \sigma_{max}^2$$
 (IV.13)

where  $E_2(\omega)$  is the imaginary part of the complex dynamic modulus  $E(i\omega)$ ;  $E(i\omega)=E_1(\omega)+iE_2(\omega) = \frac{\sigma_{max}}{\varepsilon_{max}}(\cos \delta + i\sin \delta)$  (IV.14)  $J_2(\omega)$  is the imaginary part of the complex dynamic

compliance 
$$J(i\omega)$$
;  
 $J(i\omega)=J_1(\omega)-iJ_2(\omega) = \frac{\varepsilon_{max}}{\sigma_{max}} (\cos \delta - i\sin \delta)$  (IV.15)

Bueche (12) calculated the heat generated when a triangular force (Eq. (IV.16)) was applied to the rubber.

$$\sigma = \begin{cases} (\sigma_{\max}/\Gamma)t & 0 \le t \le \Gamma \\ (\sigma_{\max}/\Gamma)(2\Gamma - t) & \Gamma \le t \le 2\Gamma \text{ (IV.16)} \\ 0 & \text{Otherwise} \end{cases}$$

Heat = 
$$6.6 Qn_{max}^{2}$$
 (IV.17)

where Q is the slope of the long-time portion of the curve of J vs. log t.

n is the frequency of the force impulses to the rubber.

 $\boldsymbol{\sigma}_{max}$  is the maximum tensile stress experienced by the rubber.

Accordingly, the creep-compliance curve has an extra advantage in connection with computing the heat build-up in rubber under repeated flexing. Since the slopes of the curves are very small, the vulcanized NR and SBR show relatively small heat build-up. The vulcanized SBR has more heat development than NR during compressive deformation, because it yields a larger slope in the creep curve (0.0650 for SBR and 0.0307 for NR in the plot of log  $\varepsilon$  vs. log t).

### IV.F. PHYSICAL PROPERTIES OF SWOLLEN RUBBERS

First, the swelling power of rubbers in two kinds of organic solvents, benzene and kerosene (C<sub>14</sub>H<sub>30</sub>), were investigated. Since the unvulcanized rubbers (NR and SBR) have weak resistance to these solvents and will dissolve and diffuse out, the following discussions are restricted to vulcanizates only.

The crosslinked parts of rubber swell when put in the solvent until the osmotic forces trying to dissolve the polymer are balanced by the elastic forces due to the stretched segments of polymer chains. These elastic retractive forces are inversely proportional to the molecular weight of the polymer between points of crosslinking (28).

The swelling rate is a function of the kind of solvent, the composition of the sample, and experimental conditions(40). Changing the composition of the ingredients of rubber can adjust its resistance to solvents. Technical test methods of this character should be carried out in rubber laboratories so that the suitability of newly developed rubber mixtures for practical service conditions can be judged by laboratory tests.

Swelling is usually expressed as the swelling ratio q, which is defined as the ratio of the volume of the swollen gel to the original unswollen one (79). The plots of the swollen ratio vs. time for NR and SBR in kerosene and benzene are shown in Figures IV-49 and -50, respectively. The swelling power of benzene is 1.4 and 2.0 as great as that of kerosene for NR and SBR, respectively. It is further evident from these figures that, because of this very high rate of swelling in benzene, a period of 48 hours is sufficient to obtain a correct idea of the behavior of the sample in minimum swelling, whereas this same length of time in kerosene gives completely misleading values. Since such a high rate of swelling as that in benzene is not ordinarily encountered, it is always advisable to continue the measurements for at least one week, in which case the swelling is measured each day, to ascertain whether the swelling maximum is practically reached, for example, in 3 or 4 days. In





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addition to possessing that higher swelling power, benzene has greater interaction with the nonpolymeric components of NR and SBR than kerosene, and then a small amount of soluble ingredients will be extracted to cause a slight reduction in dimensions. Generally, the extraction of soluble ingredients is negligible compared with the actual swelling. This fact happens after 2 days for NR and 6 days for SBR. On the other hand, with high volatile characteristics, considerable loss of benzene in the interval of time between removal of the test specimen from benzene and its final measurement may cause error.

In making measurements of the resistance to swelling, the accompanying changes in physical properties of the material are also of interest. The samples dipped in solvents for different periods of time (25 hours, 50 hours, and 100 hours) were employed to do the same creep tests as those of the unswollen rubbers. Figures IV-51 through -54 illustrate the results that are compared with those of the ordinary ones.

The swelling process of rubber corresponds to an isotropic expansion of the network, which is accompanied by a reduction in the network entropy. This condition gives the swollen sample much more freedom for segmental motion so that it can be more easily deformed than the unswollen one (90). The creep result depends upon the length of the swelling period because the swelling ratios

50 D 40 C В 30 TOTAL STRAIN (%) A 20 Nominal Stress: 300 psi Curve A: Ordinary Sample B: With Swelling Period of 25 Hrs. C: With Swelling 10 Period of 50 Hrs. D: With Swelling Period of 100 Hrs. 0 2 4 6 8 10 12 TIME (MIN) Figure IV-51. Representative Creep Curves for Swollen

VNR in Kerosene.



VNR



VSBR in Kerosene.

50 40 D C B 30 TOTAL STRAIN (%) ٩ Α 20 Nominal Stress: 300 psi Curve A: Ordinary Sample B: With Swelling Period of 25 Hrs. C: With Swelling 10 Period of 50 Hrs. D: With Swelling Period of 100 Hrs. 0 6 2 4 8 10 12

> Figure IV-54. Representative Creep Curves for Swollen VSBR. in Benzene.

TIME (MIN)

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of NR and SBR increase with time for kerosene and benzene before achieving swelling equilibrium. Accordingly, the modulus of rubber will reduce. Take as an example, the unswollen NR has a modulus E = 300/0.2520 = 1190 psi at the 20-second elastic strain. The corresponding moduli for the swollen ones are:

> E = 300/0.3662 = 819.2 psi (swelling in kerosene) E = 300/0.4234 = 708.6 psi (swelling in benzene)

The reduction factors of modulus are 1.453 and 1.679 for the swelling of NR in kerosene and benzene, respectively. The linear dimensions increased by the swelling are 1.186 (in kerosene) and 1.424 (in benzene). Theoretically, swelling of rubber reduces its Young's modulus by a factor of  $1/\gamma$  ( $\gamma$  is linear dimension increased by the swelling) but leaves the form of the stress-strain curve unchanged (92).

The results of rebound tests for these swollen rubbers (dipped in liquids for 25 hours) are shown in Figures IV-55 through -58. Their values of fractional recovery (FR) are listed in Table IV-11.

#### TABLE IV-11

|                  | Time of Removin | g the Load    |
|------------------|-----------------|---------------|
| Rubber & Solvent | 20 Sec.         | <u>l Min.</u> |
| NR in Kerosene   | 92.19%          | 92.88%        |
| NR in Benzene    | 87.19%          | 87.94%        |
| SBR in Kerosene  | 85.71%          | 88.31%        |
| SBR in Benzene   | 91.16%          | 89.46%        |

## Fractional Recovery of Swollen Rubber





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Figure IV-56. The Result of Rebound Test for Swollen (in Benzene) VNR at 80°F and 200 psi of Nominal Stress with a Loading Interval of 20 Seconds.



Figure IV-57. The Result of Rebound Test for Swollen (in Kerosene) VSBR at 80<sup>°</sup>F and 200 psi of Nominal Stress with a Loading Interval of 20 Seconds.



Figure IV-58. The Result of Rebound Test for Swollen (in Benzene) VSBR at 80°F and 200 psi of Nominal Stress with a Loading Interval of 20 Seconds. 122

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IV.G. COMPRESSION OF RUBBER BLOCK

Both the change of shape and the change of size have contributions to a compressive deformation. Shear modulus G governs the response of a material to a change of shape and bulk modulus K responds to a change of size.

Poisson's ratio  $\nu$ , as normally defined for uniform

$$v = -\frac{\varepsilon_{\text{transverse}}}{\varepsilon_{\text{axial}}}$$
(IV.18)

simple deformation, is also related to the shear and bulk moduli for isotropic material in the following equation, if the elastic properties in tension are assumed to be equal to those in compression (58):

$$v = \frac{3K - 2G}{6K + 2G}$$
 (IV.19)

For most material, other than elastomers, these two contributions are of similar magnitude, their Poisson's ratios are substantially less than 0.5, and they have little variation of compression modulus with shape. Accordingly, the usual assumption that the compression modulus is equal to Young's modulus is permissible. Since rubber has a low shear modulus but a relatively high bulk modulus, any restriction on its freedom to change shape can have a very marked effect on its apparent stiffness in compression (50,53), resulting in a large difference between the compression modulus and Young's modulus. The variation of the apparent compression modulus with the shape of the compression block will be discussed in this section.

For a compressed rubber block, the applied force F may be written in a form as:

$$F = f_c AE\varepsilon \qquad (IV.20)$$

where A is the cross-sectional area of the block

- E is the Young's modulus for the rubber
- $\varepsilon$  is the strain
- f is a numerical factor representing the restrictive effects of the bonded surfaces.

Gent et al (43) assumed that the total displacements arises from the superposition of two simple displacements: (1) the pure homogeneous deformation defined by the displacement of one rigid bounding plate toward the other, and (2) the subsequent shear displacements necessary to restore points in the planes of the bonded surfaces to their original positions in these planes. The corresponding forces  $F_1$  and  $F_2$  which must be applied to the bonded surfaces were then derived, the total force F being given by their sum. The factor  $f_c$  is thus equal to the sum of the two terms, given by

$$f_{cl} = \frac{F_{l}}{AE\varepsilon}$$
 (IV.21)

and

$$f_{c2} = \frac{F_2}{AE\varepsilon}$$
 (IV.22)

The derivation of the factors  $F_1$  and  $F_2$ , and hence of the components  $f_{c1}$  and  $f_{c2}$  of the factor  $f_c$ , is outlined below for blocks of infinitely long rectangular cross section; it is then generalized to deal with blocks of any cross section.

# IV.G.1. Rectangular Blocks of Infinite Length

In this case, the pure homogeneous deformation consists of a compressive strain  $\varepsilon$  in the vertical direction, and zero strain in the length direction, and an expansion in the width direction because the rubber block is assumed to be incompressible.

The rubber block is placed in a state of pure shear and the force  $F_1$  which has to be applied to the bonded surfaces to maintain such a deformation is given by

$$\mathbf{F}_1 = 4/3 \ \mathrm{EW}\varepsilon \qquad (IV.23)$$

per unit length, where E is Young's modulus of rubber and W is the width of the block (86).

In order to calculate the corresponding other force  $F_2$  which also has to be applied to the bonded surfaces, it is necessary to make a simplifying assumption that the horizontal planes remain plane during the deformation, and this assumption seems probable when the width W is much greater than the Height H. Vertical sections consequently take up parabolic forms, as represented diagrammatically in Figure IV-59.




Consider a plane at a distance x from the central vertical plane, then

$$xH = x(H-d) + 2/3 k_H$$
 (IV.24)

from the volume constancy assumption. That means the volume contained between the vertical surface and the central plane in the undeformed state shall be equal to the volume contained between the deformed vertical section and the central plane when it takes up the parabolic form. (The term 2/3 k<sub>x</sub>H is the approximate volume contained between the parabolic front of maximum displacement k<sub>x</sub> and the vertical plane at x when the compression is small.) The maximum displacement of the parabolic front k<sub>x</sub> becomes

$$k_x = 3/2 (xd/H)$$
 (IV.25)

In an elementary section of width dx, the small displacement  $k_x$  may be maintained by the action of an excess hydrostatic pressure acting on one curved face, where  $dP_x$  is given by classical elasticity theory in the form

$$dP_{x} = -8/3 \left(\frac{Ek_{x}}{H^{2}}\right) dx$$
 (IV.26)

The pressure  $P_x$  is then obtained by integration,

$$P_{x} = \int_{W/2}^{x} dP_{x} = 2Ed(W^{2}/4 - x^{2})/H^{3}$$
 (IV.27)

The pressure acts on the right bonded planes also. The corresponding force  $F_2$  acting on each of these surfaces may be obtained by integrating such terms as  $P_x$ dx between the limits x=W/2 and x=-W/2, to give

$$F_2 = EdW^3/3H^3$$
 (IV.28)

The apparent value of Young's modulus for the rubber block is given by

$$E_{a} = F/W\varepsilon \qquad (IV.29)$$

Hence

$$E_a = E \{4/3 + 1/3(W/H)^2\}$$
 (IV.30)

IV.G.2. Blocks of Any Cross Section

The term  $f_{cl}$  ranges from unity for symmetrical cross sections to 4/3 for cross sections in which the lateral displacements are confined to one direction only. Gent and Meinecke (44) got an empirical form for  $f_{cl}$ :

$$f_{cl} = 4/3 - 2/3(LW + H^2)/(L^2 + W^2 + 2H^2)$$
 (IV.31)

where 2L and 2W denote the sides of a rectangular cross section or the axes of an elliptical one. This relation satisfies the principal requirements: (i) it is symmetrical in L and W; (2) it yields a value of unity when L=W for all values of H, and also when H>>L,W; (3) it yields a value of 4/3 when L>>W,H or when W>>L,H.

The compression stiffness factors for various cross sections are given in Table IV-12.

# TABLE IV-12

### Compression Stiffness Factors for

Various Cross Sections

| Cross-section                       | fcl              | fc2   |
|-------------------------------------|------------------|---|
| Circle, radius R                    | 1                | $R^2/2H^2$  |
| Ellipse, semi-axes L and W          | from Eq. (IV.31) | $L^2 W^2 / (L^2 + W^2) H^2$                               |
| Square, side 2L                     | 1                | $0.141(2L)^2/H^2$   |
| Rectangle, sides 2L and 2W          | from Eq. (IV.31) | $\frac{1}{3}$ (2L) <sup>2</sup> /H <sup>2</sup>           |
|                                     |                  | x $[1 - \frac{192}{\pi^5} \frac{L}{W} \sum_{n=1,3,5}^{E}$ |
|                                     |                  | $\frac{1}{n^{5}} \tanh (\frac{n\pi W}{2L})]$              |
| Equilateral Triangle,<br>altitude Z | 1                | z <sup>2</sup> /15H <sup>2</sup>                          |

The apparent Young's modulus of NR and of SBR then can be calculated for the square sample.

