VISCOELASTIC EVALUATION OF SILICONE
RUBBER AND ETHYLENE PROPYLENE

N. R. Gordon

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By

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VISCOELASTIC EVALUATION OF SILICONERUBBER AND ETHYLENE PROPYLENEABSTRACT

Initial evaluation studies were made on two materials to determine their suitability as alternates to a silicone rubber for reactor applications. Of the two materials studied, ethylene propylene and chlorosulfonated polyethylene, the ethylene propylene has the lowest compression set and stress relaxation; and consequently, appears to be the best candidate. It has a higher stress relaxation rate than the silicone but its radiation resistance is superior.

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INTRODUCTION

The research described in this report is a preliminary effort to determine which elastomeric materials can be used as O-rings in Reactor applications. At the present time only one material, a silicone rubber, is specified for use in the Hanford reactors. The specification of additional materials would create a competitive supply with the possibility of cost savings. The purpose of this research was to evaluate the usefulness of three materials (ethylene propylene, chlorosulfonated polyethylene, and chlorosulfonated polyethylene blends) for reactor applications.

SUMMARY AND CONCLUSIONS

This report describes a preliminary investigation of three materials proposed as alternates for silicone rubber in O-ring applications. The materials included in this study were silicone (for comparison), ethylene propylene, chlorosulfonated polyethylene, and blends of chlorosulfonated polyethylene with 50% neoprene or 50% nitrile rubber. The properties initially measured on these materials were stress-strain relationships, tear strength, and compression set. A knowledge of these properties would provide a means of selecting which materials warranted further investigation. On this basis further studies on the chlorosulfonated polyethylene materials were discontinued because of their comparatively high compression set values.

The second phase of the program was the determination of time-dependent properties by stress relaxation measurements. These measurements show the changes in a material under constant strain as a function of time. The results show that the silicone rubber has a much lower rate of relaxation than does ethylene propylene, although the rate for the latter appears within acceptable limits.

As a final phase of the work, some stress-relaxation experiments were conducted on irradiated silicone and ethylene propylene. These tests show that even though the ethylene propylene relaxes faster than the silicone, it is much more radiation resistant. Consequently, the modulus of ethylene propylene changes less than silicone over an extended period of time in a radiation environment.

Based on the limited amount of work on radiation effects the ethylene propylene appears superior to the silicone. However, it is recommended that the studies of the effects of radiation on stress relaxation be continued to provide a more complete characterization of both materials.

DISCUSSION

BACKGROUND

One of the most demanding uses for elastomers in the Hanford reactors has been a cooling tube O-ring seal. This seal is subjected to both hot water and radiation. To date a silicone elastomer has demonstrated the longest useful life for this particular application. A nitrile elastomer with superior radiation resistance was tried at one time, but its creep and stress relaxation properties were so poor that it had an unsatisfactory life span.

At the present time there is no backup material qualified as a replacement for the silicone rubber. A two phase testing program is being instituted to find other useful materials. The first phase of this program is a preliminary study on materials that appear suitable for reactor use. Phase two of the program tests these materials under operating conditions, using a testing jig installed on the rear face of a reactor. This report describes results from phase one of the program.

Past Evaluation Techniques

In the past, testing techniques for evaluating elastomeric materials for reactor applications have been quite restrictive. The major test parameters have been ultimate tensile strength and ultimate elongation at an extension rate of twenty inches per minute.⁽¹⁾ In addition to these, the hardness of the materials has been determined. The effect of radiation on the materials has been determined by exposing test specimens to a ⁶⁰Co gamma flux. Although the data obtained by these techniques have been accurate and reproducible, they are not adequate for making reliable recommendations

for reactor use. The time dependency of the material's properties has been ignored, leaving a lack of knowledge of creep or stress relaxation. Such a premise can lead to untimely and unexpected failures.

Proposed Evaluation Techniques

Rough screening of materials was obtained by measuring compression set, tear strength, and stress-strain curves. Compression set normally provides an indication of the time dependence of a material under stress. Tear strength provides a measure of the materials strength during handling. Stress-strain curves provide information on the interrelations of strength and elongation as well as the ultimate properties.

A more accurate evaluation of the materials can best be accomplished by measuring one of the time dependent properties, i.e., creep or stress relaxation. Since there is a mathematical relationship between the two, stress relaxation is usually determined because the experiment is easier to perform.

Stress Relaxation and Creep

Stress relaxation of a material is defined as: the time dependent decrease in force applied by a material which is stretched to a predetermined length and held at that point, or: the decrease in stress at constant strain. Creep is defined as: the time dependent change in length of a material under a constant load, or: the change in strain at constant stress.

