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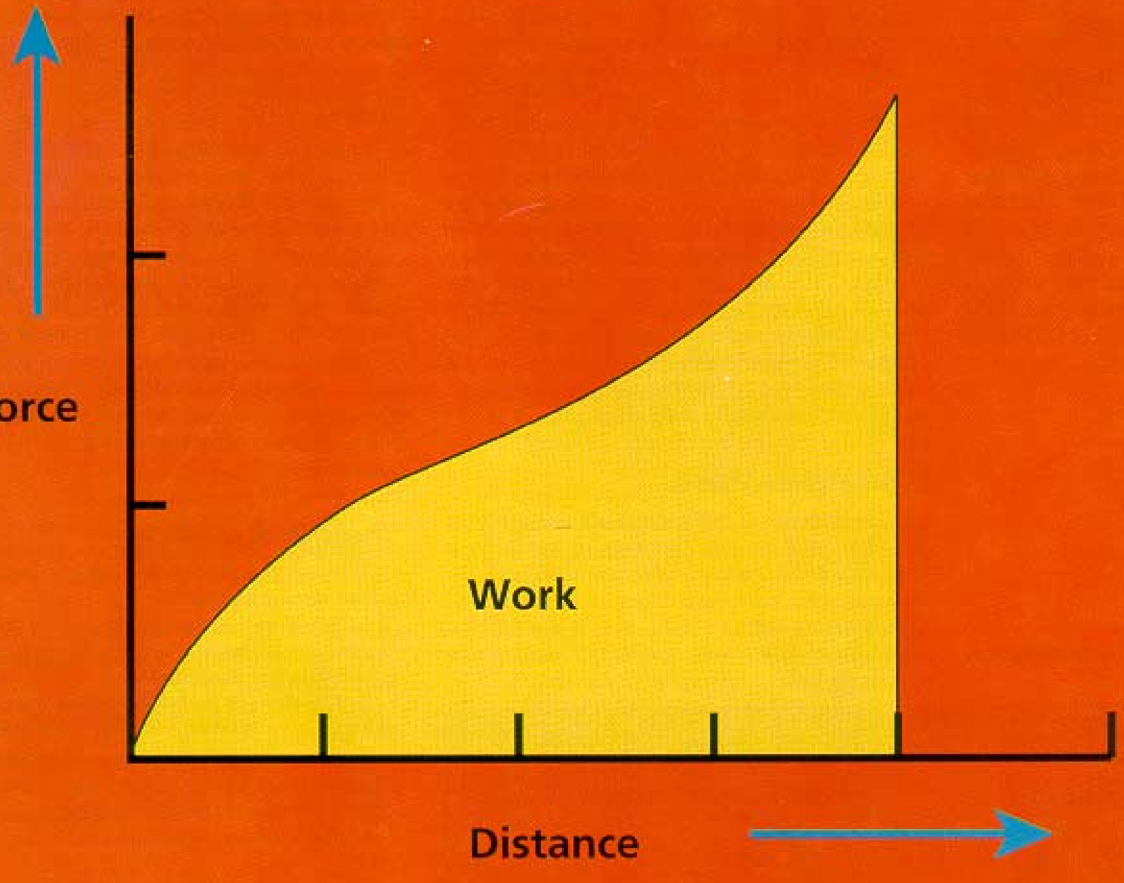
Rubber under strain: an engineering approach



Computer formulation: more bang for the buck

Compounding changes require creativity

By Daniel L. Hertz, Jr.

An analysis of rubber under strain from an engineering perspective

The stress-strain curve, "work" and its measurement, SIF, fillers and theories of elasticity all come into play in the study of rubber under strain.