 $E_a = (1 + 0.141 \times (\frac{0.394}{0.275})^2) \times 1406.2 \text{ psi} = 1812 \text{ psi} \text{ (for NR)}$  $E_a = (1 + 0.141 \times (\frac{0.394}{0.278})^2) \times 1157.4 \text{ psi} = 1485 \text{ psi} \text{ (for SBR)}$ 

#### CHAPTER V

### CONCLUSIONS AND RECOMMENDATIONS

V.A. CONCLUSIONS:

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Vulcanized rubbers have a limited range of linearity They behave linearly only in a range of applied stresses and at specified time. They demonstrate their nonlinear behavior in that doubling the load in a creep test cannot just double the magnitude of deformation after a given length of time. In some cases, the stress dependence of the creep follows approximately a hyperbolic sine function:

$$\varepsilon(t) = S(t) \sinh \left(\frac{\sigma}{\sigma_m}\right)$$
 (V.1)

where  $\varepsilon(t)$  is the creep deformation at any time t.

S(t) is a function defining the time dependence of the creep.

o is the applied stress.

 $\sigma_{m}$  is a material constant.

For VNR:  $\epsilon(t) = 292.7(\sinh \frac{\sigma}{3000})t^{0.0307}$ (#10963) For VSBR:  $\epsilon(t) = 254.4(\sinh \frac{\sigma}{2800})t^{0.0650}$ (#1180)

The ability of vulcanized rubbers to recover means that higher allowable stresses will be possible under intermittent loading conditions for a few cycles than with continuous loading.

Creep response of vulcanized rubbers begins in a way qualitatively similar to the retarded elastic response of a crosslinked polymer. However, instead of rubbery equilibrium, steady viscous flow results eventually, and upon loading the recovery is not complete, i.e., a permanent set remains.

For both vulcanized and unvulcanized rubber, their creep stages change from primary to secondary only during the first 100 hours at stresses below 1000 psi.

Modulus is defined as "a constant or coefficient that expresses, usually numerically, the degree in which a property is possessed by a substance or body" (Webster's New Collegiate Dictionary). In fact, it has a physical meaning of representing "resistance" when mentioned in mechanics. The Young's modulus of vulcanized natural rubber is greater than that of vulcanized SBR. In general, natural rubber possesses lower creep characteristics than other elastomers do. In addition, natural rubber has high resilience, it is inexpensive and easy to manufacture. These are the principal reasons for using natural rubber in making rubber springs. About 55% of all the natural rubber consumed is used in tires.

The Mullins softening effect does not exist in the compressive deformation of vulcanized rubbers which were compressed previously. The stress-strain curves of these relaxed samples are steeper than the original ones.

The vulcanized natural and synthetic rubbers have relatively small heat up during compressive deformation. SBR has more heat development than NR.

The unique effect of the swelling is to reduce the modulus inversely proportional to the increase of the dimension in the direction of deformation measured, without changing the form of the stress-strain relations.

### V.B. RECOMMENDATIONS

The mechanical properties of elastomers are not only determined from the polymer itself but also are influenced greatly by the compounding ingredients (e.g. fillers, vulcanizing agents, etc.). Since the detailed composition of the ingredients other than polymer is not clear, the discussions and conclusions written above are not general and are restricted to the specified natural rubber (#10963) and SBR (#1180).

The creep results are generally temperature dependent, and the material constant  $\sigma_m$  in the relation of the stress dependence of the creep

$$\varepsilon(t) = m'(\sinh \frac{\sigma}{\sigma_m}) t^n$$

is affected by the temperature change. Since the glasstransition temperature  $T_g$  of rubbers (about -70°C) are somewhat lower than ordinary service temperatures, a few degrees variation (±2°F) around room temperature will not influence the experimental results greatly. To remove the inaccuracy caused by temperature changes, the construction of a master curve is suggested. This can be done by running the creep experiments under different temperatures and time periods.

The evident effect of swelling of a specimen caused by a solvent is an increase in volume. The measurement of the dimensions of the swelling rubbers (volumetric method) in this experiment is just simple and crude. An indirect technique, the gravimetric method which measures the weight of liquid absorbed, can be employed to correct the result obtained from the volumetric method. It is widely used because of its simplicity; however, it may easily give false results due to the extraction of compounding ingredients. The gravimetric method is therefore applicable only when an extraction of components soluble in the swelling liquid is not a complicating factor.

All the samples used in this experiment are square in shape for easy implementation. A round disc specimen would be better than the square one for the swelling measurement, since determination of volume becomes very simple, only two dimensions (diameter and thickness) are required to be measured before and after swelling, and the swelling effects are calculated from these figures.

In some other applications (e.g. pipe couplings, closures and other interference fits), stress relaxation requires more attention than creep (75). Stress relaxation is the effect of time and temperature on the rate of decay of stress at a fixed level of strain. In stress-relaxation measurements the test specimen is rapidly deformed to a given value, and the stress required to hold the length constant is measured as a function of time.

It would be of interest and value to extend the present studies to creep of rubber under biaxial loading in compression; in fact, it would be desirable to include triaxial loading since in many applications this condition obtains. Until experimental data of this kind become available, little progress in understanding the basic phenomena involved can be obtained from mathematical analysis alone.

# NOMENCLATURE

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| $a_{\mathrm{T}}$  | shifting factor   |
|-------------------|---|
| A <sub>i</sub>    | polynomial coefficient                                  |
| A <sub>r</sub>    | amplitude ratio   |
| Е                 | Young's modulus   |
| Ea                | apparent Young's modulus                                |
| ΔE                | activation energy                                       |
| f                 | external force  |
| fc,fcl,fc2        | numerical factor  |
| fo                | displacement frequency                                  |
| <sup>f</sup> -3db | displacement frequency for which output<br>is down 3 db |
| F,F1,F2           | external force  |
| F                 | Helmholtz free energy                                   |
| G                 | shear modulus   |
| G                 | change of Gibbs free energy                             |
| Н                 | height of rubber block                                  |
| н                 | enthalpy  |
| <b>J</b> .        | compliance  |
| k                 | Boltzmann constant                                      |
| k x               | the parabolic front of maximum displacement             |
| К                 | bulk modulus  |
| L                 | bond length   |

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| of r | ubber | blc       | )C}           | ς               |
|------|-------|-----------|---------------|-----------------|
|      | of r  | of rubber | of rubber blo | of rubber block |

| L <sub>f</sub> | molar | latent | heat | of | fusion | for | the | solvent |
|----------------|-------|--------|------|----|--------|-----|-----|---------|
|----------------|-------|--------|------|----|--------|-----|-----|---------|

m the strain value at t=1 minute

m' numerical constant

n numerical constant

n frequency of the force impulses

n the number of chains in a unit volume of the rubber block

N the number of rigid bonds in a chain

P,p external pressure

P vapor pressure

P saturated vapor pressure

q swelling ratio

Q the slope of the curve of J vs log t

r chain distance

r mean-square of chain distance

R gas constant

R<sub>i</sub> the end-to-end length of the j<sup>th</sup> molecule

s entropy of chain

S entropy of network

T absolute temperature

T<sub>f</sub> melting point temperature

T<sub>g</sub> glass transition temperature

U internal energy

V volume

W width of rubber block

W<sub>g</sub> strain energy

X,Y,Z rectangular Cartesian coordinates

Greek

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| α                            | valence angle  |
|------------------------------|--|
| β                            | proportional constant                                |
| γ                            | linear dimension increase by the swelling            |
| η                            | viscosity  |
| ε.                           | strain   |
| θ                            | response time  |
| Θ                            | phase angle between displacement and electric output |
| λi                           | extension ratio (i=1,2,3)                            |
| π                            | osmotic pressure                                     |
| φ                            | $= \beta/RT$   |
| ν                            | frequency of jump                                    |
| ν                            | Poisson's ratio                                      |
| $\xi_{i}, \eta_{i}, \nu_{i}$ | segmental coordinates                                |
| σ                            | stress   |
| σ <sub>m</sub>               | stress constant of material                          |
| σo                           | stress constant of material                          |
| <sup>σ</sup> ni              | nominal stress (i=x,y,z)                             |
| σti                          | true stress (i=x,y,z)                                |
| τ                            | retardation time                                     |
| г .                          | time interval  |
| ω                            | angular frequency                                    |
| δ                            | phase angle  |

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# APPENDIX A

# ELASTOMERS

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The term elastomer is derived from "elastic" and "polymer" and has an even broader meaning. It removes two limitations that were included under the definition of a rubber (100). When stretched, an elastomer need not return to approximately its original dimensions. Thus, the concept of time required to regain shape, which is involved in the properties of snap and rebound in a rubber, need not be possessed by all elastomers. The second limitation that does not apply to elastomer is that of vulcanizability. Rubbers are included in the much broader classification of elastomers.

### A.I. NATURAL RUBBER (5,100)

The main source of natural rubber is the rubber tree called Hevea Brasilliensis. The rubber exists in the tree in the form of a milky latex consisting of colloidal globules about 0.09 to 1.85 microns in diameter suspended in an aqueous medium. This latex is contained in the inner bark and is entirely separated from the sap. The composition of the latex is approximately as follows:

| water            | 60%  |
|------------------|------|
| rubber           | 35%  |
| protein          | 2%   |
| fatty materials  | 1%   |
| carbohydrates    | 18   |
| inorganic matter | 0.4% |

The monomer that forms natural rubber is isoprene  

$$(CH_2=C-CH-CH_2)$$
 and the polymer structure is the cis-isomer  
 $CH_3$   
of 1.4 - polyisoprene.  $--(CH_2-C-CH-CH_2)_n$ 



Figure A-1. Isomers of Polyisoprene

Natural rubber exists in two geometric configurations, i.e. cis- and trans- isomers. The standard rubber, such as sheets and crepes, is the cis-polyisoprene form, while gutta-percha or balata is the trans-polyisoprene form. The latter is much less flexible, primarily because the transform crystallizes more readily. Also, it is small in commercial importance. Originally used in underwater cable insulation, balata is now utilized only in golf ball covers and special adhesives.

The presence of the double bonds largely determines the chemical reactivity of the molecules. This characteristic leads to the principal advantage as well as disadvantage of natural rubber. The advantage is that it may be combined readily with sulfur to form vulcanized rubber, which is much more valuable. However, the double bond is easily subject to oxidation, especially in the presence of light, which results in a deterioration of strength and caused cracking.

## A.II. SYNTHETIC RUBBERS

Some polymers, which meet those molecular structure requirements of rubber stated in Chapter I, have achieved commercial success by chemical synthesis. The following several kinds are the most common:

(1) Polyisoprene (5,19)

This substance became the first synthetic rubber because isoprene is the main constituent in natural rubber. Subsequently, the product, marketed as Coral Rubber, which was polymerized successfully in 1956 (by the use of lithium or Ziegler-type catalysts) to give a pure cis-polyisoprene, is a synthetic material virtually identical with natural rubber.

There appears to be no appreciable difference in either the processing or product performance of natural Hevea rubber and synthetic cis-polyisoprene except in those cases where the protein, fatty acids, ash, etc., present in natural rubber, affect its performance. In order to make the synthetic products exactly similar in performance, it is necessary to add these materials.

(2) Polybutadiene (9,19)

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Butadiene (CH<sub>2</sub>=CH-CH=CH<sub>2</sub>) differs from isoprene in having no side group except hydrogen atoms, so its polymerized product might be expected to form an elastomer with a faster response to stress than natural rubber. In the polymerization reaction nearly all types of polymerization catalysts can be applied: free-radical, ionic, Ziegler, metallic, and Alfin. Just like polyisoprene, different isomers are possible:



Figure A-2. Isomers of Polybutadiene

The stereospecific polymerization of butadiene to a pure cis-1, 4-polybutadiene was achieved, and as anticipated, the product has an even greater resilience than natural rubber.

## (3) Butadiene and Styrene Copolymer (9,19)

The presence of the styrene gives a much tougher elastomer and possesses a higher tensile strength than butadiene alone. Buna-S or GR-S (government rubberstyrene), which is now designated as SBR, is the product of copolymerization of butadiene with styrene (in a 3:1 ratio by weight) in emulsion at about 5°C. The existence of the double bonds in the chain still allows the polymer to be vulcanized by using sulfur in much the same way as in natural rubber.

SBR is a general-purpose rubber widely used for tires, mechanical goods, insulation, etc.. It is superior to natural rubber in permeability, aging, and heat resistance in many products. It is inferior in working ability, tear resistance, cut growth, tackiness, and heat buildup due to hysteresis. It is normally preferred if it yields products of equal quality and cost. Nearly 50 percent of the total tonnage of rubber consumed in the United States is SBR.

(4) Butadiene and Acrylonitrile Copolymers (9,19)

Emulsified polymerization of butadiene with 20-40 percent acrylonitrile gives synthetic elastomers known as nitrile rubbers (NBR). As with SBR, gum stocks have

extremely low strength and carbon blacks or other reinforcing agents are required in all products. Other compounding and vulcanizing ingredients are similar to those used with natural rubber and SBR. Nitrile rubber, when properly compounded and vulcanized, is characterized by high resistance to swelling in organic solvents, high abrasion resistance, low compression set, low water absorption.

Although it is similar to SBR in many respects, the replacement of the phenyl side groups by the much more polar groups improves its resistance to oil without increasing the inter- and intra- molecular forces and therefore reduces resilience at ordinary temperature. The properties of this synthetic rubber make it extremely useful in the manufacture of carburetor diaphragms, fuel tanks, hose, and gaskets. It is used in molded articles, especially mountings for machinery and shoes for service where oils are present.

(5) Butyl Rubber (9,19)

Isobutylene  $CH_2 = C(CH_3)_2$  may be polymerized to give a high polymer which consists of chemically saturated chains that cannot be vulcanized by conventional methods. However, when isobutylene is copolymerized with 2-4 percent of isoprene at -95°C, the product contains sufficient chain unsaturation (from the isoprene part) to permit vulcanization with sulfur, resulting in so-called butyl rubber.

