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ARTICLE

Development of a Quantitative, Radiation-Resistant Feeding Pump for Use in Extraction Chromatography Techniques for MA(III) Recovery

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Japan Atomic Energy Agency has been working on development of extraction chromatography technology for recovery of trivalent minor actinides (MA(III): Am, Cm) from high-level radioactive liquid waste generated in reprocessing of spent nuclear fuel. In this project, a diaphragm pump with radiation resistant is being developed for use in feeding the liquid on the recovery system. In this study, the degradation behavior of ethylene-propylene-diene (EPDM) rubber, selected as a candidate diaphragm material for diaphragm pumps, was quantitatively evaluated by irradiation tests. The rubber samples were immersed in nitric acid solution under tensile load and irradiated with gamma rays. After irradiation tests, tensile testing and dynamic mechanical analysis were conducted to the rubber samples. When the total dose increased, scission of the molecular chains on the rubber samples progressed in priority resulting in a decrease in the molecular weight. On the other hand, the viscoelasticity of the rubber is maintained even after irradiation of about 3.0 MGy. Irradiation tests were also performed on diaphragm pumps incorporating this EPDM rubber. The degradation behavior was similar to that of the rubber samples with the same total dose.

KEYWORDS: minor actinide, radiation-resistant, EPDM, diaphragm pump, gamma irradiation, tensile testing, dynamic mechanical analysis

I. Introduction

Japan Atomic Energy Agency (JAEA) has been conducting chemical testing for the recovery of trivalent minor actinides, americium (Am) and curium (Cm), from high-level radioactive liquid waste generated by the reprocessing of spent fuel from nuclear power plants, and engineering studies on the minor actinides recovery system for safety evaluation of the system and development of the equipment.[1)] As one of the recovery techniques for minor actinides, the extraction chromatography method, in which an adsorbent loaded with an extractant is packed in a column and the adsorption and elution are controlled, is being studied.[2-4)] It is important to control the flow rate when pumping the liquid to the column, and a quantifiable pump is required for the system. JAEA is considering the application of a diaphragm pump as a quantifiable pump. The diaphragm material incorporated in the diaphragm pump is an organic material, and radioactive liquid directly contacts the material when pumping, so it is necessary to improve the durability of the pump, especially the diaphragm, against radiation. There have been many studies on degradation of polymers due to irradiation, including degradation due to heat and radiation and their dose effects, but there have been few studies about radiation degradation of the materials in a nitric acid environment.[5-9)] In previous study, gamma-ray irradiation tests were conducted for EPDM and Fluor elastomers and one of the most radiation resistant diaphragm materials was selected as a candidate for inclusion in the diaphragm pump. In this study, irradiation tests were conducted on the candidate material under several total radiation dose to evaluate the effects on the mechanical properties and molecular structure of the rubber samples as total radiation dose increases. The candidate material was also processed into an actual diaphragm material, and irradiation tests were conducted on a pump in which the material was incorporated.

II. Experimental

1. Evaluation of Dose Effects of Irradiation Tests on EPDM Rubber Samples

The dumbbell-shaped rubber samples (size: 6 mm (2 mm at center) x 35 mm x 2 mm) were prepared by cutting commercially available radiation-resistant EPDM rubber sheets. The rubber samples were placed in a SUS container with a tensile load with a stress of about 1 MPa which was referenced to the discharge pressure during pump operation. A 3 mol/L nitric acid solution was added in the container so that the sample was immersed. The set acid concentration is the concentration expected in the feed solution in the MA recovery system. The container was placed at an irradiation chamber in which gamma radiation dose rate was 5.1 to 6.0 kGy/h and removed at a predetermined time on which the total dose was approximately 0.5, 1.0, 2.0, and 3.0 MGy. Dose rates were measured with an alanine dosimeter. As a comparison, the samples were prepared by under nitric acid immersion and gamma irradiation, gamma irradiation only, tensile loading only. The gamma irradiation tests were conducted at the Takasaki Institute for Advanced Quantum Science at National Institute for Quantum Science and