Stress relaxation in tension is defined mathematically by the equation:

$$E(t) = \frac{F(t)}{A_0 \Delta l / l_0} = \frac{\sigma(t)}{\epsilon} \quad (1)$$

where $E(t)$ is the modulus of elasticity as a function of time, $F(t)$ is the applied force as a function of time, A_0 is the unstressed cross sectional area, l_0 is the unstressed length, Δl is the change in length, $\sigma(t)$ is the stress as a function of time, and ϵ is the applied strain. A typical stress relaxation curve is shown in Figure 1.

Creep is generally defined mathematically as:

$$D(t) = \frac{\Delta l(t)/l_0}{F/A_0} = \frac{\epsilon(t)}{\sigma} \quad (2)$$

where $D(t)$ is the tensile compliance as a function of time, $\epsilon(t)$ is the strain as a function of time and σ is the applied stress. A typical creep curve is shown in Figure 2. It would appear that equation (2) is merely the reciprocal of equation (1). However, this is not exactly true. In equation (1) force is measured as a function of time and in equation (2) the change in length is measured as a function of time. If the material is isotropic and if the total strain is kept low the difference in modulus between the two is negligible and either can be used for design purposes. Stress relaxation was measured in this study since an O ring normally fails by that mechanism.

Boltzmann Superposition Principle

In a creep experiment, if stress σ_0 is applied to a material at time zero, the strain after time t_0 is given as:

$$\epsilon(t_0) = \frac{1}{E(t_0)} \sigma_0 \quad (3)$$

The addition of another stress at time t_0 will then give a strain at time t of

$$\epsilon(t) = \frac{\sigma_0}{E(t)} + \frac{\sigma(t)}{E(t-t_0)} \quad (4)$$

indicating the additive nature of the property. This is the basis of the Boltzmann superposition principle and serves as a definition of a linear viscoelastic material. A linear material whose structure (crystallinity, degree of cross linking, et.) does not change during the course of the experiment will obey this principle.⁽²⁾ Because of this restriction an elastomer in a reactor environment does not function as a linear viscoelastic material since its structure is continually affected by the radiation environment. However, if testing is performed outside of a radiation field, the material will obey the principle. By irradiating the material to various radiation levels then measuring the resulting changes, an indication of the influences of the radiation environment can be obtained.

Time-Temperature Superposition

The viscoelastic functions of materials are not only time dependent but also have a temperature dependency. Theoretical studies by Rouse⁽³⁾ were conducted on polymer solutions to describe this dependency in terms of relaxation time, τ_p . From these studies he developed the relationship:

$$\tau_p = f(a, \zeta_0, \frac{1}{T}) \quad (5)$$

where a is the monomer length, ζ_0 is the frictional coefficient and T is the absolute temperature. The temperature dependence of a in this function is expected to be very small. Using the Rouse function and the relationship between viscosity, η , and relaxation time in a solvent-free system, Ferry⁽⁴⁾ has developed a constant for the ratio of temperature dependent properties. He refers to this constant as the "shift factor" defined as:

$$a_T = \frac{\eta \ T_0 \ \rho_0}{\eta_0 \ T \ \rho} \quad (6)$$

The subscript o denotes properties at an arbitrary reference temperature T_o . By applying the "shift factor" to experimental results Ferry then formulated the equation:

$$\text{Log } A_T = -C_1^o(T-T_o)/(C_2^o + T-T_o) \quad (7)$$

where C_1^o and C_2^o are empirical constants. Williams, Landel and Ferry⁽⁴⁾ further simplified this equation by using the glass transition temperature of the material, T_g , as the reference temperature and obtained the relationship

$$\text{Log } A_{T_g} = -C_1^g(T-T_g)/(C_2^g + T-T_g) \quad (8)$$

The form of this equation has been found to fit many different systems over the temperature range from T_g to $t_g + 100$.

By using these relationships it is possible to measure a time dependent property of a material for short periods of time at several elevated temperatures and combine the data into a master curve extending to longer times at a lower reference temperature. The applicability of the equation is limited to amorphous polymers up to temperatures about 100°C above their glass transition temperatures. This relationship can also be applied to semi crystalline polymers if the mechanical properties are controlled by the amorphous regions of the polymer. Also, if the experiments are performed at the same strain the contributions of the crystalline regions are held constant and superposition can be made on the basis of the amorphous components.

Using time-temperature superposition, master curves for polyethylene at yield strain have been developed which coincide quite accurately with actual burst tests for polyethylene pipe.⁽⁵⁾ This provides fairly

conclusive proof that stress relaxation experiments utilizing time-temperature superposition can provide data adequate for design purposes.