(Many of the properties of butyl are dependent upon its extremely low unsaturation.) The polymerization can be expressed as follows:

$$\begin{bmatrix} CH_{3} \\ C \\ C \\ C \\ CH_{3} \end{bmatrix} = CH_{2} + CH_{2} = C - CH = CH_{2} \rightarrow \left[ \begin{pmatrix} CH_{3} \\ - C \\ C \\ CH_{3} \end{bmatrix} - CH_{2} - CH_{2} - \int_{100} 100 \\ \begin{pmatrix} - CH_{2} - C \\ - CH_{2} - C \end{bmatrix} + CH_{2} - CH_{2} - \int_{100} 100 \\ \begin{pmatrix} - CH_{2} - C \\ - CH_{3} \end{bmatrix} + CH_{2} - CH_{2} - \int_{100} 100 \\ \begin{pmatrix} - CH_{2} - C \\ - CH_{3} \end{bmatrix} + CH_{2} - CH_{2} - \int_{100} 100 \\ \begin{pmatrix} - CH_{2} - C \\ - CH_{3} \end{bmatrix} + CH_{2} - CH_{2} - \int_{100} 100 \\ \begin{pmatrix} - CH_{2} - C \\ - CH_{3} \end{bmatrix} + CH_{2} - CH_{2} - \int_{100} 100 \\ \begin{pmatrix} - CH_{2} - C \\ - CH_{3} \end{bmatrix} + CH_{2} - CH_{2} - \int_{100} 100 \\ \begin{pmatrix} - CH_{2} - C \\ - CH_{3} \end{bmatrix} + CH_{2} - CH_{2} - CH_{2} - CH_{2} - \int_{100} 100 \\ \end{pmatrix}$$

where x varies from 2 to 4 and n from 350 to 1,000.

Since these copolymers contain very little residual unsaturation, they are chemically inert and are superior to natural rubber for many purposes. Butyl is much more impermeable to the passage of gases and much more resistant to sunlight than others. Low unsaturation also contributes to high resistance to ozone and good electrical properties, so that it is an outstanding elastomeric material for electrical insulation. Butyl rubber retains its high elasticity at temperatures well below ambient comparable to rubber at ambient temperature. This means that bond rotations in its chains are more hindered than in natural rubber.

(6) Neoprene (Polychloroprene) (19)

Chloroprene closely resembles isoprene in molecular form, the methyl group of isoprene being replaced by a

chlorine atom. The chloroprene is then polymerized in the presence of a suitable catalyst to polychloroprene, usually called neoprene:

$$\begin{array}{c} n \quad CH_2 = C \quad - \quad CH = CH_2 \rightarrow -f \quad CH_2 \quad - \quad C = CH \quad - \quad CH_2 \quad - \\ | \\ Cl \quad & \\ \end{array}$$

Polychloroprene is manufactured commercially on a large scale by emulsion polymerization. Emulsions are formed with the aid of soaps or amino wetting agents in aqueous solution.

The polychloroprenes are similar to natural rubber in their properties but are greatly superior in resistance to sunlight, atmospheric oxygen, and ozone, gas diffusion, heat, oils, solvent, and chemicals. Abrasion resistance, particularly at higher temperatures, is better than natural rubber.

### (7) Polysulfide Elastomers (19,57)

The condensation reactions by the emulsion method between organic dihalides and sodium polysulfide produce polysulfide elastomers, most commonly known as Thiokols. The generalized reaction for their formation is usually expressed as follows, although two or three atoms of sulfur can be introduced instead of four:

n ClCH<sub>2</sub> - R - CH<sub>2</sub>Cl + n Na<sub>2</sub> S<sub>4</sub> + 2n NaCl + -  $H_2 - S - R - S - CH_2 - S - R - S - CH_2 -$ 

The dihalide may be a normal paraffin with chlorine atoms on the terminal carbons, dichloropropylene hydrin, dihaloethers like dichlorodiethyl ether, or dichloroethyl formaldehyde.

Regardless of the initial physical state of the polymers (i.e. crude rubber, latex, or liquid polymers), the properties of the high-molecular-weight materials depend mainly upon their chemical structure. The polysulfide polymers are outstanding for solvent and oil resistance, impermeability to vapors and gases, and resistance to oxygen, light, and ozone. Although they do not have high tensile strength, abrasion, or tear resistance, they are suitable in general for certain mechanical rubber goods. Other disadvantages are the poor odor and compressionset resistance.

### (8) Silicone Elastomers (19,63)

Bimethyl dichlorosilane can be hydrolyzed to the unstable diol:

$$Cl - Si - Cl + 2H_{2}O \neq HO - Si - OH + 2HCl$$

$$CH_{3} - Cl + 2H_{2}O \neq HO - Si - OH + 2HCl$$

$$CH_{3} - CH_{3} - OH + 2HCl$$

and then polycondensed to give high molecular weight elastomers, called silicone elastomers as follows:

n HO 
$$\begin{array}{c} CH_3 \\ | & 3 \\ Si \\ | & - \\ 0 \\ | \\ CH_3 \end{array}$$
  $OH \rightarrow OH \rightarrow$ 

Although the elastomer is poor in tensile strength, this disadvantage can be overcome by compounding with silica dust. Chemically this kind of rubber is stable up to almost 300°C and retains good flexibility at temperatures of -70°C or lower. Its greatest advantage exists in the extraordinarily wide temperature range over which it exhibits elasticity; this characteristic is superior to that of mainly hydrocarbon rubbers.

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APPENDIX B

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VULCANIZATION

In an assemblage of many polymer molecules, there may exist entanglements; hence a fraction of the final points in the network will be physical crosslinks. These entanglements are independent of the structure of the polymer. Generally, the physical entanglements cannot act as permanent crosslinks unless they are held in place by adjacent chemical crosslinks.

A chemical crosslinkage produced between two chains by the elimination of one molecule of hydrogen has four chain elements attached (Figure B-1). When a stress is applied to any one of the links, it will be transmitted to the other three segments, so the chemical crosslink is elastically effective (96).



Figure B-1. Types and Structures of Crosslinkages.

The dimensional stability of a vulcanized polymer depends on the perfection of the network and on the stability of the crosslinkage employed. The vulcanizing agent will generally have an effect on the chemical stability and

temperature resistance of the network. In principle, all types of chemical bonds are useful for obtaining a crosslinked network; the only criterion is polyfunctionality (19).

However, after vulcanization, there are still many double bonds in the rubber network. In order to prevent oxidative degradation at these sites and to obtain a stable product, it is necessary to add antioxidant. In addition, the strength properties can be greatly increased by adding a filler; e.g., carbon black is the most common.

One way of linking polymer molecules together to form a network is by the combination of radical entities R. with another molecules to yield a covalent bond between them:

 $R \cdot + R \cdot \rightarrow R - R$ 

Polymer radicals can be produced by high-energy irradiation or chemical reaction with free radicals. The resulting polymer radicals can in principle undergo several possible reactions. The following are several prevailing vulcanization agents in use today (6,19).

(1) Sulfur Vulcanization:

The polysulfide linkage, although not so stable as the carbon-carbon bonds, gives reasonable dimensional stability to the polymer and has the best balance of properties for most purposes.

The presence of the polysulfide linkage in the vulcanizates can confer high strength. The reason is that

when a vulcanizate is stretched, a proportion of the chains in the network carry an excessive stress which may lead to rupture, thus passing on to an adjacent elastic element (6). Breaking of this and further linkage in turn will lead to failure of the specimen. The polysulfide linkage, by adjustment under stress and reformation elsewhere in the network, is thought to prevent catastrophic failure of this type.

The polysulfide linkage can be formed under a wide variety of conditions from room temperature up to 250°C with times varying from days to seconds. It does not have any toxicity problem or other operating difficulty, and it is cheap.

Sulfur itself will crosslink polymers which contain large amounts of unsaturation (like polyisoprene, polybutadiene) but the reaction is slow and inefficient. Much faster reaction can be achieved with the addition of zinc oxide, a fatty acid, and organic accelerator. From 1 to 2 percent of sulfur and about half that amount of accelerator are employed. The various compositions will possess specific technological characteristics — temperature and speed of operation, safety in processing, and presence or absence of discoloration, etc.

The initial phase of the thermally induced reaction of sulfur with olefins involves the gradual formation of organic polysulfide molecules, which function as initiators

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of a free-radical chain reaction. This slow initial phase combines with olefin molecules to form polysulfides (101):



Once sufficient polysulfide molecules are present, they serve as the primary source of polysulphenyl radicals and the reaction rate accelerates.

$$R-S_x-S_x-R = 2R-S_x$$

This catalytic effect of the polysulfide products is attributed to the greater ease of thermally induced homolytic cleavage of linear organic polysulfide molecules relative to cyclic  $S_8$  sulfur molecules. The bulk of the reaction products are formed by the free-radical chain sequence shown as follows:


$$\dot{c} = c - \dot{c} + S_8 \longrightarrow \dot{c} = c - \dot{c} - S_8 = R - S_x$$

In any of the above or subsequent equations where sulfur is shown as reactant, an organic polysulfide molecule,  $R-S_x-R$ , can act as a substitute for the sulfur molecule.

### (2) Peroxides

Organic peroxides are capable of crosslinking saturated and unsaturated polymers. This type of vulcanization agent does not enter into the polymer chains but produces radicals which form carbon-carbon linkage with adjacent polymer chains. In the unsaturated case the reactions are rapid and efficient, but unless there are some particular reasons for the use of the peroxide, sulfur vulcanization is generally preferred. Although most organic peroxides can be used to crosslink polymers, the most stable ones are adopted, particularly those which do not evolve gases or vapors (e.g. carbon dioxide or water). Dimethyl peroxides and 2,5-dimethyl-2, 5-di (t-butyldioxy)-hex-3-yne are representatives of these peroxides:

(3) High-Energy Radiation:

Free radicals can be produced within polymeric materials without chain scission by means of highenergy radiation. Gamma ray sources are most often employed because of the problems of uniformity associated with the use of less penetrating electron beams. Radiation crosslinking may be carried out either in vacuum or in air. In the latter case the free radicals initially formed will react with oxygen to make peroxides which can lead to crosslinking after decomposition.

This method has the advantage of producing a cross-linked network with no extra network chemical species (hydrogen is the main product formed). However, the cost and inconvenience of handling large amounts of radioactive source and loss of energy in molds and other equipment have made it economically unattractive compared with conventional crosslinking processes.

(4) Metal Oxide and Organic Bases

Polyvalent metal oxides are used to crosslink polymers containing halogen, thiol, carboxyl, or ester groups. The most important examples are polychloroprene, chlorosulfonated polyethylene, and acrylic acid or acyclic ester polymers and copolymers. Oxides of zinc, magnesium, lead, and calcium are used.

(5) Phenyl-Formaldehyde Resols

At low degrees of condensation phenol-formaldehyde resols are effective for crosslinking unsaturated elastomers. If the resol, is multifunctional, it will crosslink the polymer directly, or a novolac resin in conjunction with formaldehyde or hexamethylenetetramine may be used. The major merit of this type of crosslink is good heat resistance, since there is no tendency for reversion.

(6) Dimaleimides

Dimaleimides are effective for crosslinking unsaturated polymers, such as natural rubber, SBR, or polychlororpene. The maleimides require activation by peroxides, high-energy radiation, or accelerators such as tetramethylthiuramdisulfide.

#### APPENDIX C

## RUBBER ELASTICITY

C.1. STATISTICAL FORM OF LONG-CHAIN MOLECULES

The kinetic or statistical theory of rubber elasticity is based upon the following several assumptions (14,85):

- (a) The rubber is incompressible.
- (b) The individual molecules of the rubber has very long chains, each of which is capable of assuming a variety of configurations in response to the thermal vibration or "micro-Brownian" motion of their constituent atoms.
- (c) The molecular chains are interlinked so as to form a coherent network, but the number of crosslinks is relatively small and is not sufficient to interfere markedly with the motion of the chains.
- (d) The chains deform in an affine manner. Consider an idealized model based upon these

assumptions that the angle between successive bonds (i.e., the valence angle) is fixed, but completely free rotation of any given bond with respect to adjacent bonds in the chain is allowed. The actual conformation will be subjected to continual fluctuation due to thermal agitation and cannot be defined explicitly. However, some of the system properties can be specified in terms of certain average values by statistical methods.

It may be shown (see Appendix D) that the root-meansquare (r.m.s.) value of the distance r between the ends of a chain containing n bonds (subchains), when n is very large, is given by

$$(r^2)^{1/2} = \sqrt{n\ell} \left[ \frac{1-\cos\alpha}{1+\cos\alpha} \right]^{1/2}$$
 (C.1)

where l is the bond length and  $\alpha$  is the valence angle. Eg. (C.1) illustrates that the mean dimensions of any chains with freely rotational bonds are proportional to the square root of the number of subchains or links which it contains.

The general configuration of the long-chain molecule is independent of the precise geometry of the chain, provided only that the number of bonds about which free rotation can occur is sufficiently large. The particular geometry of this chain only affects the mean-square length or average dimensions of the chain, not its general form.

Suppose that one end of the randomly joined chain A to be fixed at the origin of a Cartesisn system OX, OY, OZ and allow the other end B to move in a random manner throughout the available space (Figure C-1).



Figure C-1. The Affine Deformation of Chains.

For any particular position P, having coordinates (x,y,z), the associated probability that the end point B shall be located within a small volume element dV in the vicinity of the point P, which may be taken as a rectangular block of volume dx dy dz for convenience, is given by (see Appendix E)

 $P(x,y,z) dx dy dz = b^3 \pi^{3/2} \exp \{-b^2(x^2 + y^2 + z^2)\} dx dy dz$ 

(C.2)

where 
$$b^2 = 3/(2nl^2)$$

This form shows that all positions B are not equally probable although the motion of the chain is random. The probability density P(x,y,z) falls continuously as r increases, but it has a maximum value when r=O, that is when the two ends of the chains are coincident.

Since entropy is a property of a statistical system, it is legitimate to regard a single chain as a statistical system, if the number of crosslinks is sufficiently large. According to the general principles of statistical thermodynamics, the entropy is proportional to the logarithm of the number of possible configuations coresponding to any specified state.

In a vulcanized rubber, the original molecules are connected together at certain points due to the vulcanization process so as to form a network. These points of crosslinkage will restrict the motion of the ends of the intervening segments of molecules or network chains to a small element of volume in the neighborhood of certain points. This situation can be treated by assuming one end of the chain to be fixed at the origin 0 while the other is confined to a small volume element dV in the neighborhood of the point P at a distance r from 0. Under this restriction, the number of conformations available to the chain is proportional to the probability which is equal to the probability density P(r) multiplied by the size of the volume element dV.

