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ACCELERATED THERMAL AGING OF RUBBER MODIFIED EPOXY ENCAPSULANTS*

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ABSTRACT

A program is outlined to enable prediction of physical properties of rubber modified epoxy encapsulants over the life time of the extended life neutron generators. Preliminary results show that the chief aging phenomenon occurring is increased crosslink density of the epoxy matrix. No changes in the rubber phase have been detected. The effect of increased epoxy crosslink density has been higher volume resistivity at 66°C, increased tensile strength, and decreased ultimate elongation.

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INTRODUCTION

Material requirements for War Reserve (WR) applications are particularly stringent due to the high reliability requirements of the completed weapon system. For this reason, introduction of new materials into war reserve applications has always been difficult. As the expected life of weapon components has become longer, a need has arisen to predict material properties over the life of the component. For new materials, where no previous experience exists, it is of greater importance to be able to provide properties over the life of the weapon so that the reliability requirements of the weapon can be assured.

The expected life of weapon components is sufficiently long to make real time aging impractical. Use of time/temperature superposition offers a means to enable prediction of material properties over a time period much longer than the time span of the test. Aging of organic materials where a single aging process dominates generally follows the Arrhenius equation. This means that the log of the time required to achieve a particular level of change is inversely proportional to the reciprocal of the absolute temperature. The degree to which aging can be accelerated, however, is limited by the transitions which occur in the material. In glassy organic materials, the transition which limits acceleration is the glass/rubber transition. Molecular motion, oxygen diffusion, and gas permeability undergo changes in slope at the glass/rubber transition temperature. The aging of these materials above the glass transition temperature occurs by a different rate process making extrapolation through the glass/rubber transition temperature a possible source of large error.

A new material which is being introduced into neutron generators is rubber modified epoxy. This material differs from epoxies which had been used in the past through the presence of a dispersed rubber phase present in the epoxy matrix. The presence of these dispersed rubber particles imparts the epoxy with a much greater resistance to thermal shock and impact without significant loss in the physical properties. An aging program for this material has been designed and preliminary results will be reported in this paper.

MATERIALS SELECTED FOR AGING

The rubber used for modifying the epoxy is a carboxy terminated butadiene/acrylonitrile copolymer containing 18% acrylonitrile with an average molecular weight of 3500 g/mole. This rubber is produced by B. F. Goodrich Chemical Compnay, Inc., and is designated as CTBN 1300X8. Each rubber molecule is chemically attached to two epoxy molecules prior to the epoxy cure. The ratio of epoxy to rubber is 9:1 on a weight basis. The volume fraction of rubber found in the cured resin is ~ 10% with an average particle size of ~ 1 μm. The epoxy

used is Shell Chemical's Epon 828 which is a diglycidyl ether of bisphenol A with a molecular weight of 370 g/mole.

Seven epoxy/rubber/curing agent/filler/cure schedule combinations were selected for aging. They were as follows:

1. Epoxy/rubber/diethanol amine/cured at 100 psi; 2 hours at room temperature, 6 hour ramp to 54°C, 6 hours at 54°C, 6 hour ramp to 93°C, and 16 hours at 93°C.

2. Epoxy/rubber/diethanol amine/cured 16 hours at 71°C.

3. Epoxy/rubber/diethanol amine/cured 7 days at 85°C.

4. Epoxy/diethanol amine cured as Item 1.

5. Epoxy/rubber/diethanol amine/glass microspheres/cured 2 hours at room temperature and 24 hours at 66°C.

6. Epoxy/rubber/diethanol amine/glass microsphere/cured at Item 1.

7. Epoxy/rubber/Shell curing agent Z/aluminum oxide/cured as Item 1.

Selection of these materials was done to allow characterization of epoxies used in the neutron generators and to enable separation of effects due to the addition of rubber, cure schedule, curing agent and fillers.