About the author

Daniel L. Hertz is president of Seals Eastern Inc. and member of the Elastomer*ics editorial advisory board. He has chaired the education committees of the ACS Rubber Division, the New York Rubber Group and the Energy Rubber Group. He serves on the advisory boards of* CHEMTEC *and the Polymer Technology Consortium-Texas A&M. He attended Stevens Institute of Technology in 1952 and received an honorary degree in 1982.*

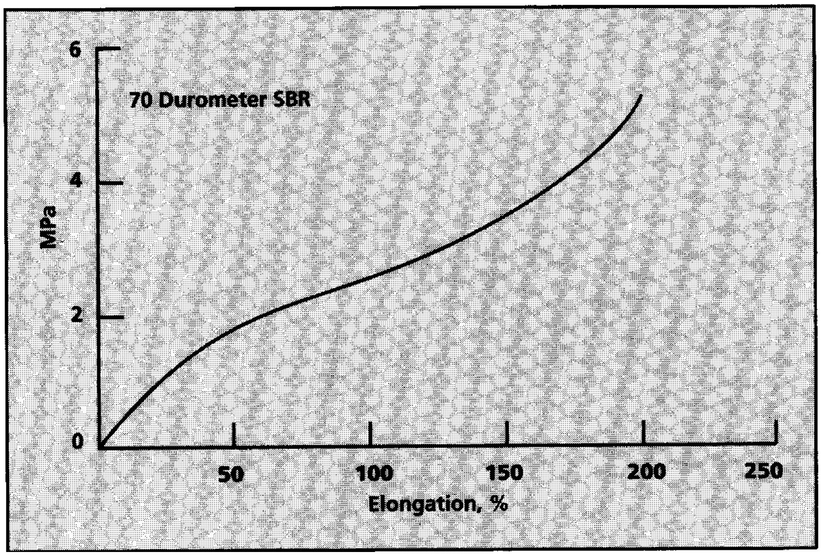
Rubber is an engineering material; even the die-hard chemists and chemical engineers that historically have dominated our industry are beginning to appreciate this fact. In an engineering sense, molded elastomeric products may be designed for use under strain (o-rings), stress (oilfield packers) or energy (tank treads, etc.). In a recent paper, Young (1) has made an outstanding contribution in this field.

There are no static applications of rubber - this broad statement is safe to make. All of the following are relevant in understanding the processes involved in the deformation of an elastomeric component: stress-strain curve; "work" as a by-product; molecular and phenomenological theories of elasticity; stress intensification factor (SIF); effect of fillers; and measurement of "work" as quality control and aging prediction. This article will discuss each of these factors individually.

Stress-strain curve

The tensilgram (Figure 1) is certainly as fundamental as one can get. In actuality it represents a stress-strain curve (Figure 2), whose terms we now can identify. *Stress is* the force acting across a *unit area* in a solid material in resisting the separation, compression or shearing that tends to be induced by external forces. *Strain is* the change in length of an object in some direction per unit undistorted length in some direction (not necessarily the same direction). The nine possible strains form a second-rank tensor.

Figure 1. A tensilgram.



Work

In an engineering sense, work (W), a scalar quantity, has been performed since the effort has involved both a magnitude (force) and a direction (distance). Newton's laws remind us that this work will not disappear without the appearance of heat or mechanical force, both measurable in joules (2). The actual value of work is the area under the stress-strain curve (Figure 3). In a recent educational paper Peacock (3) notes this value as "strain energy/ unit volume" using the value at 20% extension, which is quite reasonable in a design sense.

Theories of elasticity

What is this substance we are using as an engineering material?

1. Super-condensed gas (C_2 + C_4 gases) – gas viscosity $\cong 10^{-5}$ Pascal second (Pa•s); elastomer (η) $\cong 10^{9}$ Pascal second (Pa•s).

2. Density (ρ) is $\cong$ 1000 times greater than the gas.

3. Also referred to as a super-cooled liquid because of its ability to become "glassy" with only a narrow temperature shift.

4. Amorphous - essentially in the rubbery state.

The information in the first statement clearly suggests that thermodynamics is a prime consideration in the understanding of an elastomeric response.