The entropy of the chain is therefore given by

$$S = k \ln P(x,y,z) dV \qquad (C.3)$$

Substitution of the expression for P(x,y,z) yields

$$S = k \{ln(constant) - b^2r^2 + ln dV\} = c - kb^2r^2$$

(C.4)

where c is an arbitrary constant which includes the volume element term ln dV.

Now, consider a pure homogeneous strain in which a unit cube is deformed into a rectangular parallel-piped having three edge lengths,  $\lambda_1$ ,  $\lambda_2$ , and  $\lambda_3$ . The three principal extension ratios are still along three mutually perpendicular coordinate axes. The extension ratio  $\lambda_1$  has the value greater or less than 1 depending upon whether it corresponds to a stretch or a compression, provided the assumption for constancy of volume (i.e.,  $\lambda_1\lambda_2\lambda_3 = 1$ ) is satisfied.

Suppose that an individual chain (Figure C-1) has an end-to-end distance represented by the vector  $\vec{r}_0$ , with components  $(x_0, y_0, z_0)$  in the unstrained state of the network, and let (x, y, z) be the components of the vector  $\vec{r}$  of of the same chain after deformation. Then by the affine deformation assumption:

 $x = \lambda_1 x_0$   $y = \lambda_2 y_0$   $z = \lambda_3 z_0$  (C.5)

The entropy of the chain in the original state is

$$s_o = c - kb^2 r_o^2 = c - kb^2 (x_o^2 + y_o^2 + z_o^2)$$
(C.6)

The entropy of the same chain in the strained state is obtained by substituting the value of (x,y,z) given by Eq. (C.5) for  $(x_0, y_0, z_0)$ , i.e.,

$$s = c - kb^{2} (\lambda_{1}^{2} x_{0}^{2} + \lambda_{2}^{2} y_{0}^{2} + \lambda_{3}^{2} z_{0}^{2})$$
 (C.7)

The contribution to the total entropy of deformation due to this chain will be

$$\Delta s = s - s_0 = -kb^2 \{ (\lambda_1^2 - 1)x_0^2 + (\lambda_2^2 - 1)y_0^2 + (\lambda_3^2 - 1)z_0^2 \}$$
(C.8)

The total entropy for all the N chains contained in a unit volume of the network is obtained by summation of the expression (28)

$$\Delta S = \Sigma \Delta S = -kb^{2} \{ (\lambda_{1}^{2} - 1) \Sigma x_{0}^{2} + (\lambda_{2}^{2} - 1) \Sigma y_{0}^{2} + (\lambda_{3}^{2} - 1) \Sigma z_{0}^{2} \}$$
(C.9)

Here b is assumed constant which is equivalent to assuming the chain contour length or chain molecular weight is the same as for all the chains.

Since the directions of the chain vectors  $\dot{\vec{r}}_{0}$  in the unstrained state are entirely random, there will be no preference for the x, y, or z directions and hence, remembering that

$$\Sigma x_0^2 + \Sigma y_0^2 + \Sigma z_0^2 = \Sigma r_0^2 \qquad (C.10)$$

It may be written that

$$\Sigma x_0^2 = \Sigma y_0^2 = \Sigma z_0^2 = 1/3 \Sigma r_0^2$$
 (C.11)

But  $\Sigma r_0^2 = N r_0^2$  where  $r_0^2$  is the mean-square length of the chain in the unstrained state. Hence Eq. (C.9) becomes

$$\Delta S = -1/3 \text{ Nkb}^2 \frac{1}{r_0^2} (\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \qquad (C.12)$$

If one more assumption, that the mean-square chain vector length in the unstrained state is the same as for corresponding set of free chains, is introduced, the mean-square length of the chains  $r_0^2$  will be equal to  $3/(2b^2)$ . The total entropy  $\Delta S$  will become

$$\Delta S = -1/2 \text{ Nk} (\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \qquad (C.13)$$

which does not contain the parameter b, and hence is not directly dependent on the chain contour length.

### C.II. THERMODYNAMIC CONSIDERATIONS OF STRESS AND STRAIN

The deformation process of rubber is assumed to take place reversibly. When a stress is applied to a sample of crosslinked rubber, equilibrium is established fairly rapidly. Once at equilibrium, the properties of the rubber can be described by thermodynamics (83,102).

Combining the first and second laws of thermodynamics one can write:

$$dU = TdS - dW$$
(C.14)

From the definition of Helmholtz free energy

$$\mathbf{F} = \mathbf{U} - \mathbf{TS} \tag{C.15}$$

At constant temperature,

$$(dF)_{\pi} = (dU)_{\pi} - T(dS)_{\pi}$$
 (C.16)

From Eqs. (C.14) and (C.15),

$$(dF)_{T} = -(dW)_{T}$$
 (C.17)

If a tensile force f acts upon a piece of rubber of length L, the work done by the system is -fdL. If the volume of the system increases by dV as a result of this strain, then

$$dW = -fdL + PdV$$
 (C.18)

where P is the external pressure. Hence

$$(dF)_{T} = f(dL)_{T} - P(dV)_{T}$$
(C.19)

Since dV is very small during an elastic extension at atmospheric pressure and consequently the  $P(dV)_{T}$  term is negligible compared with  $f(dL)_{T}$ ,

$$(dF)_{T} = f(dL)_{T}$$
(C.20)

Combining Eqs. (C.16) and (C.20),

$$f = \left(\frac{\partial F}{\partial L}\right)_{TV} = \left(\frac{\partial U}{\partial L}\right)_{TV} - T \left(\frac{\partial S}{\partial L}\right)_{TV} \quad (C.21)$$

The first and second terms on the right-hand side of Eq. (C.21) are the energy and entropy contributions to the tensile force, respectively. In polymers, energy elasticity represents the storage of energy resulting from the elastic straining of bond angles and length-like springs from their equilibrium values. Entropy elasticity is caused by the decreases in entropy upon straining (63).

Assume constant volume and constant tensile force,

$$dU = T dS + f dL$$

then

$$\left(\frac{\partial L}{\partial T}\right)_{f,V} = \frac{1}{f} \left(\frac{\partial U}{\partial T}\right)_{f,V} - \frac{T}{f} \left(\frac{\partial S}{\partial T}\right)_{f,V}$$
(C.22)

i.e., the energy term causes an increase in length (positive  $(\frac{\partial L}{\partial T})_{f,V}$ ) which is the normal result of thermal expansion for most materials, reflecting the increment of the average distance between molecular centers with temperature. As for the entropy term, all factors in it are positive, i.e.,  $\frac{T}{f}(\frac{\partial S}{\partial T})_{f,V} > 0$ , but the preceding negative sign means a decrease in length with temperature. At very small extension in a piece of rubber, the thermal extension more than offsets the increase of entropy, and the length increases with temperature. However, when temperature is raised above the so-called thermal-elastic inversion point, the length of rubber will contract with increasing temperature.

This result is due to the entropy effect overwhelming the normal thermal expansion. (In other materials, where the structural units are confined to a single arrangement, i.e., the molecules cannot readily interchange, the entropy term is negligible, so their lengths increase with increasing temperature generally.)

Differentiating Eq. (C.15)

$$dF = dU - TdS - SdT$$
$$= TdS - dW - TdS - SdT$$
(C.23)

so that

$$(dF)_{V} = f(dL)_{V} - S(dT)_{V} \qquad (C.24)$$

By using the exact thermodynamic Maxwell relation

$$-\left(\frac{\partial S}{\partial L}\right)_{T,V} = \left(\frac{\partial f}{\partial T}\right)_{L,V}$$
(C.25)

Substituting for  $\left(\frac{\partial S}{\partial L}\right)_{T,V}$  in Eq. (C.21),

$$\mathbf{f} = \left(\frac{\partial \mathbf{U}}{\partial \mathbf{L}}\right)_{\mathbf{T},\mathbf{V}} + \mathbf{T}\left(\frac{\partial \mathbf{f}}{\partial \mathbf{T}}\right)_{\mathbf{L},\mathbf{V}}$$
(C.26)

Thus

$$(\frac{\partial f}{\partial T})_{L,V} = -\frac{1}{T} (\frac{\partial U}{\partial L})_{T,V} + \frac{f}{T}$$
 (C.27)

Since energy will be stored springlike in the strained bond angles and lengths when extended, the partial derivative is positive. With a negative sign in front, the first term on the right-hand side of Eq. (C.27) predicts a relaxation of the tensile force with increasing temperature (88). In fact, this energy term reflects the ordinary thermal expansion. Next the second term causes the tensile force to increase with temperature, which is a direct result of thermal agitation of the expanded chains (the tendency acts toward high entropy (2)).

As explained above, at small strain the energy elasticity is more prominent than the entropy term, so the tensile force f decreases when temperature is increased. But, at reasonably large values of f, the negative effect of the energy term is overwhelmed by the positive entropy effect, and the force increases with temperature (81). In other words, when a rubber is stressed at constant strain, the tension increases when the temperature is increased to a level.

#### APPENDIX D

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## FREELY ROTATING TETRAHEDRAL CHAIN

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The freely rotating tetrahedral chain is typical of many linear polymers. It consists of a number of carbon atoms joined together and each chain bond is assumed to be able to rotate freely on the valence cone as illustrated in Figure D-1 (a).



#### Figure D-1. Typical Segments Along a Freely Rotating Tetrahedral Chain

The mean square end-to-end length  $\overline{r^2}$  is the straight-line distance between the two ends of the mole-cule. By definition,

$$\overline{r^2} = 1/q \frac{q}{j=1} R_j^2$$
 (D.1)

where  $R_{j}$  is the end-to-end length of the j-th molecule.

Since a chain is composed of N rigid bonds connected end to end, if one assigns to each bond, say the i-th, a vector  $\dot{k}_i$ , which points from the beginning to the end of the bond, then

$$\overline{R_{j}} = \sum_{i=1}^{N} \overline{\ell_{i}}$$
(D.2)

and

$$\overline{r^2} = \frac{1}{q} \sum_{\substack{j=1 \\ j=1 \\ j=1 \\ j=1 \\ j=1 \\ j=1 \\ j=1 \\ j}^2$$
(D.3)

This equation is a perfectly general form for a linear polymer (97).

Expanding Eq. (D.3)

$$\overline{r^{2}} = 1/q \sum_{j=1}^{q} \ell_{1}^{2} + \ell_{2}^{2} + \dots + \ell_{N}^{2} + \overline{\ell_{1} \cdot \ell_{2}} + \overline{\ell_{1} \cdot \ell_{3}} + \dots + \overline{\ell_{N-1} \cdot \ell_{N}}_{j}$$
(D.4)

where  $\overline{\ell_n} \cdot \overline{\ell_m} = |\ell_n| \cdot |\ell_m| \cos \alpha$ , and  $\alpha$  is the angle between  $\overline{\ell_n}$  and  $\overline{\ell_m}$ . Now,  $\ell_1^2 = \ell_2^2 = \ldots = \ell_N^2 = \ell^2$ , hence

$$\overline{\mathbf{r}^{2}} = 1/q \sum_{j=1}^{q} (N\ell^{2} + \ell_{1} \cdot \ell_{2} + \ell_{1} \cdot \ell_{3} + \dots + \ell_{N-1} \cdot \ell_{N})_{j}$$

(D.5)

Since the quantity  $Nl^2$  is the same for any molecule,

$$\overline{r^2} = N\ell^2 + 1/q \sum_{j=1}^{q} (\overline{\ell_1} \cdot \overline{\ell_2} + \overline{\ell_1} \cdot \overline{\ell_3} + \dots + \overline{\ell_{N-1}} \cdot \overline{\ell_N})_j$$

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(D.6)

Consider the bond  $\overline{l_{n+2}}$  (Figure D-1(b).), which can rotate on its valence cone without disturbing the lower-numbered bonds in the chain. Obviously, as it alone rotates, its average value over a long period of time will be a vector of magnitude  $l\cos\alpha$  pointing along vector  $\overline{l_{n+1}}$ . Hence

$$\ell_{n+1} \cdot \ell_{n+2} = \ell_{n+1} \cdot \ell_{n+1} \cos \alpha = \ell^2 \cos \alpha \quad (D.7)$$

Similarly, the average value of the vector  $l_{n+1}$  will be  $l_n \cos \alpha$ . Thus, it follows that

$$\mathcal{L}_{n} \cdot \mathcal{L}_{n+2} = \mathcal{L}_{n} \cdot \mathcal{L}_{n+1} \cos \alpha = \mathcal{L}_{n} \cdot \mathcal{L}_{n} \cos^{2} \alpha = \mathcal{L}^{2} \cos^{2} \alpha$$

(D.8)

In general, 
$$\tilde{\ell}_n \cdot \tilde{\ell}_{n+p} = \ell^2 \cos^p \alpha$$
 (D-9)

Substituting these values into Eq. (D.6)

$$\overline{r^{2}} = N\ell^{2} + \ell^{2} [(\cos\alpha + \cos^{2}\alpha + \cos^{3}\alpha + ... + \cos^{N}\alpha + \cos\alpha) + (\cos\alpha + \cos^{2}\alpha + ... + \cos^{N-1}\alpha + \cos^{2}\alpha + \cos\alpha) + \cos\alpha + ... + \cos^{N-2}\alpha + ... + \cos^{N}\alpha + \cos^{N-1}\alpha + \cos^{N-2}\alpha + ... + \cos\alpha]$$
(D.10)

$$\overline{r^{2}} = N\ell^{2} + \ell^{2} [2(N-1) \cos \alpha + 2(N-2) \cos^{2} \alpha + 2(N-3) \cos^{3} \alpha + ... + 2 \cos^{N} \alpha]$$
  
=  $N\ell^{2} + 2N\ell^{2} (\cos \alpha + \cos^{2} \alpha + ... + \cos^{N} \alpha)$   
-  $2\ell^{2} (\cos \alpha + 2\cos^{2} \alpha + ... + N \cos^{N} \alpha)$  (D.11)

$$\overline{r^2} = N\ell^2 + 2N\ell^2 \left(\frac{1-\cos^{N}\alpha}{1-\cos\alpha}\right) \cos\alpha - 2\ell^2 \cos\left[\frac{1-\cos^{N}\alpha}{(1-\cos\alpha)^2}\right]$$
(D.12)

If N is very large and  $\cos \alpha$  is not too close to unity, the above relation may be simplified to yield

$$\overline{r^2} \approx \frac{1+\cos\alpha}{1-\cos\alpha} N\ell^2$$
 (D.13)

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For a tetrahedral chain,  $\cos \alpha = 1/3$ , and  $r^2 = 2N\ell^2$ .