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Technology, Japan. The samples were measured by tensile testing using a force tester (A&D Company, Limited, MCT2150) to determine elongation at break and tensile strength at break. Dynamic mechanical analysis was also conducted by using Dynamic Mechanical Analyzer (Hitachi High-Tech Corporation, DMS6100) in the range of -200 to 100°C. The molecular weight between cross-linking points was calculated from the area where the storage modulus became flat (approximately 100°C in this case), from which the cross-link density was calculated from Eq. 1.[10)]

$$n = \frac{E'}{2(1+\mu)\rho RT} \tag{1}$$

n : cross-link density [mol/Kg]
E': storage modulus [Pa]
μ : Poisson's ratio (Assumed 0.5)
ρ : density [Kg/m^3]
R : gas constant [J/mol・K]
T : absolute temperature [K]

2. Irradiation Test on Diaphragm Pumps Incorporating EPDM Diaphragm Materials

A double diaphragm pump (TACMINA CORPORATION, Smoothflow Pump, PLFXW2-06-SESE-UWX-B104) was then fabricated incorporating diaphragms molded from radiation-resistant EPDM rubber sheet with a thickness of 4 mm. It consists of two pump head sections: the pump heads connected to the driven section and the pump heads through which the actual feed solution flows, and the space between the two heads is filled with a buffer solution. Radiation-resistant EPDM diaphragms are incorporated into the pump head of the latter. **Figure 1** shows the exterior of the fabricated double diaphragm pump and the interior of the pump head incorporating EPDM diaphragms.

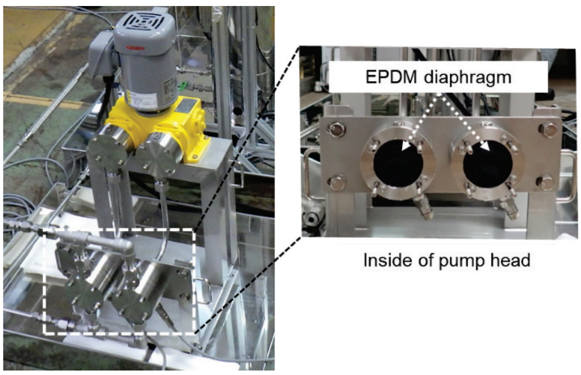


Fig. 1 Exterior view of the fabricated double diaphragm pump (left) and EPDM diaphragm incorporated in the pump head (right)

The irradiation tests on that pump were also conducted at the same facility. The pumps were gamma irradiated with water circulating. Dose rates were measured with an alanine dosimeter. Dose rates for several locations on the pump were measured and the dose rate to the diaphragm material was evaluated to be about 2.4 kGy/h. Since the pump was irradiated for 464.6 hours, the total absorbed dose was calculated to be approximately 1.1 MGy. Note that this dose rate was measured outside the stainless-steel pump head covering the diaphragm material, so the actual absorbed dose of the EPDM material inside the pump head is considered to be much lower. In this study, however, the absorbed dose is reported as approximately 1.1 MGy. Dynamic viscoelasticity measurements were performed on the diaphragm materials before and after irradiation, and the crosslink density was calculated in the same manner.

III. Results and Discussion

In an environment with little oxygen in the nitric acid solution as in the present study, gamma irradiation is said to cause both cross-linking and disintegration reactions simultaneously in the polymer structure, with one of the reactions occurring preferentially.[11)] Estimated total dose of four dumbbell-shaped rubber samples (Sample 2, 3, 4 and 5) irradiated are shown in **Table 1**. Total dose was estimated by multiplying the dose rate calculated from the alanine dosimeter measurement with the irradiation time. **Figures 2** and **3** show the results of elongation at break and strength at break obtained from tensile tests. Error bars show the data variability to the mean as a standard deviation. Both elongation at break and strength at break showed a decreasing trend with increasing dose.