To accelerate the aging as much as possible aging temperatures were selected as close as practical to the galss transition temperature of the epoxy. The five temperatures, 70, 66, 60, 55 and 50°C, were selected for aging to verify accuracy of the time/temperature superposition assumption. A logarithmic sampling schedule was designed for a four year period to identify aging phenomena with activation energies ranging from 10 to 30 kcal/mole assuming Arrhenius behavior. Tests were selected to monitor the aging phenomenon itself. These tests were glass transition temperature, density, and electron microscopy. A second set of tests was selected to identify the effect of aging on the physical properties of interest to the design engineers. These tests measured tensile properties, electrical properties, dynamic shear modulus, stress relaxation and coefficient of thermal expansion.

RESULTS

Some preliminary results from Groups 1, 4, and 5 will be given in this section. At present the total aging time ranges from a maximum of 6 months for Group 1 to a minimum of 3 months for Group 5. Only trends in data are available at this time because sufficient time has not elapsed to allow equivalent aging at the lower aging temperatures.

The first results to be examined will be the glass transition temperatures of the epoxy and rubber phases. Both the epoxy and rubber phases can age chemically through crosslinking and oxidative degradation. Increased crosslink density would be reflected through increased glass transition temperatures. Figures 1 and 2 show the glass transition temperatures for the epoxy and rubber phases respectively. All three groups showed a marked increase in epoxy glass transition temperature. This shows that filler and the presence of rubber do not have a measurable effect on the postcuring reaction of the epoxy. Figure 2 shows the rubber glass transition temperature for Groups 1 and 5 (Group 4 is omitted since it has no rubber phase). Examination of this figure shows that the rubber phase has not undergone a chemical reaction which affects the glass transition temperature as a result of aging.

Physical aging is being measured through changes in density. A glassy epoxy is not at its equilibrium volume after normal processing. As an epoxy is cooled through its glass/rubber transition, free volume is frozen into the glass. As aging proceeds, the epoxy will relax toward its equilibrium specific volume. this relaxation will have an appreciable effect on physical properties. This relaxation is being monitored via density measurements. Figure 3 shows these density measurements for Groups 1 and 4. The results to date show that any changes in density that have occurred are smaller than the sample-to-sample variation in density.

The principal type of aging that has been observed is the increased crosslink density of the epoxy matrix as reflected by the increased epoxy glass transition temperatures. This has occurred independently of the presence of rubber and glass microspheres. Now the effect of this increased crosslink density on electrical and tensile properties will be examined. Figures 4, 5, and 6 show the dielectric constant, dissipation factor, and volume resistivity. The dielectric constant and dissipation factor were measured at 1 MHz and 23°C. The volume resistivity was measured at 66°C. Dielectric constant and dissipation factor show no trends with aging with the exception of the Group 1 dielectric constant which shows an increased dielectric constant with aging. No explanation of this is known, and it is believed that this trend is scatter in the data that will disappear as more data is collected. The volume resistivity, however, shows a clear trend for all three groups shown. The increased crosslink density has the effect of increasing the volume resistivity.

Figures 7, 8, and 9 show the changes in tensile strength, modulus, and ultimate elongation respectively for Groups 1, 4, and 5. The increased crosslink density of the epoxy has the effect of increasing the tensile strength. Although in Group 5, where the effect of the glass microspheres dominates, this effect is not seen. In Group 1 where the toughening mechanisms which allow plastic deformation have reduced

effectiveness as the epoxy matrix is embrittled the ultimate elongation is considerably reduced. The modulus shows almost no trend with aging.

SUMMARY

An accelerated thermal aging program is underway for rubber modified epoxy encapsulants. The objective of this program is to make a prediction of physical properties of the rubber modified epoxy over the life of the extended life neutron generators. Preliminary results indicate that the chief aging occurring is the increased crosslinking of the epoxy matrix. This aging appears independent of the presence of the rubber modifier or the presence of glass microspheres. The principal effects of increased crosslink density of the epoxy matrix has been increased volume resistivity at 66°C and increased tensile strength.