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## APPENDIX E

CHAIN-END DISTRIBUTION FUNCTION

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The chain-end distribution function can be obtained by three different methods.

(1) Freely Orienting Chain, Statistical Procedure (14)

For a freely orienting chain, the root-mean-square value of the x component  $(\overline{l_x^2})^{1/2}$  is given by

$$\frac{1}{\frac{\mu^2}{\pi^2}} = \frac{\int_{0}^{\pi/2} \ell^2 \cos^2\alpha (2\pi\ell \sin \alpha \cdot \ell \cdot d\alpha)}{\frac{\pi}{2}}$$

$$= \frac{2\pi \ell^4 \int_0^{\pi/2} \cos^2 \alpha \sin \alpha d\alpha}{2\pi \ell^2 (-\cos\alpha) \Big|_0^{1/2}}$$
(E.1)

from which  $\overline{\ell_x^2} = \ell^2/3$ . (E.2)

That means the freely orienting chain acts like a chain having bonds that can, on the average, have components in the x, y, and z directions of  $\pm l/\sqrt{3}$ .

The probability that the component of the chain end-to-end distance is  $n(\sqrt{k}/3)$ , where N>>n, can be calculated from Eq. (E.2), which is equivalent to seeking the probability that "heads" will come up n times more than "tails" in N tosses of a coin. This probability is expressed as

$$P(n) = (\frac{1}{2})^{N} N! / [\frac{N-n}{2}]! [\frac{N+n}{2}]!$$
 (E.3)

By using Sterling's approximation to reduce factorial expressions,

$$\ln\left(\frac{N-n}{2}\right)! = \left(\frac{N-n}{2}\right)\ln\left(\frac{N-n}{2}\right) - \left(\frac{N-n}{2}\right)$$
$$\ln\left(\frac{N+n}{2}\right)! = \left(\frac{N+n}{2}\right)\ln\left(\frac{N+n}{2}\right) + \left(\frac{N+n}{2}\right)$$

Then replacing  $n^2$  by  $3x^2/l^2$ , one gets

 $\ln N! = N \ln N-N$ 

$$P(x) = (3/2\pi N\ell^2)^{1/2} \exp(-3x^2/2N\ell^2)$$
(E.4)

Therefore, the probability that the components of the distance between chain ends will be x, y, and z is given by a product of three such factors; hence,

$$P(x,y,z) = (3/2\pi N\ell^2)^{3/2} \exp \{-3(x^2 + y^2 + z^2)/2N\ell^2\}$$
(E.5)

#### (2) Diffusion Equation (80)

For a chain with n freely orienting segments, each of length  $\ell$ , end-to-end distribution function can be written as  $P(\vec{r},n)$ , where r is the vector end-to-end distance. The new distribution function for a chain containing one more segment will be  $P(\vec{r}, n+1)$ , simply due to an addition of a vector length  $\vec{\ell}$  to the previous chain.

$$\overline{P(\vec{r},n+1)} = \overline{P(\vec{r}+\vec{k},n)}$$
(E.6)

The expression  $P(\vec{r}+\vec{l},n)$  is now expanded to give:

$$P(\vec{r}+\vec{\ell},n) = P(\vec{r},n) + \left(\frac{\partial P}{\partial x} \ell_{x} + \frac{\partial P}{\partial y} \ell_{y} + \frac{\partial P}{\partial z} \ell_{z}\right)$$

$$+ \frac{1}{2!} \left[\frac{\partial^{2} P}{\partial x^{2}} \ell_{x}^{2} + \frac{\partial^{2} P}{\partial y^{2}} \ell_{y}^{2} + \frac{\partial^{2} P}{\partial z^{2}} \ell_{z}^{2} + 2\frac{\partial^{2} P}{\partial x \partial y} \ell_{x} \ell_{y}\right]$$

$$+ \dots + higher terms \qquad (E.7)$$

Since the cross-product terms and the  $l_x, l_y$  and  $l_z$  terms average out to zero for the free-orienting chains, then by neglecting the higher-order terms,

$$\overline{\mathbf{P}(\vec{\mathbf{r}}+\vec{\mathbf{l}},\mathbf{n})} = \overline{\mathbf{P}(\vec{\mathbf{r}},\mathbf{n}+1)} = \overline{\mathbf{P}(\vec{\mathbf{r}},\mathbf{n})} + \frac{\underline{\mathbf{l}}^2}{6} \left(\frac{\partial^2 \mathbf{P}}{\partial \mathbf{x}^2} + \frac{\partial^2 \mathbf{P}}{\partial \mathbf{y}^2} + \frac{\partial^2 \mathbf{P}}{\partial \mathbf{z}^2}\right)$$

or

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$$\frac{\partial \mathbf{P}}{\partial \mathbf{n}} = \frac{\mathbf{P}^2}{6} \left( \frac{\partial^2 \mathbf{P}}{\partial \mathbf{x}^2} + \frac{\partial^2 \mathbf{P}}{\partial \mathbf{y}^2} + \frac{\partial^2 \mathbf{P}}{\partial \mathbf{z}^2} \right)$$
(E.8)

This equation is analogous to the partial-differential equation for diffusion; its solutions are well known (20). In the present case, the solution is

$$P(\vec{r}) = (\frac{3}{2\pi N \ell^2})^{3/2} \exp(-\frac{3r^2}{2N \ell^2})$$
 (E.9)

where  $r^2 = x^2 + y^2 + z^2$  and the restriction is r<<Nl

### (3) Delta-Function Subchain Model (14)

This method is more general and easily extended to other problems than the previous two methods. The chain is still assumed to be made up of N freely orienting segment to be governed by the distribution function for a chain. This assumption means that the actual chain is split into Z subchains, each of average length l.

The probability that the Z chain segments are such that the chain configuration is characterized by segment coordinates  $\xi_1, \xi_2, \ldots, \xi_z$  and  $\eta_1, \eta_2, \ldots, \eta_z$  and  $\nu_1, \nu_2, \ldots, \nu_z$  is found by taking the product of the independent probabilities for the N segments

$$\prod_{i=1}^{N} \exp \{-3/2l^2\} (\xi_i^2 + \eta_i^2 + v_i^2)$$
 (E.10)

A delta function  $\Lambda$  is defined as follows:

$$\Delta = \begin{cases} 1 & \text{when } \sum_{i=1}^{Z} \xi_i = \mathbf{X}, \sum_{i=1}^{Z} \eta_i = \mathbf{Y}, \sum_{i=1}^{Z} \nu_i = \mathbf{Z} \\ i = 1 & i = 1 & i = 1 \\ 0 & \text{otherwise} \end{cases}$$
(E.11)

One of several possible representations for it is

$$\Delta = \iiint_{x} \exp \left[ jt_{x} (\Sigma \xi_{i} - \mathbf{X}) + jt_{y} (\Sigma \eta_{i} - \mathbf{Y}) \right]$$
  
+  $jt_{z} (\Sigma \nu_{i} - \mathbf{Z}) dt_{x} dt_{y} dt_{z}$  (E.12)

where  $j = \sqrt{-1}$  and the sums extend over  $1 \le N$ 

Following the procedure outlined above

$$P(\mathbf{r}) \sim \iiint_{\xi \eta \nu} \Delta \pi \exp \left[-\left(\frac{3}{2\ell^2}\right)\left(\xi_1^2 + \eta_1^2 + \nu_1^2\right) d\xi_1 \dots d\xi_2 d\eta_1 \dots d\eta_2 \right]$$
$$d\nu_1 \dots d\nu_2 \qquad (E.13)$$

with the limits ranging from  $-\infty$  to  $+\infty$ . After the integration has been carried through and the probability normalized, it is found that

$$P(r) = \left(\frac{3}{2\pi N \ell^2}\right)^{3/2} \exp\left[-\left(\frac{3}{2N \ell^2}\right) r^2\right] \quad (E.14)$$

which is identical with the result found previously. Once again the result is obviously restricted to long chains at elongations that are not too large.

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## APPENDIX F

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### BASIC EXPERIMENTAL CREEP DATA

### <u>VNR(</u>#10963)

True Stress 50 psi 100 psi 150 psi 200 psi Time Strain (%) 1 sec. 1.19 5.94 13.08 17.61 2 sec. 1.45 6.86 13.67 17.86 4 sec. 1.72 6.91 14.48 18.87 5 sec. 1.78 7.06 14.95 19.24 10 sec. 2.31 7.92 15.19 19.75 20 sec. 2.37 7.98 15.36 20.12 30 sec. 2.44 8.04 15.71 20.38 40 sec. 2.44 8.24 15.89 20.50 50 sec. 2.51 8.31 ----20.88 1 min. 2.51 8.38 16.12 21.13 2 min. 2.52 8.71 16.41 21.38 3 min. 2.54 8.97 16.47 21.45 4 min. 2.57 16.65 9.10 21.45 5 min. 2.64 9.17 17.06 21.57 6 min. 2.64 9.23 17.17 21.64 8 min. 2.70 9.30 17.41 21.70 10 min. 2.71 9.30 21.76 17.46 20 min. 2.74 9.89 17.64 22.09 30 min. 2.80 9.98 17.78 22.35 40 min. 2.85 10.12 17.94 22.58 50 min. 2.89 10.19 18.25 22.79 1 hr. 2.95 10.36 18.45 23.07 2 hr. 3.15 11.01 18.71 23.77

11.21

18.96

24.28

3 hr.

3.30

## <u>VNR</u>(#10963)

|     |     |        | True Stress |         |         |  |
|-----|-----|--------|-------------|---------|---------|--|
|     |     | 50 psi | 100 psi     | 150 psi | 200 psi |  |
| Ti  | me  |        | Strai       |         |         |  |
| 4   | hr. | 3.64   | 11.34       | 19.18   | 24.57   |  |
| 5   | hr. | 3.43   | 11.52       | 19.40   | 24.80   |  |
| 6   | hr. | 3.30   | 11.66       | 19.52   | 25.06   |  |
| 8   | hr. | 3.64   | 12.00       | 19.79   | 25.46   |  |
| 10  | hr. | 3.43   | 12.27       | 20.04   | 25.80   |  |
| 15  | hr. | 3.71   | 13.06       | 20.20   | 26.39   |  |
| 20  | hr. | 3.67   | 13.55       | 20.20   | 26.69   |  |
| 25  | hr. | 3.68   | 13.72       | 2074    | 26.84   |  |
| 30  | hr. | 3.69   | 13.54       | 20.98   | 26.84   |  |
| 35  | hr. | 3.81   | 13.39       | 21.48   | 26.90   |  |
| 40  | hr. | 4.23   | 13.14       | 22.06   | 26,93   |  |
| 45  | hr. | 4.28   | 13.44       | 22.45   | 27.16   |  |
| 50  | hr. | 4.35   | 13.77       | 22.55   | 27.40   |  |
| 55  | hr. | 4.41   | 13.71       | 22.55   | 27.42   |  |
| 60  | hr. | 4.51   | 13.80       | 22.64   | 27.49   |  |
| 65  | hr. | 4.57   | 13.82       | 22.64   | 27.55   |  |
| 70  | hr. | 4.63   | 13.85       | 22.41   | 27.67   |  |
| 75  | hr. | 4.75   | 13.40       | 22.17   | 27.74   |  |
| 80  | hr. | 4.50   | 14.29       | 22.07   | 27.94   |  |
| 85  | hr. | 4.42   | 14.30       | 22.13   | 27.96   |  |
| 90  | hr. | 4.39   | 14.35       | 22.29   | 28.05   |  |
| 95  | hr. | 4.59   | 14.47       | 22.44   | 28.19   |  |
| 100 | hr. | 4.60   | 14.72       | 22.46   | 28,33   |  |

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## <u>VNR</u>(#10963)

|         | True Stress      |         |         |                |
|---------|------------------|---------|---------|----------------|
|         | 3 <b>0</b> 0 psi | 400 psi | 500 psi | 1000 psi       |
| Time    |                  | Strai   | n (%)   |                |
| 1 sec.  | 26.33            | 31.41   | 34.98   | 41.50          |
| 2 sec.  | 26.85            | 31.45   | 35.70   | 45.40          |
| 4 sec.  | 27.11            | 31.49   | 37.51   | 47.99          |
| 5 sec.  | 27.17            | 31.49   | 38.50   | 48.64          |
| 10 sec. | 27.30            | 34.71   | 40.35   | 51.10          |
| 20 sec. | 28.40            | 35.63   | 41.42   | 51.88          |
| 30 sec. | 28.53            | 35.69   | 41.54   | 52 <b>.1</b> 4 |
| 40 sec. | 28.60            | 35.69   | 41.70   | 52.27          |
| 50 sec. | 28.73            | 35.80   | 41.92   | 52.40          |
| 1 min.  | 28.86            | 35.98   | 42.12   | 52.59          |
| 2 min.  | 29.31            | 36.09   | 42.36   | 53.05          |
| 3 min.  | 29.38            | 36.32   | 42.59   | 53.18          |
| 4 min.  | 29.77            | 36.49   | 42.81   | 53.24          |
| 5 min.  | 29.83            | 36.67   | 43.10   | 53.24          |
| 6 min.  | 29.90            | 36.72   | 43.15   | 53.31          |
| 8 min.  | 29.96            | 36.78   | 43.38   | 53.45          |
| 10 min. | 30.02            | 36.90   | 43.50   | 53.70          |
| 20 min. | 30.48            |         | 43.58   | 53.70          |
| 30 min. | 30.78            | 37.30   | 43.62   | 53.76          |
| 40 min. |                  |         | 43.62   |                |
| 50 min. | 31.63            |         |         | 53.76          |
| 1 hr.   | 31.70            | 37.70   | 43.65   | 53.76          |
| 2 hr.   | 33.64            | 38.84   | 43.74   |                |
| 3 hr.   | 33.94            | 38.84   | 43.82   | 54.18          |