Thermodynamics and elastomers. Consider something as elementary as the Ideal Gas Law:

$$PV = nRT$$

where n = number of molecules (fixed), R = gas constant and P, V and T (absolute) are variables.

Elastomers are a thermodynamic "system" since they have a definable boundary (n). We

Greek references

ε (epsilon) = practical tensile strain
η (eta) = non-newtonian viscosity
λ (lambda) = extension ratio or $\frac{\text{elongation}}{\text{elongation-original}}$
μ (mu) = Poisson's ratio
σ (sigma) = stress
ρ (rho) = density

now have to consider elastomeric properties in terms of stress, strain, time and temperature. In a compact but comprehensive review, Smith (4) neatly defines the stress-strain-time-temperature relationships for polymers. More recently, Shen (5) and Freakley (6) offer similar discussions on these relationships, which generally are defined in terms of either:

- phenomenological - the response under stress-strain under varying test conditions and the interrelation of the data; or
- molecular-which uses kinetic response based on theory of gases.

Phenomenological and molecular bases. The "phenomenological" basis (mathematical) is best described in Shen (5) and Freakley (6). These discussions include the work of Mooney (1940) and Rivlin (1948), which subsequently produced the Mooney-Rivlin coefficients. This concept is now incorporated into a constitutive equation widely used in the finite element analysis of elastomers. The "molecular" basis, primarily using thermodynamics, originally was referred to as the "statistical theory" by Gauss, and later referred to as the "Gaussian Theory" by Kuhn (1936) and the "kinetic theory" by English researchers.

Thus for "Large-Deformation, time independent properties" (4) the stress-strain curve is predicted by Equation 1:

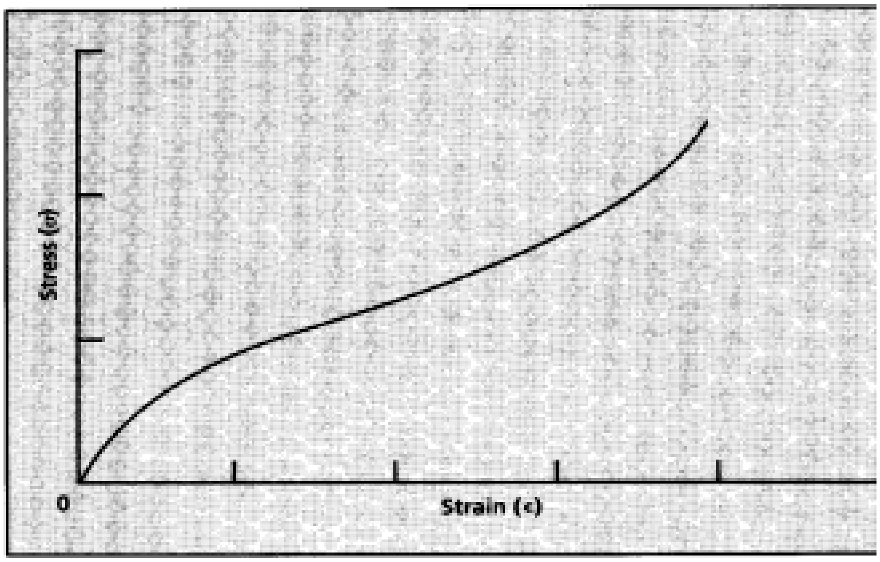
$$\sigma = NkT(\lambda - \lambda^{-2}) \quad (1)$$