FIGURE 1

EPOXY GLASS TRANSITION TEMPERATURE

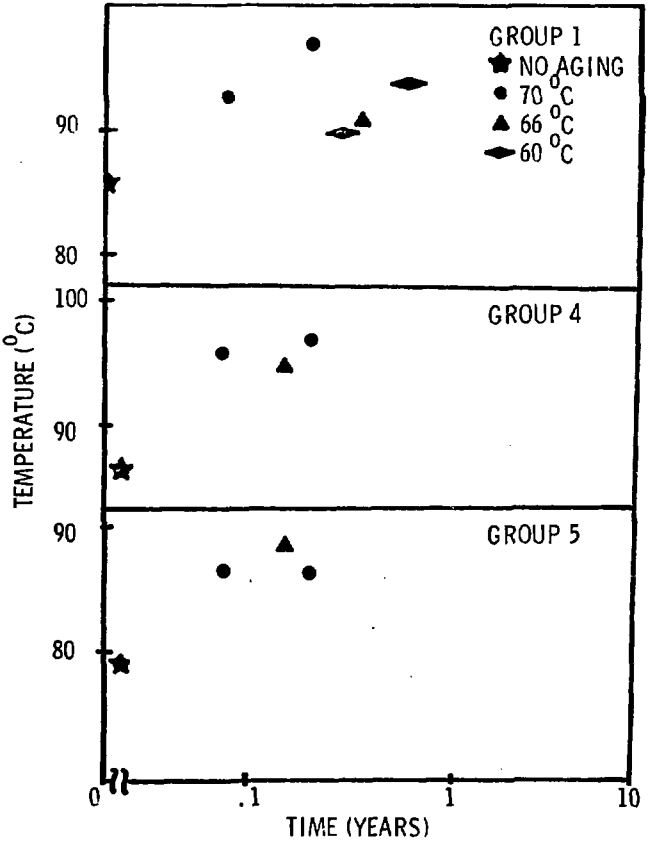

FIGURE 2

RUBBER GLASS TRANSITION TEMPERATURE

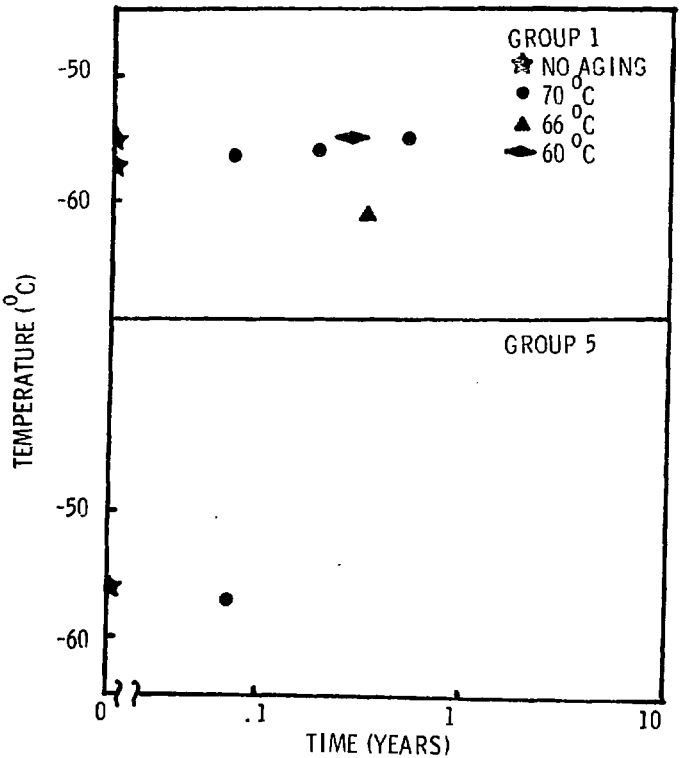

FIGURE 3

DENSITY