EXPERIMENTAL

Materials

The elastomers studies in this program were silicone rubber, chlorosulfonated polyethylene, chlorosulfonated polyethylene blended with 50% nitrile or 50% neoprene elastomer, and ethylene propylene.* The silicone was in the form of two inch diameter O rings; the chlorosulfonated polyethylene and its blends were 1/8 inch thick sheets; and the ethylene propylene was in the form of 2-1/4 inch diameter O rings and 1/8 inch thick sheet. Initial test data on the silicone and ethylene propylene were so widely scattered that it became necessary to post-cure them to obtain valid results.

Initial Screening Tests

The stress-strain relationships, compression set and tear strength of the materials evaluated were determined initially to screen out those materials which would not be comparable to the silicone for reactor use. Stress-strain curves were measured per ASTM D412-62T for the flat sheets and ASTM D1414-56T for the O rings at an extension rate of 2 inches per minute. Stress-strain curves are shown in Figure 5. Compression set was measured per ASTM D395-61 method B after 22 hours at 100°C. Notch tear strength was measured per ASTM D624 die C. Results of compression set and tear strength measurements are shown in Tables 1 and 2, respectively.

* The silicone used was Silastic 2096 from Dow Corning; the Ethylene Propylene was Nordel from Du Pont; the Chlorosulfonated Polyethylene was Hypalon 20 from Du Pont.

Table 1

Compression Set*

	<u>Measured</u>	<u>Manufacturer's Literature</u>
Chlorosulfonated Polyethylene	68%	75%
Ethylene Propylene	12.2%	12-47%**
Silicone	--	7%***

* Measured per ASTM D395-61 Method B - 22 hours at 100°C.

** 47% is for ordinary compound - 12% is for a special compound.

*** After 70 hours at 300°C.

Table 2

Notch Tear Strength*

Chlorosulfonated Polyethylene	101 lbs. per inch
50% Chlorosulfonated Polyethylene 50% Nitrile	120 lbs. per inch
50% Chlorosulfonated Polyethylene 50% Neoprene	142 lbs. per inch
Ethylene Propylene	233 lbs. per inch
Silicone	30 lbs. per inch**

* ASTM D624 die C.

** Dow Corning Literature

Compression set measurements were not made on the silicone rubber because no flat specimens were available.

The compression set of the chlorosulfonated polyethylene was so much higher than the other two materials that it was rejected from further consideration. No further tests were made on this material.

Silicone rubber had the lowest ultimate tensile strength and elongation of all the materials tested, however, this is of little relative importance for O ring applications where the part is stretched to only a small percent of its ultimate strain.

Stress Relaxation Tests

Stress relaxation tests were conducted on O ring test specimens. These specimens were extended at a rate of 2 inches per minute between 1/2 inch diameter rollers to a constant strain ($\epsilon = 0.5$ for silicone, $\epsilon = 2.0$ for ethylene propylene) and allowed to relax. The stress change was recorded continuously on a strip chart. Tests were conducted for periods of 5 minutes. Temperature of the sample was maintained at $\pm 0.5^\circ\text{C}$ in an Instron environmental test chamber. Five specimens were tested at each test temperature and averaged to give one curve at each temperature. The lowest test temperature used (1.5°C) was taken as the reference temperature. The log of the modulus of elasticity was then plotted as a function of time using T_0/T as a vertical shift factor. Figures 4 and 5 show these curves for silicone and ethylene propylene, respectively, at the various temperatures which they were tested. The ρ/ρ_0 part of the vertical shift factor was ignored since the density change is a function of thermal volume expansion and this quantity is very low for the two materials tested.

Figure 6 shows the master curves obtained for the silicone and ethylene propylene. All data were reduced to $\log E_{(t)}$ at a reference temperature of 1.5°C. (See Appendix for a description of the method for generating these curves.) From this curve it is apparent that the time dependent modulus of the silicone rubber changes less than that of the ethylene propylene.

A limited amount of work was performed on the effects of radiation on the stress relaxation of silicone and ethylene propylene as represented in Figures 7 and 8, respectively. These figures show that the change in modulus caused by the radiation environment is much less for the ethylene propylene than it is for the silicone. Using a family of curves such as these it is possible to plot the modulus of the material as a function of time and radiation dose rate. Such a curve is shown on Figures 7 and 8 at a rate of 10^6 r/hour. Although it is unlikely that these curves depict exactly what happens in a reactor they provide a valuable method of comparing the two materials. This process would also be useful for designing a part with a maximum and minimum modulus of elasticity. If these limits were designated on the stress relaxation curves the designer could predict with reasonable accuracy the useful life of the part for any radiation level, or the maximum allowable radiation for a specified life span.

RECOMMENDED ADDITIONAL STUDIES

The foregoing studies have demonstrated that simple tests such as stress-strain relationships and compression set do not provide adequate data for comparative evaluation of materials. This can only be accomplished by using time-dependent properties such as stress relaxation. Additional work should first complete the study of effects of radiation on the stress relaxation of ethylene propylene and the silicone. The curves on silicone are necessary for a basis of comparison; and ethylene propylene appears to be a promising material.