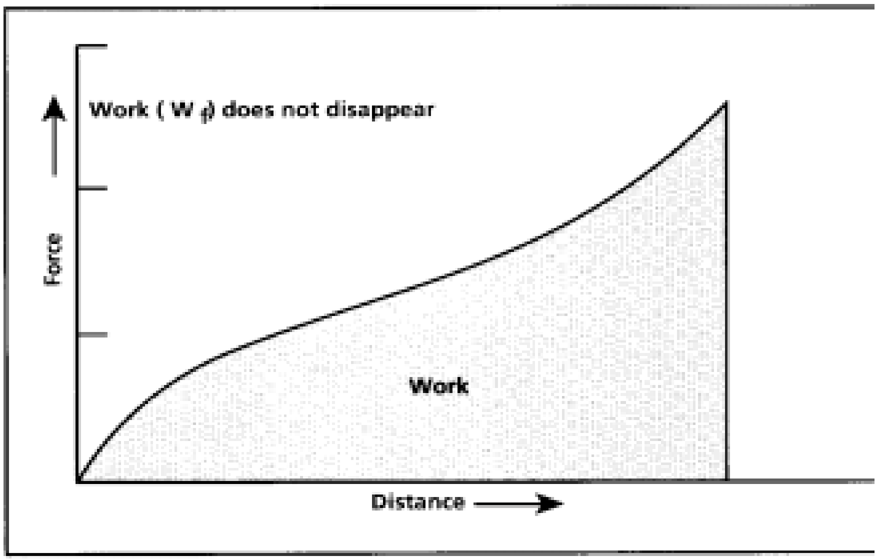
Based on molecular (kinetic) theory, this equation predicts that a tensile stress-strain curve is nonlinear (Figures 1 and 2), with stress proportional to temperature (within limits ranging from glass transition temperature T_g to = 100°C or 100°K above T_g). Smith (4) further notes the same theory to develop Equation 2:

$$G = NkT = \rho RT/M_c \quad (2)$$

where M_C equals molecular weight between crosslinks. This equation tells us two important facts: G is directly related to M_C which can change through crosslink density increases or decreases and/or chain scission (aging, chemical attack); and all elastomers have an equivalent G value at fixed temperature above their glass transition temperature, i.e. T_g + 60°C.

Molecular (kinetic) theory predicts that a shear modulus stress-strain curve is linear and stress is proportional to temperature.