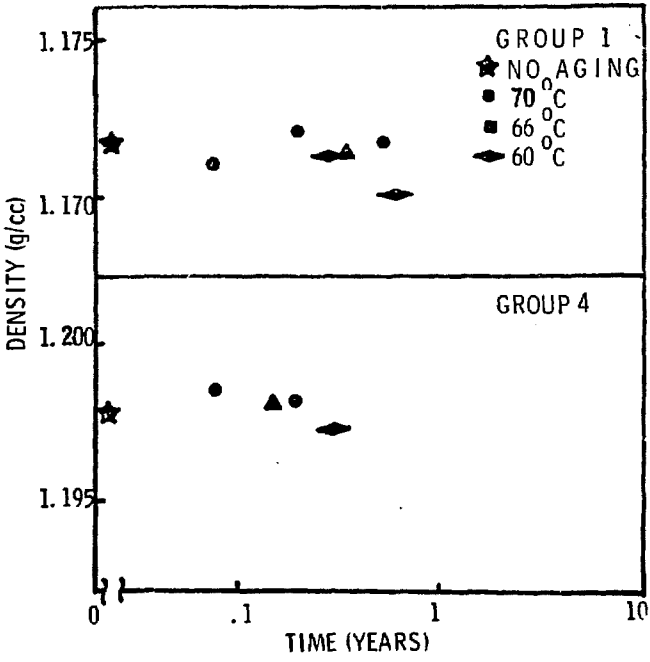

FIGURE 4

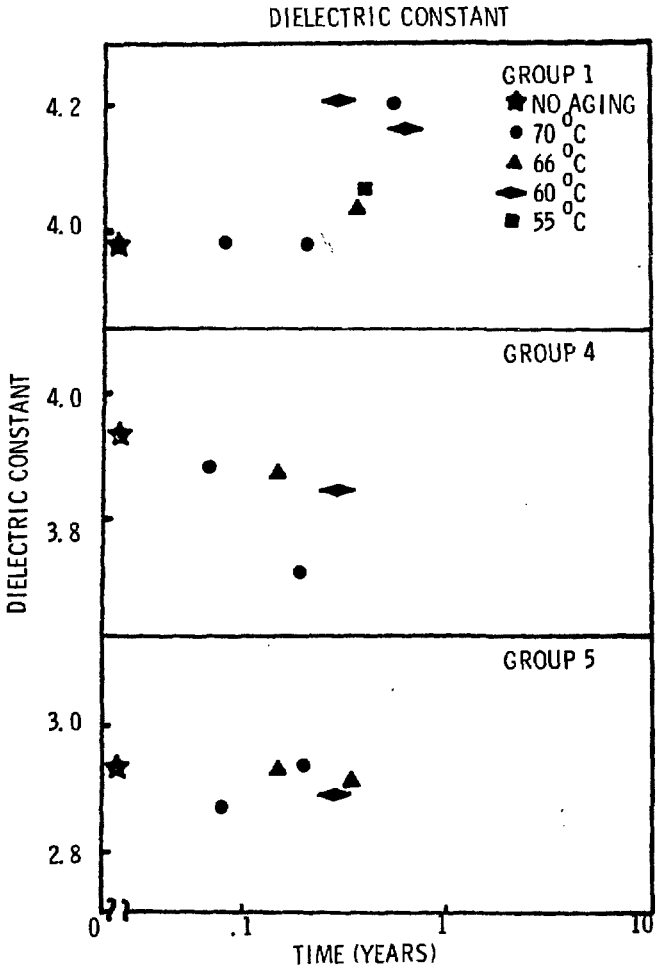
DIELECTRIC CONSTANT
GROUP 1
NO AGING
70 °C
66 °C
60 °C
55 °C
GROUP 4
GROUP 5
4.2
4.0
4.0
3.8
3.0
2.8
DIELECTRIC CONSTANT
0
.1
1
10
TIME (YEARS)