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# <u>VNR</u>(#10963)

|             |       | True Stress |                   |                  |          |  |
|-------------|-------|-------------|-------------------|------------------|----------|--|
| Тim         | e     | 300 psi     | 400 psi<br>Strain | 500 psi<br>n (%) | 1000 psi |  |
| <u> </u>    | hr    | 34 00       | 28 00             | <i>µ</i> 3 00    | <u> </u> |  |
|             | 111 e | 04.00       | 50.90             | 43.90            | 54.24    |  |
| 5           | nr.   | 34.10       | 39.08             | 43.95            | 54.80    |  |
| 6           | hr.   | 34.28       | 39.20             | 44.21            |          |  |
| 8           | hr.   | 34.52       | 39.21             | 44.42            | 54.51    |  |
| 10          | hr.   | 34.27       | 39.69             | 44.60            | 54.73    |  |
| <b>1</b> 5  | hr.   | 34.88       | 40.28             | 45.41            | 55.19    |  |
| 20          | hr.   | 35.25       | 40.44             | 46.04            | 55,29    |  |
| 25          | hr.   | 35.60       | 40.50             | 46.46            | 55.55    |  |
| 30          | hr.   |             | 40.27             |                  | 55.65    |  |
| 35          | hr.   | 35.67       | 40.85             | 46.64            | 55.77    |  |
| 40          | hr.   | 35.78       | 41.31             | 46.76            | 56.16    |  |
| 45          | hr.   | 35.99       | 41.84             | 47.01            | 56.61    |  |
| 50          | hr.   | 36.08       | 42.18             | 47.24            | 56.81    |  |
| 55          | hr.   |             | 42.22             |                  | 56.95    |  |
| 60          | hr.   | 36.39       | 42.23             | 47.24            | 56.95    |  |
| 65          | hr.   | 36.51       | 42.31             | 47.26            | 56.96    |  |
| 70          | hr.   | 36.71       | 42.31             | 47.29            | 57.06    |  |
| 75          | hr.   | 36.85       | 42.08             | 47.43            | 56.95    |  |
| 80          | hr.   | 36.98       | 41.84             | 47.69            | 56.69    |  |
| 85          | hr.   | . 36.99     | 41.75             | 47.75            | 56.56    |  |
| 90          | hr.   | 37.11       | 41.83             | 47.78            | 56.60    |  |
| 95          | hr.   | 37.25       | 41.92             | 47.85            | 56.70    |  |
| <b>1</b> 00 | hr.   | 37.29       | 42.08             | 48.01            | 56.86    |  |
|             |       |             |                   |                  |          |  |

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# <u>UnVNR</u>(#10963)

|     |      | True Stress |        |                      |         |  |
|-----|------|-------------|--------|----------------------|---------|--|
|     |      | 31 psi      | 50 psi | 100 psi              | 200 psi |  |
| Tin | ne   |             | Strai  | n (%)                | •       |  |
| 1   | sec. | 0.24        | 18,29  | 160 TH 160 TH 170 TH | 44.48   |  |
| 2   | sec. | 0.73        | 19.51  | 29.04                | 45.76   |  |
| 4   | sec. | 1.10        | 21.22  | 31.01                | 47.62   |  |
| 5   | sec. | 1.34        | 21.83  | 31.36                | 48.20   |  |
| 10  | sec. | 2.43        | 23.66  | 33.10                | 49.94   |  |
| 20  | sec. | 4.15        | 26.71  | 35.31                | 51.22   |  |
| 30  | sec. | 5.61        | 28.78  | 36.70                | 52.26   |  |
| 40  | sec. | 7.07        | 30.49  | 37.51                | 52.61   |  |
| 50  | sec. | 8.17        | 31.59  | 38.33                | 53.43   |  |
| 1   | min. | 8.90        | 32.44  | 38.79                | 53.54   |  |
| 2   | min. | 13.41       | 36.46  | 40.89                | 54.70   |  |
| 3   | min. | 16.34       | 38.90  | 41.93                | 55.40   |  |
| 4   | min. | 19.02       | 41.46  | 43.20                | 55.75   |  |
| 5   | min. | 21.71       | 45.12  | 44.37                | 56.91   |  |
| 6   | min. | 24.02       | 46.83  | 45.18                | 57.26   |  |
| 8   | min. | 26.83       | 48.78  | 45.76                | 58.42   |  |
| 10  | min. | 29.27       | 50.61  | 46.46                | 58.65   |  |
| 20  | min. | 34.39       |        | 48.08                |         |  |
| 30  | min. | 36.71       | 56.58  | 49.13                | 60.51   |  |
| 40  | min. | 37.83       |        | 49.38                |         |  |
| 50  | min. | * * * * * * |        | 50.50                |         |  |
| 1   | hr.  | 40.00       | 58.41  | 50.17                | 61.09   |  |
| 2   | hr.  | 42.19       | 61.80  | 50.99                | 62.50   |  |
| 3   | hr.  | 42.93       | 63.74  | 51.22                | 63.17   |  |

# <u>UnVNR(#10963)</u>

|     |     | True Stress    |        |         |         |
|-----|-----|----------------|--------|---------|---------|
|     |     | 31 psi         | 50 psi | 100 psi | 200 psi |
| Tin | ne  |                | Strai  | .n(%)   |         |
| 4   | hr. | 44.02          | 64.94  | 52.03   | 63.53   |
| 5   | hr. | 45.00          | 65.91  | 52.96   | 64.11   |
| 6   | hr. | 46.34          | 66.86  | 53.43   | 64.46   |
| 8   | hr. | 48.17          | 67.68  | 54.12   | 64.89   |
| 10  | hr. | 49.51          | 69.51  | 54.59   | 65.27   |
| 15  | hr. | 52.20          | 71.34  | 55.75   | 65.76   |
| 20  | hr. | 54 <b>.1</b> 5 | 72.43  | 56.44   | 66.20   |
| 25  | hr. | 55.61          | 72.99  | 56.85   | 66.41   |
| 30  | hr. | 57.38          | 73.41  | 57.26   | 66.55   |
| 35  | hr. | 58.66          | 74.05  | 57.78   | 66.68   |
| 40  | hr. | 59.94          | 74.36  | 58.42   | 66.78   |
| 45  | hr. | 61.10          | 74.39  | 58.88   | 66.78   |
| 50  | hr. | 61.22          | 74.54  | 58.88   | 66.78   |
| 55  | hr. | 61.71          | 74.63  | 59.06   | 66.99   |
| 60  | hr. | 62.13          | 75.12  | 59.64   | 67.15   |
| 65  | hr. | 62.38          | 75.83  | 60.10   | 67.60   |
| 70  | hr. | 62.86          | 75.98  | 60.51   | 67.63   |
| 75  | hr. | 62.99          | 76.10  | 60.51   | 67.71   |
| 80  | hr. | 63.29          | 76.33  | 60.98   | 67.78   |
| 85  | hr. | 63.54          | 76.68  | 61.21   | 68.00   |
| 90  | hr. | 64.08          | 76.82  | 61.79   | 67.94   |
| 95  | hr. | 64.39          | 76.84  | 62.14   | 67.94   |
| 100 | hr. | 64.51          |        | 62.08   |         |

# <u>UnVNR</u>(#10963)

|     |      | True Stress |           |                    |             |  |  |  |
|-----|------|-------------|-----------|--------------------|-------------|--|--|--|
|     |      | 300 psi     | 400 psi   | 500 psi            | 600 psi     |  |  |  |
| Tir | ne   | ·······     | Strain(%) |                    |             |  |  |  |
| 1   | sec. | 50.66       | 52.69     | 54.08              |             |  |  |  |
| 2   | sec. | 51.98       | 54.01     | 55.14              |             |  |  |  |
| 4   | sec. | 53.17       | 55.15     | 56.10              | ** ** ** ** |  |  |  |
| 5   | sec. | 53.89       | 55.63     | 56.42              |             |  |  |  |
| 10  | sec. | 55.09       | 56.29     | 57.48              |             |  |  |  |
| 20  | sec. | 56.05       | 57.00     | 58.32              | 59.49       |  |  |  |
| 30  | sec. | 56.41       | 57.60     | 58.64              | 60.98       |  |  |  |
| 40  | sec. | 56.89       | 57.84     | 58.98              | 61.19       |  |  |  |
| 50  | sec. | 57.12       | 58.08     | 59.38              | 61.56       |  |  |  |
| 1   | min. | 57.48       | 58.68     | 59.49              | 61.82       |  |  |  |
| 2   | min. | 57.96       | 58.98     | 60.34              | 62.67       |  |  |  |
| 3   | min. | 59.40       | 59.40     | 60.55              | 62.99       |  |  |  |
| 4   | min. | 60.72       | 60.12     | 60.76              | 64.26       |  |  |  |
| 5   | min. | 61.08       | 61.32     | 61.50              | 65.11       |  |  |  |
| 6   | min. | 61.44       | 61.92     | 62.25              | 65.54       |  |  |  |
| 8   | min. | 62.28       | 62.28     | 62.78              | 67.02       |  |  |  |
| 10  | min. | 62.40       | 62.86     | 63.10              | 66.28       |  |  |  |
| 20  | min. | 62,99       |           | 63.94              | 67.34       |  |  |  |
| 30  | min. | 63.47       |           | 64.37              | 67.87       |  |  |  |
| 40  | min. |             | 65.15     |                    |             |  |  |  |
| 50  | min. |             |           | tend title gam gam |             |  |  |  |
| 1   | hr.  | 64.43       | 65.63     | 65.22              | 68.61       |  |  |  |
| 2   | hr.  | 64.67       | 67.66     | 67.13              | 68.93       |  |  |  |
| 3   | hr.  | 65.35       | 68,62     | 67.82              | 69.51       |  |  |  |

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|            |     |               | True Stress |               |                                       |  |  |
|------------|-----|---------------|-------------|---------------|---------------------------------------|--|--|
|            |     | 300 psi       | 400 psi     | 500 psi       | 600 psi                               |  |  |
| Time       |     |               | Strai       | n(%)          |                                       |  |  |
| 4          | hr. | 65.87         | 69.10       | 68.24         | 70.73                                 |  |  |
| 5          | hr. | 65.99         | 69.64       | 68 <b>.61</b> | 71.21                                 |  |  |
| 6          | hr. | 66.36         | 70.06       | 68.82         | 71.69                                 |  |  |
| 8          | hr. | 66.83         | 70.66       | 69.35         | 72.43                                 |  |  |
| 10         | hr. | 67.26         | 71.01       | 69.74         | 72.90                                 |  |  |
| <b>1</b> 5 | hr. | 67.88         | 71.74       | 70.44         | 73.81                                 |  |  |
| 20         | hr. | 68.30         | 72.28       | 71.00         | 74.28                                 |  |  |
| 25         | hr. | 68.62         | 73.11       | 71.22         | 74.66                                 |  |  |
| 30         | hr. | 68.84         | 73.53       | 71.37         | 74.87                                 |  |  |
| 35         | hr. | 69.10         | 73.95       | 71.58         | 75.29                                 |  |  |
| 40         | hr. | 69.23         | 74.49       | 71.69         | 75.82                                 |  |  |
| 45         | hr. | 69.26         | 74.67       | 71.70         | 75.93                                 |  |  |
| 50         | hr. | 69.27         | 74.85       | 71.63         | 75.93                                 |  |  |
| 55         | hr. | 69.50         | 75.06       | 71.69         | 75.98                                 |  |  |
| 60         | hr. | <b>69.</b> 82 | 75.15       | 71.93         | 76.25                                 |  |  |
| 65         | hr. | 70.28         | 75.21       | 72.34         | 76.56                                 |  |  |
| 70         | hr. | 70.43         | 75.27       | 72.56         | 76.62                                 |  |  |
| 75         | hr. | 70.46         | 75.33       | 72.57         | 76.62                                 |  |  |
| 80         | hr. | 70.54         | 76.13       | 72.66         | <b>76.7</b> 8                         |  |  |
| 85         | hr. | 70.69         | 75.81       | 72.85         | 77.20                                 |  |  |
| 90         | hr. | 70.69         | 75.81       | 73.12         | 77.52                                 |  |  |
| 95         | hr. | 70.72         | 75.87       | 72.99         | 77.57                                 |  |  |
| 100        | hr. |               | 75.90       |               | 77.52                                 |  |  |
|            |     |               |             |               | · · · · · · · · · · · · · · · · · · · |  |  |

<u>UnVNR</u>(#10963)

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# <u>VSBR</u>(#1180)

|     |      | True Stress |           |         |         |  |  |
|-----|------|-------------|-----------|---------|---------|--|--|
|     |      | 100 psi     | 150 psi   | 200 psi | 250 psi |  |  |
| Tin | le   |             | Strain(%) |         |         |  |  |
| 1   | sec. | 7.65        | 12.00     | 15.43   | 19.24   |  |  |
| 2   | sec. | 7.92        | 13.06     | 15.66   | 20.50   |  |  |
| 4   | sec. |             | 13.19     | ·       | 21.01   |  |  |
| 5   | sec. | 8.44        | 13.19     | 15.90   | 21.26   |  |  |
| 10  | sec. | 8.71        | 13.24     | 16.80   | 21.38   |  |  |
| 20  | sec. | 9.10        | 13.32     | 17.14   | 21.76   |  |  |
| 30  | sec. | 9.25        | 13.59     | ·       | 22.14   |  |  |
| 40  | sec. | 9.37        | .13.64    | 17.37   | 22.14   |  |  |
| 50  | sec. | 9.44        | 13.68     | 17.37   |         |  |  |
| 1   | min. | 9.50        | 13.72     | 17.37   | 22.64   |  |  |
| 2   | min. | 10.55       | 13.98     | 17.94   | 22.89   |  |  |
| 3   | min. | 10.82       | 14.25     | 18.28   | 23.40   |  |  |
| 4   | min. | 10.95       | 14.51     | 18.40   | 23.65   |  |  |
| 5   | min. | 10.95       | 14.51     | 18.51   | 23.77   |  |  |
| 6   | min. | 10.95       | 14.51     | 18.63   | 23.90   |  |  |
| 8   | min. | 10.95       | 14.64     | 18.86   | 24.02   |  |  |
| 10  | min. | 11.61       | 14.78     | 19.08   | 25.16   |  |  |
| 20  | min. | 12.20       | 17.55     |         | 28.43   |  |  |
| 30  | min. | 12.47       |           | 20.38   | 29.84   |  |  |
| 40  | min. | 12.62       | 18.86     | 20.83   | 30.82   |  |  |
| 50  | min. | 12.76       |           | 20,99   |         |  |  |
| 1   | hr.  | 12.93       | 19.66     | 21.29   | 31.70   |  |  |
| 2   | hr.  |             |           | 24.82   | 34.34   |  |  |
| 3   | hr.  | 14.04       |           | 24.90   | 35.03   |  |  |