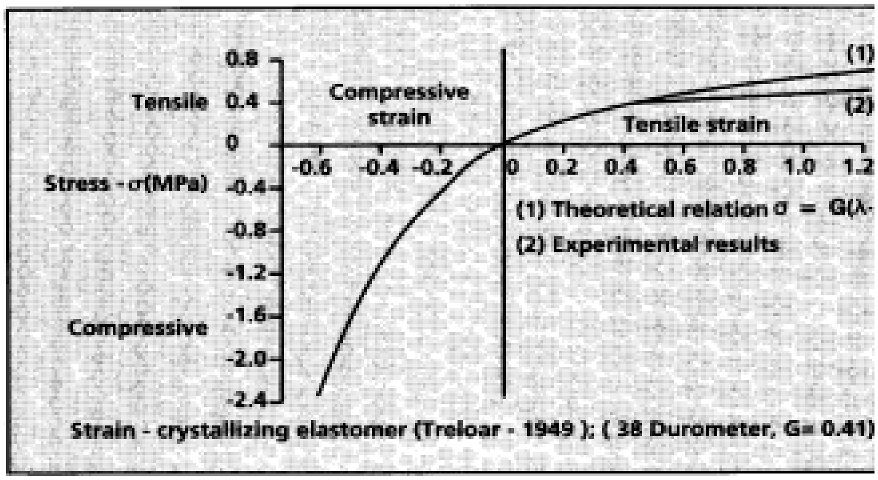


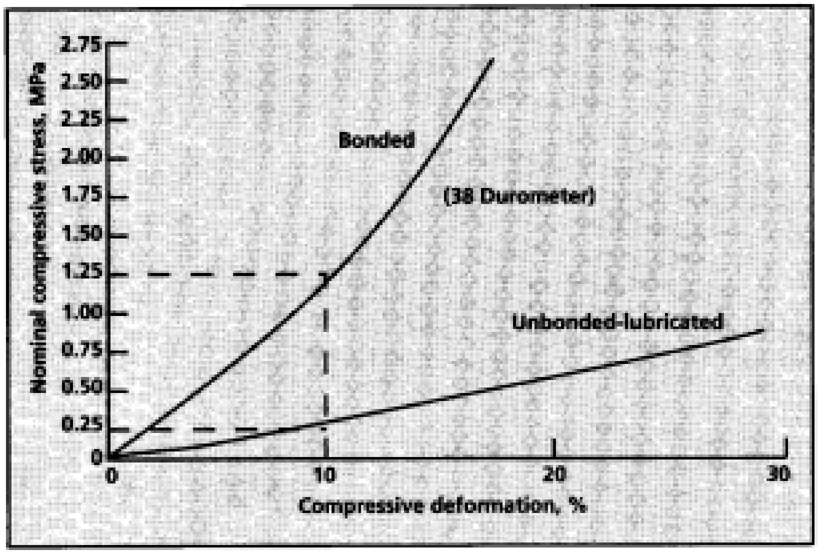
Figure 2 (top). A stress-strain curve. Figure 3 (c ter). Value of work as a under the stress-strain curve. Figure 4 (above). Uniaxial tensile–compre sion curve.

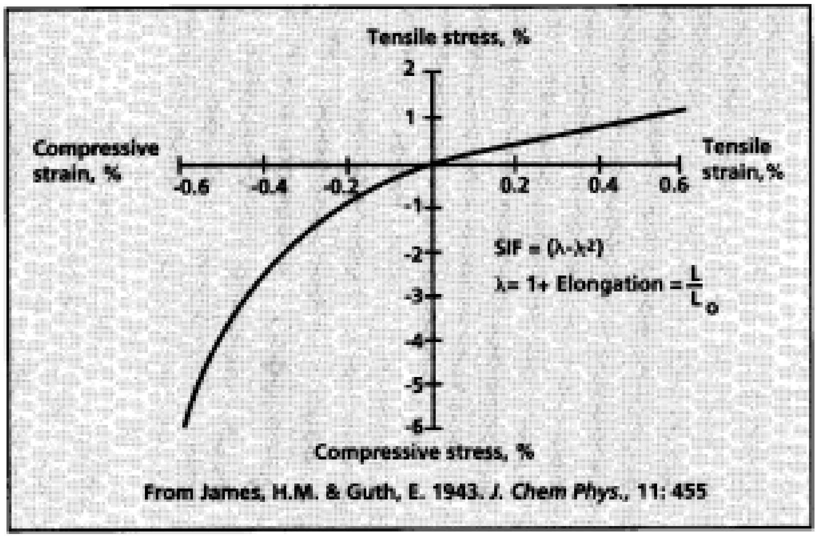
Summarizing Equations 1 and 2:

$$\sigma = NkT(\lambda - \lambda^{-2}) \quad (1)$$
$$G = NkT \quad (2)$$

in turn suggests Equation 3:

$$\sigma = G(\lambda - \lambda^{-2}) \quad (3)$$





From James, H.M. & Guth, E. 1943. *J. Chem Phys.*, 11: 455

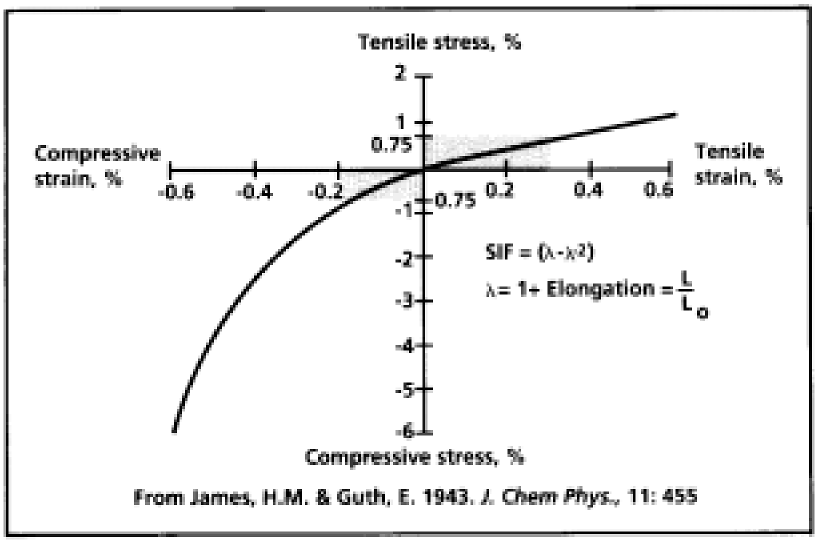


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Figure 5 (top). Stress-deformation curve. Figure 6 (center). Stress intensification factor (SIF) curve. Figure 7 (above). SIF curve with shaded area representing ideal design range for non-elastomers.

Treloar (7) compares actual results in Figure 4, a lightly filled natural rubber formulation, with the theoretical Equation 3. There is good correlation in compression and up to approximately 30% extension in tension. This relationship is correct if the specimen is well lubricated on the ends in compression (uniaxial) as opposed to being bonded (triaxial) (Figure 5).

Stress intensification factor

Referring now to the Treloar equation (Equation 3), consider the following: Shear modulus G, as previously noted, is the same for all non-crosslinked, unfilled elastomers at an equivalent temperature above their individual T_g values. Replotting the Treloar equation excluding the "G" value yields Equation 4:

$$\mathrm{SIF} = (\lambda - \lambda^{-2}) \quad (4)$$

and gives us a similar curve as shown in Figure 6. Remembering again the definition of stress, consider what is happening in the deformation of rubber whether it is under compression or tension.

> ***Under tension, to extend an elastomer 45%, an internal stress equivalent to 100% of the original must be overcome.***

Under compression, to deform an elastomer 24.5%, an internal stress equivalent to 100% of the original value must be overcome. The calculation for this reads as follows:

24.5% compression = 0.755 of original height
$\mathrm{SIF}= (0.755 - 0.755^{-2}) = -1.00$

Under tension, to extend an elastomer 46%, an internal stress equivalent to 100% of the original value must be overcome. The calculation for this reads as follows:

46% extension = 1.46 of original length
$\mathrm{SIF}= (1.46- 1.46^{-2}) = 0.991$

Smith (4) points out that the molecular (kinetic) theory is based on the principle that the bulk of these elastic forces are the results of entropy changes, i.e., this is now stored energy in the system (rubber) and the stress is directly proportional to the temperature.

Note: I am not saying that all designs should be held to 75% of this value (Figure 7), as one might do when working metals or plastics, but do consider what the elastomer is experiencing under strain. Consider the additional factor of fillers.

Fillers

Fillers serve numerous functions, but common to all is the effect brought about by increasing the viscosity of the formulation. This effect is defined by a modification of the Einstein viscosity equation by Guth (Equation 5):

$$G = G_0(1 + 2.5c^* + 14.1c^{*2}) \quad (5)$$

where c* equals volume fraction of filler.

Equation 5 illustrates increase in viscosity based on volume concentrations of fillers considered as suspended spheres.

Many fillers have more complex structures that are treated with the Guth-Smallwood equation (Equation 6):

$$G = G_0(1 + 0.67f^*c + 1.67f^2c^2) \quad (6)$$

Where f^* equals shape factor (typically $\cong$ 6).

The basic premise is the *volume* relationship, and thus the numerous filler studies based on weight equivalents often are creating false impressions on hardness change, reinforcing effects, etc. Correctly approached, filler studies should be based on equivalent volumes by correcting for density.

As noted previously, fillers increase viscosity. Equation 5 illustrates this in a logical fashion. We all know that carbon blacks behave differently even though we might have equal volumes of an N990 or N330. Obviously there is surface activity involvement, so we should at least understand "Adhesion and Wetting: Similarities and Differences" (8).

Another key factor to consider is that the addition of fillers to an elastomer automatically puts the network under strain. Consider a typical 90 durometer nitrile rubber formulation. To achieve this hardness, the polymer - filler ratio by *weight* might be 100 phr of elastomer (NBR) and 90 phr of filler (carbon black).

