4.8 Degradation of Elastomers by Heat and/or Radiation

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Abstract This article studied some problems on the degradation of elastomers by heat and/or radiation. The changes in ultimate elongation, and the increase in C=O concentration show the existence of synergistic relationship between heat and radiation as the rate constant of chemical stress relaxation shows. The temperature dependence of radiation induced degradation of fluorine containing elastomers was found to be small. The fluorin containing elastomer have less radiation resistant properties than appropriately compounded EPDM.

INTRODUCTION

The electric cable and components in container vassal of nuclear power plant are exposed by radiation and heat simultaneously during normal service condition and a simulated loss of coolant accident. Elastomers are used as the materials for the electric cables and the components because of its elastic and flexible properties. Therefor, it is important to study the temperature dependence of radiation induced degradation of elastomers. The synergistic relationship between heat and radiation is the functional problem to be also clarified. It is practically useful to investigate whether heat resistant elastomer have radiation resist properties. The article studied some problems on the degradation of elastomers by heat and/or radiation mentioned above.

EXPERIMENTAL

The fluorine containing elastomers used were AFLAS type (Asahi glass Co. Ltd.) and VITON type (Du pont). AFLAS type is copolymer of tetrafluoroethylene with propylene, and VITON type is copolymer of hexafluoropropylene with vinilyden fluoride. Each of the copolymers contains small amount of termonomer. Table 1 shows compounding receipts of those samples. The receipt of ethylene-propylene diene elastomer (EPDM) was shown elsewhere (Ito M., 1993). The sicknesses of the samples were about 0.5mm. The irradiation was performed by Co-60 ray at the constant temperature in air oven. The mechanical properties were measured by the tensile test at room temperature. The distance of jowl was 500mm, and the extension rate was 50mm/min. The volume resistivity was measured with applying electricity of 500V.
Table 1 compounding receipts of fluorine containing elastomers.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>AFLAS Type</th>
<th>Parts</th>
<th>VITON Type</th>
<th>Parts</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFLAS 150 (Asahi glass)</td>
<td>100</td>
<td>VITON B (Du pont)</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>1,3-Bis(ter-butyl peroxy isopropyl)benzene</td>
<td>1.0</td>
<td>Lead monoxide</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>Triallyl isocyanurate</td>
<td>5.0</td>
<td>DAIAK No.3 (Du pont)</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>Sodume stearate</td>
<td>1.5</td>
<td>Activated calcium carbonate</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>Mistron vapor talc</td>
<td>30</td>
<td></td>
<td></td>
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</tbody>
</table>

RESULT AND DISCUSSION

Synergistic relationship between heat and radiation on the degradation of elastomers.

Fig.1 shows increase in concentration of C=O of ethylene-propylene copolymer pure vulcanizate by heat and/or radiation. If there is the simple additivity on the increase in C=O concentration by heat and radiation, the simultaneous additions of each of the deteriorate conditions gives the data on dotted line. The simultaneous addition results higher C=O concentration than the value expected from the basis of simple additivity. Therefore the result shows the existence of a synergism between heat and radiation. Clough and Gillen (1981), and Ito (1981) concluded that there is a synergistic relationship between heat and radiation on the degradation of polymers. The former measured the decrease in ultimate elongation by heat and/or radiation but they did not define the rate of decrease in ultimate elongation. On the other hand, the latter measured the rate of chemical stress relaxation. The method proposed "coefficient of synergism" to express the magnitude of synergism.

Fig.1

Increase in concentration of C=O of EP07P by heat and/or irradiation.
- 70°C heat alone
- 3kGy/h at room temperature
- 3kGy/h at 70°C
The extrapolated line

Fig.2

Synergism of Heat and Radiation on Elongation Changes.
- Heat (140°C)
- Radiation (0.5 Mrad/h at 70°C)
- Heat and Radiation (0.5 Mrad/h at 140°C)
Recently I found out that the rate constant of decrease in ultimate elongation can define for certain elastomers. As an example, decrease in ultimate elongation of EPDM-4 by heat and/or radiation is shown in Fig. 2. The rate constant of decrease in ultimate elongation $K$ defined by equation 1.

$$\log \left( \frac{e}{e_0} \right) = -Kt$$  \hspace{1cm} (1)

where $e$ is elongation at time $t$ and $e_0$ is the initial elongation. A synergistic relationship exist on the decreasee in ultimate elongation. The slope for the simulatanious addition of heat and radiation is higher than that expected from the basis of simple additivity. The results suggests that the measurement of C=O concentration and elongation at break for the certain elastomers can give the degree of synergism.

Radiation induced degradation of fluorine containing elastomers at various temperatures.

Fig. 3 and 4 show the relationship between the weight of the samples and dose. The weight decreases with increasing dose and temperature. The scission reaction by irradiation produced low molecular products. The diffusion of those volatile products from samples to air results in the weight loss at higher temperatures. The temperature dependence of the rate of weight loss was found to be discrete. The results show that the rate of scission reaction does not affect the weight loss directly, but the diffusion of low molecular weight products from the sample to air controls the rate of the weight loss. Fig. 5 and 6 show the changes of volume resistivity by irradiation. At higher temperatures, irradiation does not affect the resistivity. This is due to the vaporization of polar molecules that decrease the value of resistivity from the samples at higher temperatures. The 25% modulus of two elastomers increases with increasing dose as shown in Fig. 7 and. VITON type doses not show the temperature dependence. AFLAS types have temperature dependence, but not remarkable one. The decrease in ultimate elongation by irradiation at various temperatures was also studied. Fig. 9 shows the dose when elongation at break decreases to 50% and when elongation decreases the half of initial values. The result shows that AFLAS type has better radiation resistant properties than VITON type.

Comparison of radiation resistant property with another elastomers.

Fig 10 shows the decreases in ultimate elongation of various elastomers by irradiation. EPDM-3 and acrylic elastomer(AC-1) have better radiation resistant properties on the view point of elongation retained. Thus, appropriately compounded EPDM and acrylic rubber were found to have excellent radiation resistant properties compared with fluorine containing heat resistant elastomers.
Fig. 3: Weight change of AFLAS type elastomer by irradiation.

Fig. 4: Weight change of VITON type elastomer by irradiation.

Fig. 5: Changes of volume resistivity of AFLAS type elastomer by irradiation.

Fig. 6: Changes of volume resistivity of VITON type elastomer by irradiation.

Fig. 7: Changes of 25% modulus of AFLAS type elastomer by irradiation.

Fig. 8: Changes of 25% modulus of VITON type elastomer by irradiation.
Fig. 9 Relationship between critical dose and reciprocal of temperature.

Fig. 10 Decrease in ultimate elongation of various elastomers by irradiation.

REFERENCES