FIGURE 5
DISSIPATION FACTOR

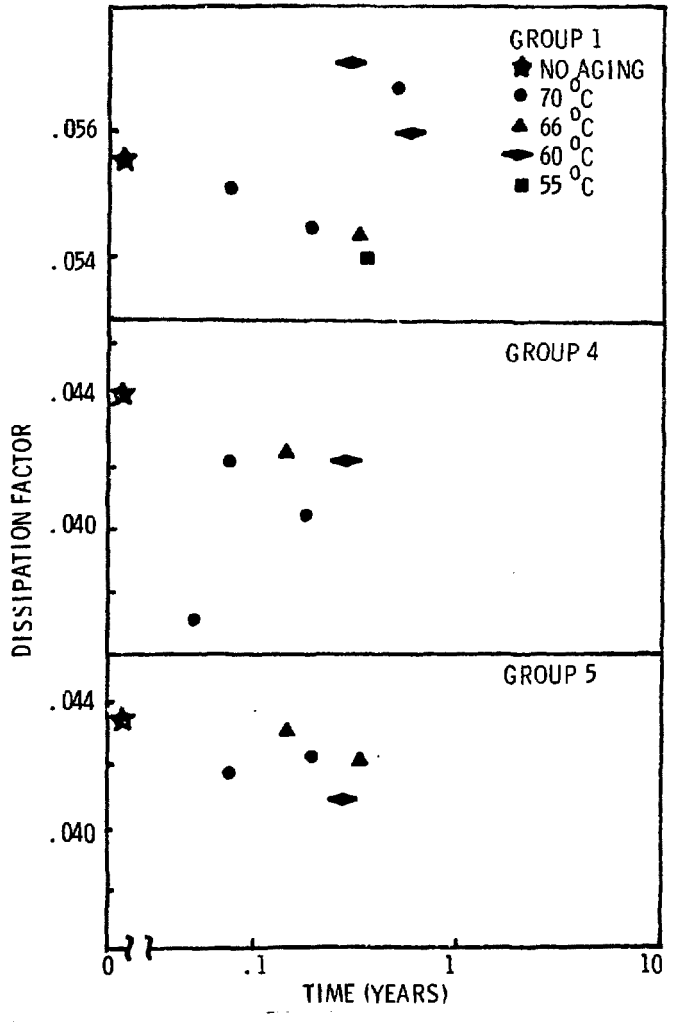

FIGURE 6

VOLUME RESISTIVITY

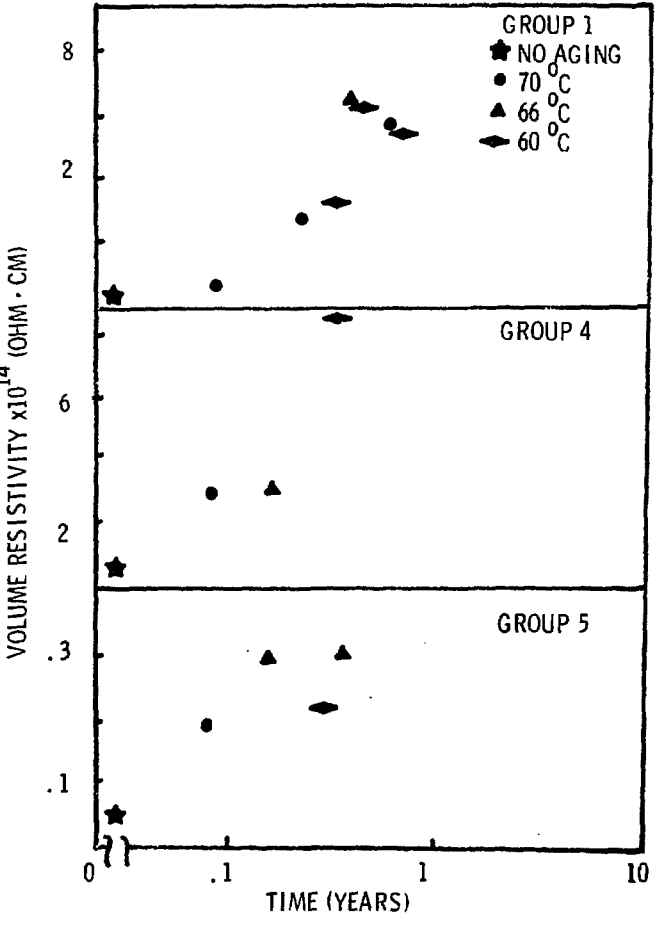

FIGURE 7