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|         | True Stress |         |               |               |
|---------|-------------|---------|---------------|---------------|
|         | 100 psi     | 150 psi | 200 psi       | 250 psi       |
| Time    |             | Strain  | n (%)         | •             |
| 4 hr.   | 14.30       | 22.42   | 25.08         | <b>35.6</b> 6 |
| 5 hr.   | 14.41       | 22.82   | 25.19         | 36.10         |
| 6 hr.   | 14.72       | 23,22   | 25.47         | 36.48         |
| 8 hr.   | 15.06       | 23.75   | 25.58         | 37.23         |
| 10 hr.  | 14.60       | 24.27   | 25.63         | 37.61         |
| 15 hr.  | 15.62       | 24.87   | 26.06         | 38.68         |
| 20 hr.  | 15.90       | 25.46   | 26.56         | 39.31         |
| 25 hr.  | 16.16       | 25.86   | 26.87         | 39.75         |
| 30 hr.  | 16.38       | 25.92   | 28.38         | 39.81         |
| 35 hr.  | 16.58       | 25.99   | 29.03         | 40.12         |
| 40 hr.  | 16.96       | 26.12   | 29.52         | 40.31         |
| 45 hr.  | 17.18       | 26.25   | 29.93         | 40.50         |
| 50 hr.  | 17.45       | 26.38   | 30.55         | 41.13         |
| 55 hr.  | 17.78       | 26.25   | 30.75         | 41.51         |
| 60 hr.  | 18.13       | 26.52   | 31.10         | 41.70         |
| 65 hr.  | 18.63       | 26.65   | 31.53         | 41.85         |
| 70 hr.  | 18.67       | 26.98   | <b>31.</b> 95 | 42.14         |
| 75 hr.  | 18.88       | 27.11   | 32.12         | 42.39         |
| 80 hr.  | 19.17       | 27.11   | 32.34         | 42.64         |
| 85 hr.  | 19.42       | 27.84   | 32.47         | 42.64         |
| 90 hr.  | 19.55       |         | 32.67         |               |
| 95 hr.  | 19.67       | 27.51   | 32.81         | 42.89         |
| 100 hr. | 19.80       | 27.31   | 32.97         | 42.96         |

|              |     |                | True Stress |         |         |  |
|--------------|-----|----------------|-------------|---------|---------|--|
|              |     | <b>100</b> psi | 150 psi     | 200 psi | 250 psi |  |
| Tin          | ne  |                | Strai       | n (%)   | ·       |  |
| 125          | hr. | 20.24          | 28.50       | 33.53   | 43.52   |  |
| 150          | hr. | 20.80          | 28.17       | 34.07   | 43.71   |  |
| 175          | hr. | 21.82          | 27.97       | 34.39   | 43.84   |  |
| 2 <b>0</b> 0 | hr. | 22.10          | 27.97       | 34.92   | 43.58   |  |
| 225          | hr. |                | 27.51       | 35.20   |         |  |
| 250          | hr. | 23.71          |             | 35.54   |         |  |
| 2 <b>7</b> 5 | hr. | 23.72          |             | 36.01   |         |  |
| 300          | hr. | 24.38          |             | 36.46   |         |  |
| 325          | hr. | 24.93          |             | 36.57   |         |  |
| 350          | hr. | 24.84          |             | 36.68   |         |  |
| 375          | hr. | 24.78          |             | 36.76   |         |  |
| 400          | hr. | 24.89          |             | 36.87   |         |  |
| 425          | hr. | 24.87          |             | 36.92   |         |  |
| 450          | hr. | 25.22          |             | 37.12   |         |  |
| 475          | hr. | 25.33          |             | 37.15   |         |  |
| 50 <b>0</b>  | hr. | 25.14          |             | 36.84   |         |  |
| 525          | hr. | 24.72          |             | 36.81   |         |  |
| 550          | hr. | 24.71          |             | 36.94   |         |  |
| 575          | hr. | 25.01          |             | 37.13   |         |  |
| 60 <b>0</b>  | hr. | 24.77          |             | 37.19   |         |  |
| 625          | hr. | 24.74          |             | 37.29   | ,       |  |
| 650          | hr. | 24.80          |             | 37.47   |         |  |
| 675          | hr. | 24.78          |             | 37.62   |         |  |
| 700          | hr. | 25.29          |             | 37.85   |         |  |

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|              |     | Tru     | le Stress |
|--------------|-----|---------|-----------|
|              |     | 100 psi | 200 psi   |
| Time         | •   |         | Strain(%) |
| 725          | hr. | 25.22   | 37.80     |
| 7 <i>5</i> 0 | hr. | 25.12   | 37.93     |
| 775          | hr. | 25.67   | 38.11     |
| 800          | hr. | 25.55   | 38.08     |
| <b>110</b> 0 | hr. | 26.21   | 39.54     |
| 1125         | hr. | 26.42   | 39.70     |
| 1150         | hr. | 26.78   | 39.86     |
| 1175         | hr. | 26.53   | 39.71     |
| 1200         | hr. | 26.29   | 39.69     |
|              |     |         | -         |

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|    |      | True Stress |               |         |          |  |
|----|------|-------------|---------------|---------|----------|--|
|    |      | 300 psi     | 400 psi       | 500 psi | 1000 psi |  |
| Ti | le   |             | Strai         | n(%)    |          |  |
| 1  | sec. | 22.96       | 27.93         |         | 46.73    |  |
| 2  | sec. | 23.19       | 28.65         | 35.05   | 47.31    |  |
| 4  | sec. | 23.46       | 28.79         | 36.24   | 47.90    |  |
| 5  | sec. | 23.67       | 28.91         | 36.45   | 47.93    |  |
| 10 | sec. | 26.94       | 31.92         | 37.27   | 48.01    |  |
| 20 | sec. | 27.67       | 32.38         | 37.50   | 48.48    |  |
| 30 | sec. |             | 32.85         | 37.76   | 48.56    |  |
| 40 | sec. | 27.92       | 33.18         | 38.08   | 48.60    |  |
| 50 | sec. |             | 33.30         | 38.26   | 48.81    |  |
| 1  | min. | 28.05       | 33.41         | 38.43   | 48.95    |  |
| 2  | min. | 28.80       | 33.64         | 38.55   | 49.06    |  |
| 3  | min. | 28.93       |               | 38.90   | 49.18    |  |
| 4  | min. | 29.18       | 34.21         | 38.90   | 49.30    |  |
| 5  | min. | 29.43       | 34.33         | 39.02   | 49.42    |  |
| 6  | min. | 29.56       | 34.44         | 39.14   | 49.42    |  |
| 8  | min. | 29.68       | 34.56         | 39.60   | 49.53    |  |
| 10 | min. | 29.68       | 34.79         | 39.72   | 49.65    |  |
| 20 | min. | 31.57       | 37.20         | 42.17   | 51.40    |  |
| 30 | min. | 31.82       | 37.89         | 42.76   | 51.64    |  |
| 40 | min. | 32.08       | 37.89         | 42.76   | 52.07    |  |
| 50 | min. |             |               | 42.98   | 52.41    |  |
| 1  | hr.  | 32.45       | <b>3</b> 8.23 | 43.27   | 52.63    |  |
| 2  | hr.  | 36.72       | 39.26         | 44.24   | 53,60    |  |
| 3  | hr.  | 36.75       | 39.85         | 44.79   | 53.98    |  |

|     |     |                     | True Stress(psi) |         |                |  |
|-----|-----|---------------------|------------------|---------|----------------|--|
|     |     | 300 psi             | 400 psi          | 500 psi | 1000 psi       |  |
| Ti  | me  |                     | Strain           | n (%)   |                |  |
| 4   | hr. | 36.77               | 40.40            | 45.28   | 54.36          |  |
| 5   | hr. | 36.80               | 40.82            | 45.65   | 54.70          |  |
| 6   | hr. | 36.82               | 4 <b>1.1</b> 5   | 45.98   | 54.96          |  |
| 8   | hr. | 36.86               | 41.70            | 46.54   | 5 <b>5.2</b> 8 |  |
| 10  | hr. | 36.94               | 42.15            | 46.92   | 55.51          |  |
| 15  | hr. | 37.24               | 42.74            | 47.62   | 55.97          |  |
| 20  | hr. | 38.01               | 42.95            | 48.33   | 56.30          |  |
| 25  | hr. | 400 mga ann ann ann | 43.21            | 49.03   | 56.52          |  |
| 30  | hr. | <b>38.6</b> 8       | 43.51            | 49.40   | 56.62          |  |
| 35  | hr. | 40.11               | 43.85            | 49.73   | 56.77          |  |
| 40  | hr. | 40.78               | 44.09            | 50.00   | 56.92          |  |
| 45  | hr. | 41.16               | 44.20            | 50.15   | 57.09          |  |
| 50  | hr. | 41.40               | 44.30            | 50.41   | 57.11          |  |
| 55  | hr. | 41.58               | 44.50            | 50.59   | 57.11          |  |
| 60  | hr. | 41.76               | 44.73            | 50.86   | 57,21          |  |
| 65  | hr. | 42.02               | 44.90            | 51.05   | 57.27          |  |
| 70  | hr. | 42.20               | 44.97            | 51.14   | 57.50          |  |
| 75  | hr. | 42.79               | 45.17            | 51.10   | 57.69          |  |
| 80  | hr. | 43.04               | 45.38            | 51.16   | 57.76          |  |
| 85  | hr. | 43.28               | 45.56            | 51.09   | 57.88          |  |
| 90  | hr. | 43.52               | 45.59            | 51.30   | 58.05          |  |
| 95  | hr. | 43.74               | 45.54            | 51.31   | 58.09          |  |
| 100 | hr. | 43.84               | 45.58            | 51.65   | 57.94          |  |

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|         | True Stress |         |         |                       |
|---------|-------------|---------|---------|-----------------------|
|         | 300 psi     | 400 psi | 500 psi | 1000 psi              |
| Time    | <u> </u>    | Strai   | n(%)    |                       |
| 125 hr. | 44.53       | 46.41   | 51.82   | 57.87                 |
| 150 hr. | 44.97       | 46.39   | 51.83   | 58.36                 |
| 175 hr. | 45.31       | 46.50   | 52.10   | 58.68                 |
| 200 hr. | 45.52       | 46.95   | 52.73   | 58.64                 |
| 225 hr. | 45.65       | 47.35   | 52.97   | وروي ويقل فأح أسد إحد |
| 250 hr. | 46.01       | 47.67   | 52.93   |                       |
| 275 hr. | 46.65       | 47.68   | 52.98   |                       |
| 300 hr. | 46.93       | 47.78   | 53.13   |                       |
| 325 hr. | 46.94       | 47.90   | 53.14   |                       |
| 350 hr. | 47.04       | 48.12   | 53.56   |                       |
| 375 hr. | 47.22       | 48.43   | 53.42   |                       |
| 400 hr. | 47.36       | 48.30   | 53.25   | ****                  |
| 425 hr. | 47.74       | 48.00   | 52.87   |                       |
| 450 hr. | 47.76       | 47.77   | 53.11   |                       |
| 475 hr. | 47.66       | 48.12   | 53.42   |                       |
| 500 hr. | 47.43       | 48.22   | 53.28   | 60.61                 |
| 525 hr. | 47.72       |         |         | 60.90                 |
| 550 hr. | 48.05       |         |         | 60.99                 |
| 575 hr. | 47.81       |         |         | 60.71                 |
| 600 hr. | 47.94       |         |         | 60.69                 |
| 625 hr. | 48.05       |         |         |                       |
| 650 hr. | 48.31       |         |         |                       |
| 675 hr. | 48.55       |         |         |                       |
| 700 hr. | 48.49       |         |         |                       |

|              |     | True Stress |                   |                 |          |
|--------------|-----|-------------|-------------------|-----------------|----------|
| Time         |     | 300 psi     | 400 psi<br>Strain | 500 psi<br>n(%) | 1000 psi |
| 725          | hr. | 48.53       |                   |                 |          |
| 7 <i>5</i> 0 | hr, | 48.77       |                   |                 |          |
| 775          | hr. | 48.68       |                   |                 |          |
| 1075         | hr. | 48.96       |                   |                 |          |
| 1100         | hr. | 50.45       |                   |                 |          |
| 1125         | hr. | 50.69       |                   |                 |          |
| 1150         | hr. | 50.35       |                   |                 |          |
| 1175         | hr. | 50.35       |                   |                 |          |
| 1200         | hr. |             |                   |                 |          |

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|    |      |               | True Stress |         |         |
|----|------|---------------|-------------|---------|---------|
|    |      | 30 psi        | 50 psi      | 100 psi | 150 psi |
| Ti | me   | <u></u>       | Strai       | .n (%)  |         |
| 1  | sec. |               | 2.10        | 8.05    | 12.86   |
| 2  | sec. |               | 2.80        | 11.04   | 19.03   |
| 4  | sec. |               | 3.37        | 14.02   | 23.72   |
| 5  | sec. |               | 4.06        | ****    | 24.90   |
| 10 | sec. |               | 5.66        | 22.64   | 30.63   |
| 20 | sec. | 1.76          | 7.41        | 23.64   | 35.47   |
| 30 | sec. | 2.13          | 9.23        | 26.88   | 38.19   |
| 40 | sec. | 2.79          | 9.93        | 28.96   | 40.17   |
| 50 | sec  | 3.08          | 11.19       | 30.65   | 41.93   |
| 1  | min. | 3.23          | 11.54       | 31.43   | 42.67   |
| 2  | min. | 5.29          | 15,24       | 35.65   | 48.25   |
| 3  | min. | 6.17          | 16.99       | 37.92   | 49.86   |
| 4  | min. | 7.34          | 18.67       | 39.54   | 51.77   |
| 5  | min. | 7.86          | 19.72       | 40.78   | 52.73   |
| 6  | min. | 8.66          | 21.05       | 41.88   | 53.31   |
| 8  | min. | 8.88          | 21.47       | 43.64   |         |
| 10 | min. | 8.88          | 23.50       | 45.19   | 56.19   |
| 20 | min. | 10.57         | 26.65       | 47.27   | 57.34   |
| 30 | min. | 10.70         | 28,39       |         |         |
| 40 | min. |               | 30.03       |         |         |
| 50 | min. |               | 32.14       |         | 61.78   |
| 1  | hr.  | 15.56         | 33.99       | 51.95   | 63.14   |
| 2  | hr.  | <b>1</b> 8.94 | 38.04       | 54.54   | 64 00   |
| 3  | hr.  | 20.70         | 40.98       | 56.23   | 66.15   |