A review of the literature supplied information on chlorosulfonated polyethylene with appears to conflict with the conclusions on this study.⁽⁶⁾ Although no values were given for compression set, the stress relaxation quoted is very similar to ethylene propylene as shown in Figure 8. This would indicate that either compression set measurements are not valid criteria for evaluating time dependent properties of a material, or the stress relaxation measurements in the referenced paper are for a significantly different chlorosulfonated polyethylene than those studied in this work. However, both materials were made by the same manufacturer and bear the same designation.

Because of the uncertainties involved, further studies should be conducted on the chlorosulfonated polyethylene to determine its stress relaxation and how this property is affected by radiation.

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APPENDIX

Method for Developing a Master Curve

The master curves for the silicone and ethylene propylene shown in Figure 6 were developed from the relaxation curves at varying temperatures (shown in Figures 4 and 5). Tables 3 and 4 contain the accumulated information to form the master curve. The values in the $\Delta \log A_T$ column were obtained by measuring the horizontal separation between the individual relaxation curves in Figures 4 and 5 with a linear scale. $\log A_T$ then becomes a sum of the $\Delta \log A_T$ values with the reference temperature (1.5°C) having a $\log A_T$ value of zero. The calculated value of $\log A_T$ is obtained by using the equation:

$$\log A_T = -C_1^0 (T-T_0)/(C_2^0 + T-T_0) \quad (9)$$

The values of C_1^0 and C_2^0 are obtained by plotting $T-T_0/\log A_T$ as a function of $T-T_0$ (Figures 9 and 10). From the curve, C_1^0 is $-1/\text{slope}$ and C_2^0 is intercept/slope . The variation from a straight line for ethylene propylene at the higher temperatures results because these temperatures exceed the glass transition temperature by more than 100°C and equation 9 is no longer valid.

With the values of $\log A_T$ the master curves can be formed. First the individual relaxation curves are shifted vertically by multiplying E by T_0/T . They are then shifted horizontally by the factor $\log A_T$. The master curves are shown in Figures 11 and 12.

Table 3

Determination of Log A_T Values for Silicone

<u>°C</u>	<u>$\Delta \log A_T$</u>	<u>$\log A_T$</u>	<u>$T-T_0$</u>	<u>$T-T_0/\log A_T$</u>	<u>$\log A_T$ (calc)</u>
1.7	6.6				
13.0		- 6.6	11.3	-1.72	- 6.19
	3.35				
19.0		- 9.95	17.3	-1.74	- 8.88
	0				
25.5		- 9.95	23.8	-2.39	-11.5
	-1.5				
29.5		- 8.45	27.8	-3.29	-12.9
	3.35				
35.0		-11.80	33.3	-2.82	-12.5
	0.35				
37.8		-12.15	36.1	-2.97	-15.5
	3.45				
40.0		-15.60	38.3	-2.46	-16.2
	4.60				
43.3		-20.20	41.6	-2.06	-17.1
	0				
49.0		-20.20	47.3	-2.35	-18.6
	6.4				
54.5		-26.60	52.8	-1.98	-19.9

Table 4

Determination of log A_T Values for Nordel Ethylene

<u>°C</u>	<u>$\Delta \log A_T$</u>	<u>$\log A_T$</u>	<u>$T-T_0$</u>	<u>$T-T_0/\log A_T$</u>	<u>$\log A_T$ (calc)</u>
1.5	1.05				
7		-1.05	5.5	-5.23	-1.22
	0.93				
12.8		-1.98	11.3	-5.72	-2.27
	1.31				
25		-3.29	23.5	-7.13	-3.98
	0.69				
32		-3.98	30.5	-7.66	-4.23
	0.94				
43.3		-4.92	41.8	-8.52	-5.73
	1.30				
54		-6.22	52.5	-8.44	-6.47
	3.03				
64		-9.25	62.5	-6.77	-7.02

FIGURE 1
Typical Stress Relaxation Curve

FIGURE 2
Typical Creep Curve

FIGURE 3
Stress Strain Curves

FIGURE 5
Stress Relaxation NORDEL Ethylene-Propylene

FIGURE 6
Stress Relaxation Master Curves at $T_0 = 1.5^\circ\text{C}$

FIGURE 7
Effects of Radiation on Stress Relaxation of Silicone

FIGURE 8
Effects of Radiation on Stress Relaxation of Ethylene Propylene

FIGURE 9
Determination of Constants of WLF Equation for Silicone

FIGURE 10
Determination of Constants of WLF Equation for Ethylene Propylene

FIGURE 11
Master Stress Relaxation Curve for Silicone

FIGURE 12
Master Stress Relaxation Curve for Ethylene-Propylene

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