TENSILE STRENGTH

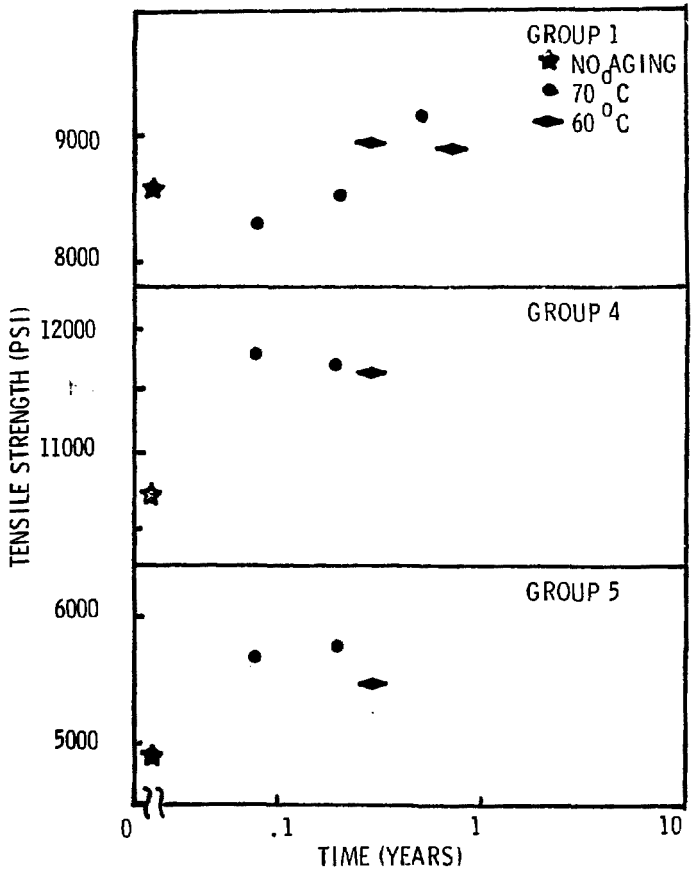

FIGURE 8

ELASTIC MODULUS

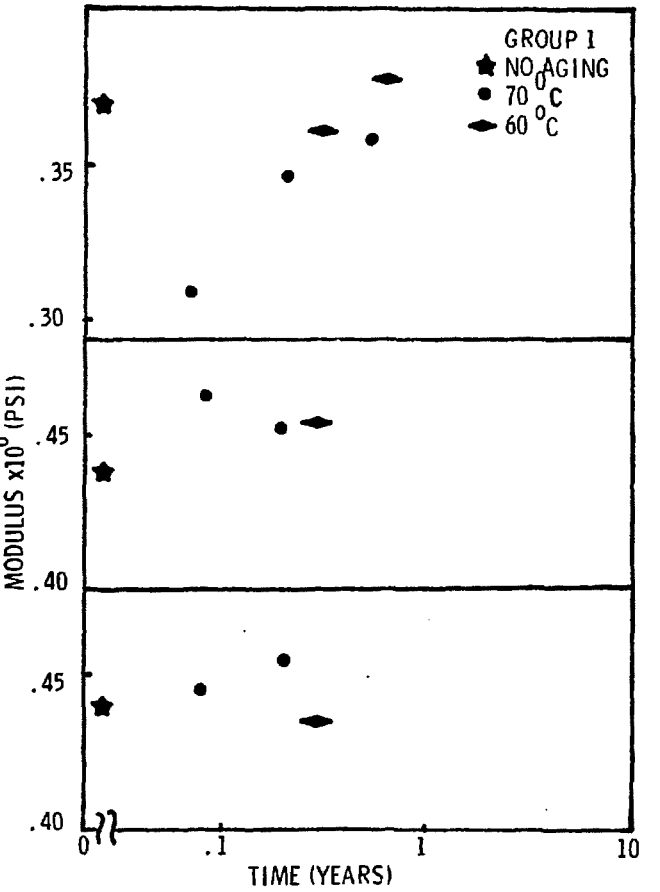

FIGURE 9

ULTIMATE ELONGATION