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|            |     | True Stress                           |               |         |         |  |
|------------|-----|---------------------------------------|---------------|---------|---------|--|
|            |     | 30 psi                                | 50 psi        | 100 psi | 150 psi |  |
| Tim        | e   | · · · · · · · · · · · · · · · · · · · | Strai         | n(%)    |         |  |
| 4          | hr. | 22.10                                 | 42.40         | 57.27   | 63.74   |  |
| 5          | hr. | 23.49                                 | 43.64         | 58.31   | 65.87   |  |
| 6          | hr. | 23.64                                 | 44.62         | 58.96   | 65.14   |  |
| 8          | hr. | 25.26                                 | 45.59         | 60.00   | 66.09   |  |
| <b>1</b> 0 | hr. | 25.55                                 | 45.80         | 61.17   | 67.04   |  |
| 15         | hr. | 26.58                                 | 47.41         | 61.56   | 69.17   |  |
| 20         | hr. | 28.49                                 | 48.88         | 62.86   | 71.60   |  |
| 25         | hr. | 30.03                                 | 50.28         | 64.42   | 71.89   |  |
| 30         | hr. | 31.04                                 | 51.23         | 65.19   | 73.43   |  |
| 35         | hr. | 31.47                                 | 51.73         | 65.44   | 74.83   |  |
| 40         | hr. | 31.70                                 | 52.04         | 65.56   |         |  |
| 45         | hr. | 31.69                                 | 52.24         | 65.43   | 74.09   |  |
| 50         | hr. | 32.36                                 | 52.90         | 65.69   | 74.52   |  |
| 55         | hr. | 33.02                                 | 53.45         | 65.99   | 74.90   |  |
| 60         | hr. | 33.41                                 | 53.72         | 66.13   | 74.68   |  |
| 65         | hr. |                                       |               |         | 74.56   |  |
| 70         | hr. | 34.57                                 | 54.87         | 66.68   | 74.91   |  |
| 75         | hr. | 35.07                                 | 55 <b>.31</b> | 67.02   | 75.16   |  |
| 80         | hr. | 35.52                                 | 55.73         | 67.40   | 75.62   |  |
| 85         | hr. | 35.71                                 | 56.01         | 67.39   | 76.09   |  |
| 90         | hr. | 35,96                                 | 56.26         | 67.54   | 76.49   |  |
| 95         | hr. | 36.48                                 | 56.72         | 67.84   | 76.62   |  |
| 100        | hr. | 37.00                                 | 56.97         | 68.08   | 76.66   |  |

|    |      | True Stress    |             |         |         |
|----|------|----------------|-------------|---------|---------|
|    |      | <b>200</b> psi | 300 psi     | 400 psi | 500 psi |
| Ti | ne   |                | Strain      | n (%)   | •       |
| 1  | sec. | 26.43          | 35.97       | 41.79   | 51.92   |
| 2  | sec. | 29.37          | 41.81       | 46.83   | 54.47   |
| 4  | sec. | 32.87          | 45.71       | 50.43   | 57.02   |
| 5  | sec. | 40.00          | 47.01       | 50.58   | 58.17   |
| 10 | sec. | 41.03          | 50.51       | 53.31   | 60.22   |
| 20 | sec. | 42.10          | 54.81       | 57.78   | 63.41   |
| 30 | sec. | 45.17          | 57.14       | 59.65   | 65.26   |
| 40 | sec. | 47.69          | 57.92       | 60.81   | 67.22   |
| 50 | sec. | 49.09          | 58.95       | 61.82   | 68.31   |
| 1  | min. | 50.35          | 59.86       | 62.18   | 69.50   |
| 2  | min. | 53.46          | 61.94       | 63.90   | 72.22   |
| 3  | min. | 55.17          | 63.76       | 65.27   | 72.92   |
| 4  | min. | 56.22          | 64.67       | 66.14   | 73.69   |
| 5  | min. | 57.27          | 65.06       | 66.71   | 74.07   |
| 6  | min. | 57.90          | 65.77       | 67.29   | 74.39   |
| 8  | min. | 58.81          | 66.23       | 67.80   | 74.84   |
| 10 | min. | 59.58          | 67.01       | 68.16   | 75.35   |
| 20 | min. | 61.75          |             |         | 75.64   |
| 30 | min. | 62,50          | 69.47       | 73.78   |         |
| 40 | min. |                |             |         | 77.78   |
| 50 | min. | مو بنو من مع   | ** ** ** ** | *       | 78.32   |
| 1  | hr.  | 64.90          | 70.51       | 74.50   | 79.05   |
| 2  | hr.  | 65.87          | 72.07       | 75.50   | 80.72   |
| 3  | hr.  | 66.85          | 72.46       | 76.37   | 81.86   |

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|      |     | True Stress |         |         |         |
|------|-----|-------------|---------|---------|---------|
|      |     | 200 psi     | 300 psi | 400 psi | 500 psi |
| Ti   | me  |             | Strai   | n (%)   | •       |
| 4    | hr. | 67.34       | 73.76   | 76.58   | 82.89   |
| 5    | hr. | 67.69       | 73.89   | 77.23   | 83.40   |
| 6    | hr. | 68.25       | 74.67   | 77.81   | 83.65   |
| 8    | hr. | 68.74       | 75.32   | 78.53   | 84.29   |
| 10   | hr. | 69.09       | 76.29   | 79.03   | 84.55   |
| 15   | hr. | 71.75       | 78.11   | 81.05   | 85.06   |
| 20   | hr. | 72.80       | 79.21   | 82.49   | 86.33   |
| 25   | hr. | 73.29       | 80.45   | 84.08   | 87.55   |
| 30   | hr. | 74.69       | 81.55   | 84.94   | 88.16   |
| 35   | hr. | 75.80       | 82.01   | 85.88   | 88.31   |
| 40   | hr. | 74.83       | 80.90   | 84.29   | 88.42   |
| 45   | hr. | 75.59       | 81.81   | 85.30   | 88.34   |
| 50   | hr. | 76.12       | 82.40   | 85.62   | 88.65   |
| 55   | hr. | 76.25       | 82.75   | 85.91   | 88.91   |
| 60   | hr. | 76.28       | 82,63   | 85.86   | 89.04   |
| 65   | hr. | 76.40       | 82.40   | 85.75   |         |
| 70   | hr. | 76.76       | 82,51   | 86.15   | 89.66   |
| 75   | hr. | 76.95       | 82.80   | 86.44   | 90.01   |
| 80   | hr. | 77.29       | 83.16   | 86.64   | 90.22   |
| 85   | hr. | . 77.56     | 83.49   | 87.00   | 90.17   |
| 90   | hr. | 77.89       | 83.80   | 87.15   | 90.40   |
| · 95 | hr. | 78.08       | 83.99   | 87.28   | 90.55   |
| 100  | hr. | 78.07       | 84.01   | 87.35   | 90.87   |

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APPENDIX G

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COMPUTER PROGRAM FOR REGRESSION ANALYSIS

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IMPLICIT REAL#8(A-H.O-Z)
     CHARACTER R*8(6) .NAME*64
      DIMENSION S(10,11), Y(6,12), F(12), X(6,12), C(6,12), EE(6,12), ER(6)
     *•XL(9)•YY(3•12)•YF(3•12)•YB(3•12)•YFA(3•12)•IW(10)•FF(10)•P(10)•
     *DE(20,20),T(50)
      DATA XL/1.66D00,1.25D00,.83D00.42D00.5*0.0000/
      DATA EN/64 0.001000/
      DATA EE, Y, C, X, YFA, P/334*0.0000/
      DATA T/1.0D00.2.0D00.3.0D00.5.0D00.8.0D00.10.0D00.15.0D00.20.0D00.
     +25.0000,30.0000,40.0000,50.0000,00.0000,37+0.0000/
      READ(5.1) ITUTAL.IW
1
      FGRMAT(1112)
      READ(5.2) F
2
      FORMAT(12F4.0)
      WRITE(6,119)
      DO 4 I=1,ITCTAL
      READ(5,5)(X(1,J),J=1,7)
4
5
      FORMAT(12F6.3)
      DO 50 M=1.ITGTAL
      ERR=0.
      DO 9 K=2.10
      KM = K - 1
      KP=K+1
      DO 10 I= 1.K
      DC 11 J= 1.K
      1F(1.GT.J) GD TD 11
      S(1, J) = 0.
      N = I W (M)
      DO 12 L=1.N
      IX=0
      1F((DABS( F(L) ).LT.0.00001).AND.((1+J-2).EQ.0)) IX=1
      S(I,J)=S(I,J)+(F(L)+DFLOAT(IX))++(I+J-2)
      CONTINUE
12
      S(J,I) = S(I,J)
11
      CONTINUE
      S(I.KP)=0.
      DC 15 L=1.N
      IX=Ü
      IF((DABS( F(L))+LT+0+00001)+AND+((I-1)+EQ+0)) IX=1
      S(1,KP)=S(1,KP)+X(M,L)+(F(L)+DFLUAT(1X))++(1-1)
15
      CONTINUE
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SUBROUTINE GJ(A.N.NP) IMPLICIT REAL+8(A-H, D-Z) DIMENSION A(10.11)  $DO 1 I = 1 \cdot N$ IF(DABS(A(I,I)).LT.0.0001) GD TD 109 CONTINUE 1 GO TO 1234 DC 51 ID=1.N 109 IF(DABS(A(ID,ID)).EC. 0.0 ) GO TO 51 IF(ID.EQ.N) GD TO 17 IID=1D+100 52 JD=110.N .EQ. 0.000 ) GD TO 52 IF (DABS(A(JD.ID)) DO 53 LD=1.NP ADM=A(1D,LD) A(1D,LD) = A(JD,LD)53 A(JD,LD)=ADM GO TO 51 52 CONTINUE IF(ID.LE.2) GO TO 10 17 LD = 10 - 1DO 54 KD=1.LD IF((DABS(A(KD, JD)).LT.0.0001).AND.(DABS(A(JD.KC)).LT.0.0001)) GO 6 TC 54 DD 55 MD=1.NP ADM = A(KD, MD)A(KD,MD) = A(JD,MD)A(JD,MD) = ADM55 GO TU 51 54 CONTINUE WRITE(6,987) , 987 SITHERE IS NO SOLUTION FOR THIS SET, BECAUSE THE DETERMINANT OF THI ES INPUT MATRIX IS POSSIBLY EQUAL TO ZERO. .) GC TC 10 51 CONTINUE 1234 DO 1010 1=1.N AI = A(I, 1)DC 101 J=2+NP 101 A(1, J-1) = A(1, J) / A1A(I,NP)=1./AI DÚ 102 K=1.N IF(K.EQ.1) GO TO 102 AK=A(K,1)DD 103 L=2.NP 103 A(K,L-1) = A(K,L) - A(1,L-1) + AK $A(K, NP) = -A(I, NP) \neq AK$ 1 02 CONTINUE 1010 CONTINUE 10 FETURA END

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|     | ٠ <u>ــ</u> .   |  |
|-----|---|--|
| 10  | CONTINUE  |  |
| ••  | CALL GJ(S,K,KP)   |  |
|     | 5=0.  |  |
|     | DC 101 I=1.N  |  |
|     | Y(M,1) = S(K,1)   |  |
|     | DO 100 J=1,KM   |  |
| 100 | Y(M,I) = Y(M,I) * F(I) + S(K-J,I)   |  |
| 101 | EE(M,1)=(Y(M,1)-X(M,1))**2  |  |
|     | DC 102 1=1+N  |  |
| 102 | E=E+EE(M.I)   |  |
|     | IF(K.EQ.N) GO TO 73   |  |
|     | E=E/DFLOAT(N-K)   |  |
| 73  | CONTINUE  |  |
|     | DC 13 I=1,K   |  |
|     | C(M,I) = S(I,I)   |  |
| 13  | CONTINUE  |  |
|     | IF((DABS(ERR-E)) .LT. ER(M)) GD TU 50   |  |
|     | ERR=E   |  |
| 9   | CONTINUE  |  |
| 50  | CONTINUE  |  |
|     | DO 111 M=1.IIOTAL   |  |
| ••• | WRITE(6,112)  |  |
| 112 |   |  |
|     | N=1W(M)   |  |
| 113 | DU 113 1-14N<br>Nottele 116 Ello VIN IN VIN IN EELN IN  |  |
| 115 | WRITELD, 1147 FLIJ, ALM, 17, T(M, 17, CC(M, 17)<br>FORMAT//, FY, F7, 2, Ay, FR, 5, 2/34, 015, 71) |  |
| 111 |   |  |
|     | WEITE((, 115)   |  |
| 115 | EDRMAT(1H) /// 28X THE COEFFICIENTS OF CURVING FITTING FOR FACH C                                 |  |
| ••• | EOMPONENT. 1///)  |  |
|     | DD 117 I=1.N  |  |
|     | J=1+1   |  |
| 117 | $k \in ITE(0, 118) = J \circ (C(k, 1) \circ K = 1, 6)$  |  |
|     | white(0,119)  |  |
|     | DC 222 1=1+4  |  |
|     | DC 222 J=1.13   |  |
| 222 | DE(I,J)=C(1,2)+2,*C(1,3)*T(J)+3,*C(1,4)*T(J)**2+4,*C(1,5)*T(J)**3+                                |  |
|     | 85,*C(1,6)*T(J)**4+0,*C(1,7)*T(J)**5  |  |
|     | WRITE(6,202)((DE(1,J),I=1,4),J=1,13)  |  |
| 202 | FORMAT(28X,41HTHE STPAIN RATE VALUES FOR EACH COMPONENT,///,                                      |  |
|     | 621X+4E15+6+/)  |  |
| 118 | $F_{GRMAT}(4X, *A(*, 12, *)) = *, 0X, 6E15, 0, /)$  |  |
|     | WF1TE(0,119)  |  |
| 115 | FORMAT (1H1+///)  |  |
|     | STOP  |  |
|     | LND   |  |
|     |   |  |

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