Converting this from weight to volume:

Elastomer (NBR)	100.0	d.	1.00
Filler (carbon black)	50.0	d.	1.80
Total volume	150.0		

Converting this volume change back to linear change we use the accepted relationship for change in an isotropic solid, i.e. volume = 3S (1 +S/100), where S is linear change. This works out to be about a 15% prestrain in the elastomer. Now consider an o-ring of this formulation, compressed 20%. A substantial strain has been applied to a network already under strain, typically at an elevated temperature. Small wonder that high hardness o-rings often fracture in service.

Measurement of "work"

For routine testing one should consider using the following (Equation 7) from Freakley & Payne (6), p. 27:

$$W = G/2(\lambda^2 + 2/\lambda - 3) \quad (7)$$

Peacock (3) points out that although an X & MR chart of durometer (a measure of viscosity) was under statistical control, a comparable X & MR chart plotting the same batches for "Work at 20% extension" shifted abruptly from 200 Ib/in.^{2} to 150 Ib/in.^{2}. Investigation revealed an incorrect postcure of test slabs (not product), and a corrected postcure brought the values back into statistical control. The point to be made is that durometer is not a measure of polymer - filler interaction, but only a measure of viscosity.

Since G is directly related to W, changes in network M_C due to aging (see Equation 3) will be immediately reflected in the W value. M_C (molecular weight between crosslinks) has always been subject to considerable debate (9,10).

Durometer is not a measure of polymer-filler interaction, but only a measure of viscosity.

Conclusion

To summarize:

- Using the concept "work (W) = the area under the stress strain curve" is a more global measurement of elastomeric network under strain.

- The interrelationships between work (W) and shear modulus (G) (as shown in Equation 7), and G and M_C is well defined.

- A change in M_C that can be initiated mechanically, chemically or thermally will be reflected in the W quantity and will be an indicator of the long-term stability of the elastomer system.

- Stress Intensification Factor and the effects of fillers should be understood and taken into consideration in critical applications where elastomeric components are under deformation.

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This article is based on a paper originally presented at the Akron Rubber Group, Jan. 24, 1991.

Seals Eastern Case Histories

Aerospace and Military Technology

Seals Eastern was the sole-source for all fuel and oxidizer seals in the "Lance" missile system. Fluorosilicone and phenylsilicone rubber were molded and bonded to complex, large-diameter aluminum structures in a clean-room environment. Extensive studies on crosslinking, bonding technology, surface chemistry and elastomers ended with the production of a highly successful missile system. The quality and process controls necessary for this complex project led to the level of quality we are noted for today.

Automotive Applications

Seals Eastern is a high volume manufacturer of tight-tolerance rubber/metal bonded seals for high-reliability drive train components. Precision tooling, modern molding techniques and automated handling equipment make us a consistent high-quality, low-cost supplier. In the new world of just-in-time (JIT) inventory, manufacturing must parallel with data on a real-time basis. Materials management by demand-supply analysis is accomplished using an integrated systems approach i.e.: customer order processing--linked to--materials resource planning--linked to--work order processing --linked to--shop floor control. Through such controls we offer our customers job traceability and punctual delivery.

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Our country's future energy supply, "sour" gas -- a high pressure, high-temperature combination of natural gas, carbon dioxide and hydrogen sulfide -- is a very harsh environment for any seal. Seals Eastern's contribution of advanced technical papers deals with the problem of sealing in this environment. Our numerous patents have provided the solutions. We are a major supplier of heat resistant seals and packers for critical high-pressure well completions. Unique molding techniques, total quality control and consistent performance are our assurances of quality for our oil field and geothermal customers.

Nuclear Applications

High-pressure superheated steam and excessive radiation levels are the critical environment in the event of a loss of cooling accident (LOCA) within a nuclear reactor. Seals Eastern has developed high-temperature formulations that withstand this event without excessive softening.

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