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Effect of Solvent Environments on the Swelling Behavior of Elastomers Commonly used in Weapon Components*

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Abstract

The equilibrium swelling of a number of elastomeric seals, commonly used in weapon components, was determined after they were exposed to a saturated solvent environment. The dimensional stability of these elastomers in the solvents varied considerably. Reasons for this are discussed and a method by which one may estimate the degree of swelling that these elastomers will undergo in a solvent environment is presented.

Polymeric materials are used for a variety of applications in weapon components. These applications include electronic packaging, environmental O-ring seals and EMR gaskets. The materials come in contact with a variety of chemical environments which may have a detrimental effect on the material properties. For example preflight controllers come in contact with the jet fuel JP4, a mixture of organic solvents (1), which has been shown to swell the silicone EMR gasket appreciably.

The choice of a particular material depends on the properties desired and the environments with which it will come in contact. For example, silicones have a high permeability to moisture and swell considerably when exposed to saturated fuel environments. They, however, possess excellent low temperature capabilities. Conversely, VITON has excellent water permeation characteristics and excellent resistance to JP4 but exhibits poor low temperature properties. One important problem that faces the component engineer is the choice of a material that will withstand a variety of solvent environments with which it may come in contact during cleaning of the component, or during storage. Some elastomeric materials are known to undergo considerable swelling in the presence of particular solvents. Under these conditions the osmotic forces that produce this swelling are so high that they can cause the material to rupture (1). Non-elastomeric polymers, on the other hand, undergo a dissolution process in the presence of a good solvent. The aim of this paper is to study the behavior of elastomers in different solvent environments. This work was motivated by the fact that the silicone gaskets that are used for EMR protection in preflight controllers can undergo swelling on the order of 200% in the presence of JP4, whereas the fluorosilicones, the new replacement, undergo only minor changes in dimensions. This behavior will be addressed in detail. Moreover a method is presented which allows one to predict the degree of swelling that elastomers commonly used in weapon components will undergo in the presence of different solvent environments.

The experiments performed were rather simple, involving measuring the dimensional stability and weight change of the elastomers in the presence of different solvents. The weight changes were performed using electronic microbalances and Mettler balances. The materials were silicone, fluorosilicone, VITON and ethylene-propylene-diene (EPDM) elastomers. Table 1 summarizes the swelling behavior of the elastomers in 3 solvents, JP4, pentane and acetone. V_0 was the initial volume and V was the equilibrium volume of the elastomer.

Elastomer	$\mathbf{(V\text{-}V_0)/V_0}$	**Solvent**
Silicone	2.1	JP4
Silicone	0.4	Acetone
Fluorosilicone	0.16	JP4
Fluorosilicone	1.8	Acetone
Fluorosilicone	0.22	Pentane
VITON	.01<	JP4
VITON	1.6	Acetone
EPDM	1.1	JP4
EPDM	0.01<	Acetone

It is clear that the silicone and EPDM elastomers undergo considerable swelling in JP4 whereas VITON and the fluorosilicones do not. In the presence of acetone, however, VITON and the fluorosilicones undergo considerable swelling whereas the silicone and EPDM elastomers do not.

We can examine these observations in detail. Unlike hydrophilic substances that undergo swelling in the presence of water because of strong molecular interactions between the molecules, the swelling of elastomers by solvents is quite different. The swelling results from the large increase in the combinatorial entropy of mixing, ΔS_{mix}, that results as the solvent and elastomer molecules intermix. The degree of swelling is offset by two factors, a free energy contribution that arises from the elastic restoring forces, ΔG_{elas}, and the enthalpic interactions between the solvent and elastomer molecules, ΔH_{mix}, which is usually positive for elastomer solvent systems.

In comparing the equilibrium swelling of an elastomer in a series of solvents the term in the free energy that is affected is the enthalpic term. This term has the form (2,3)

$$\Delta H_{mix} \sim (\delta_1 - \delta_2)^2 \qquad (1)$$

δ_1 and δ_2 are solubility parameters of the solvent and elastomer, respectively. The solubility parameter is defined as the square root of the cohesive energy density, where the cohesive energy density is the heat of vaporization per unit volume. Swelling is maximum when the enthalpic contribution is smallest, ie. $\delta_1=\delta_2$. This is the underlining reason that elastomers typically behave differently in different solvent environments.

The solubility parameter of acetone is 9.9 $(cal/cm^3)^{1/2}$ and is 7.4 $(cal/cm^3)^{1/2}$ for pentane. The solvents that compose JP4 have values that range from 7.1 to 7.6$(cal/cm^3)^{1/2}$ (4). The results in table 1 suggest that the solubility parameters of the silicone and EPDM elastomers are close to that of the solvents that constitute JP4. That the swelling of these materials in acetone was insignificant is consistent with this result. The values of the solubility parameters of VITON (a fluoropolymer) and fluorosilicones are close to 9.9$(cal/cm^3)^{1/2}$, the δ of acetone. By comparing the relative degrees of swelling, the solubility parameters of the elastomers increase in the following order, EPDM, silicone, fluorosilicone and VITON. These observations suggest that adding a fluorinated chemical group to the silicone chemical structure increased its polarity thus rendering it dimensionally stable in the presence of JP4.

It follows that the swelling of any of these elastomers can be predicted based on the solubility parameter of the solvent which is readily available in handbooks (4-5). Another approach is to calculate the solubility parameters from chemical group contributions, but this is often not possible since the exact formulations of many of these elastomers are frequently unknown.

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