Table 1 Estimated total dose of each rubber samples

Sample	1	2	3	4	5
Estimated Total Dose (MGy)	0 (raw material)	0.54	1.2	2.3	3.3

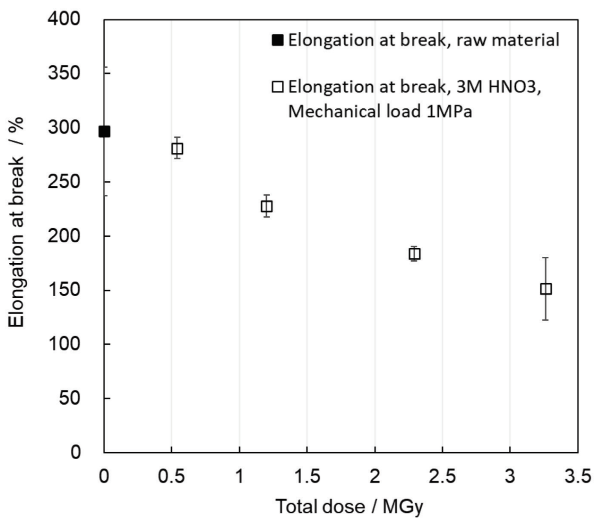
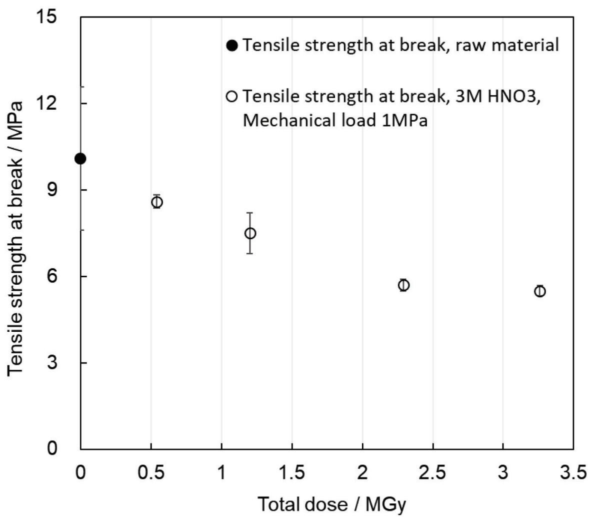


Fig. 2 Elongation at break resulting from variations in absorption dose of gamma rays



Fi g. 3 Tensile strength at break resulting from variations in absorption dose of gamma rays

On the other hand, the elongation at break was more than 100% even after irradiation of about 3 MGy, as indicated by the results of Sample 5, indicating that the viscoelasticity of the rubber is maintained to a certain degree. In terms of tensile strength at break, the decrease in strength became slower above about 2 MGy as indicated by the results of Sample 4 and 5, which suggests radiation-induced degradation progresses more slowly under these conditions above 2 MGy. **Figure 4** shows the cross-link density calculated from the results of dynamic mechanical analysis. Similar to strength at break and elongation at break, the cross-link density also showed a decreasing trend with increasing total dose. This is considered to be due to the priority progression of the scission of the molecular chains of the rubber samples, leading to a

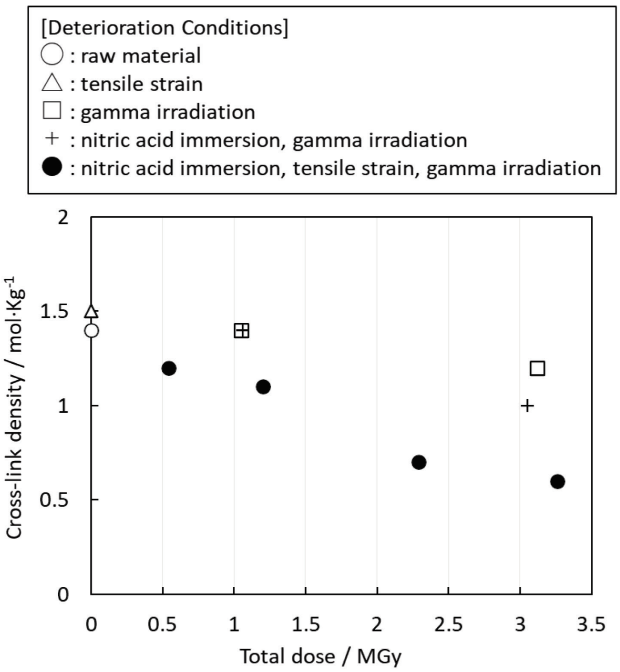


Fig. 4 Cross-link density determined from Dynamic Mechanical Analysis

decrease in molecular weight. The cross-link density results for the degradation conditions of nitric acid immersion and gamma irradiation, gamma irradiation only, and tensile load only showed that the degradation progressed more easily when the three degradation conditions of nitric acid immersion, gamma irradiation, and tensile load were combined.

No failure of the pump itself due to gamma radiation or any damage to the diaphragm material that would have caused the pump to shut down occurred. **Figure 5** shows the diaphragm material before and after irradiation of a double diaphragm pump incorporating EPDM, a rubber of the same type and with the same characteristics as the dumbbell-shaped rubber sample used in the irradiation test. The difference between the diaphragm and the rubber sample is the shape and the thickness of the rubber. The diaphragm pump works by deformation of the diaphragm material due to the reciprocating motion of the pump shaft, which causes the solution to flow. Therefore, although the diaphragm material changed shape after operation, no deterioration of the material itself was visually observed. The crosslink density calculated by dynamic viscoelasticity measurement of the raw diaphragm material was 1.5 mol/Kg. Then, the value after the irradiation test was 1.0 mol/Kg. These values are close to the result of the raw rubber sample and the rubber sample after irradiation of about 1 MGy under three degradation conditions. Both crosslink density was 1.4 mol/Kg and 1.1 mol/Kg. This suggests that in this system, the degradation of the diaphragm material in the irradiation test on the diaphragm pump can be predicted by the degradation test on the rubber samples. As previously mentioned, if the dose to the pump was less accurate, the degradation would be more progressed than the result in the dumbbell-shaped rubber sample. Furthermore, the irradiation test on the pump in this case did not expose the pump to nitric acid. This may be because the dumbbell-shaped rubber sample does not reflect the stress caused by the reciprocating motion, and further study is needed to improve the prediction accuracy.

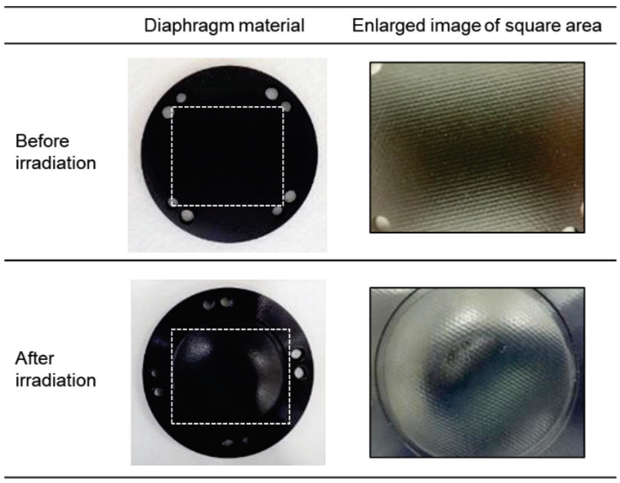


Fig. 5 Diaphragm before and after irradiation

IV. Conclusion

In this study, the degradation behavior of EPDM rubber to be incorporated into the diaphragm pump on the minor actinide recovery system was quantitatively evaluated. When the integrated dose was varied from about 0.5 to 3.0 MGy, the mechanical properties of the rubber which immersed nitric acid solution showed a decreasing trend, which was considered to be due to the priority progression of the scission of the molecular chains of the rubber, leading to a decrease in molecular weight. The degradation behavior of the same kind of rubber incorporated in the pump was similar to that of the rubber samples with the same total dose. This result suggests that the irradiation test with the rubber samples can simulate the degradation of actual pumps. In the future, we plan to conduct further irradiation tests on pumps with higher integrated doses and with circulating nitric acid solutions to evaluate applicability of the EPDM rubber to a diaphragm pump on minor actinide recovery system.

Acknowledgment

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