Proceedings of the 15th International Symposium on the
Packaging and Transportation of Radioactive Materials
PATRAM 2007
October 21-26, 2007, Miami, Florida, USA

OPTIMIZATION OF FABRICATION CONDITION OF METAL CASK NEUTRON SHIELDING PART WHICH APPLIED SIMULATION OF CURING BEHAVIOR OF EPOXY RESIN

Naoki Kumagai
Power & Industrial Systems R & D Laboratory,
Hitachi, Ltd.

Mamoru Kamoshida
Hitachi Works,
Hitachi-GE Nuclear Energy Ltd.

Koji Fujimura
Power & Industrial Systems
R & D Laboratory, Hitachi, Ltd.

Takeshi Hiranuma
Hitachi Works, Hitachi-GE
Nuclear Energy Ltd.

Masashi Shimizu
Hitachi Works, Hitachi-GE
Nuclear Energy Ltd.

ABSTRACT

A new neutron shielding resin was developed for a dual-purpose metal cask. The resin is composed of a cycloaliphatic epoxy, anhydrous acid, catalyst, aluminum hydroxide, and boron tetracarbide. Because the curing reaction of the resin was moderate at room temperature, a large amount of resin was treated at one time and the frequency of mixing of the components and pouring the resin into the cask was reduced. The feasibility of a fabrication process for treating a large volume of resin was investigated using a chemical reaction simulation and mock-up test. The results of the mock-up test were that no significant voids or cracks were found in the resin, and uniform elemental composition was found. A simulation method we created was effective in predicting the curing behavior of our resin and is suitable for optimizing the fabrication conditions of the resin in the metal cask.

INTRODUCTION

A dual-purpose metal cask was developed for transporting and storing spent nuclear fuel[1-2]. One of the most important safety functions of the dual-purpose metal cask is shielding gamma rays and neutrons emitted from spent fuel. Inner and outer shells made of carbon steel are used for gamma rays, while a polymer based resin is used for neutrons because it contains many hydrogen atoms.

We developed a new resin for enhancing the quality assurance of the metal cask by using materials whose composition and properties are well understood. The composition of the resin was summarized in a previous paper[3]. In this paper, we describe the representative properties such as long-term durability and the fabrication process of our resin.

The resin is prepared by mixing liquid epoxy, liquid hardening reagents, fire retardant, and neutron absorbing material. The mixture is poured into the neutron shielding part of the metal cask, and it is hardened by the chemical reaction of epoxy and hardening reagents. The fabrication conditions need to be optimized by considering the properties of the chemical reaction of epoxy and hardening reagents. A chemical reaction simulation method was developed

to optimize the fabrication conditions. The simulation and mock-up tests were used to determine the validity of a fabrication method for our resin.

OUTLINE OF THE DEVELOPED RESIN

<u>Composition of the resin</u>
The base polymer of our resin was composed of a cycloaliphatic epoxy hardened with anhydrous acid. A catalytic reagent was added to the system to increase the curing reaction rate of epoxy and anhydrous acid at room temperature. Aluminum hydroxide and boron tetracarbide were added to the base polymer as fire retardant and neutron absorbing material, respectively.
The basic specifications of the resin are summarized in Table 1. We expected a high shielding ability because the resin contains a high concentration of hydrogen and boron.

Table 1. Specifications of our resin

Item	Specification
Base resin	Epoxy
Fire retardant	Aluminum hydroxide
Neutron absorbing material	Boron tetracarbide
Hydrogen content	$\geqq 0.086$ g-H/cm^3
Boron content	$\geqq 0.0191$ g-B$_4$C/cm^3

<u>Degradation behavior</u>
The thermal degradation behavior of the resin was investigated in a thermal degradation test. The resin specimen (2 cm $\phi \times 7$ cmH) was heated in an electric furnace, and the weight loss of the specimen was determined. The parameters of the thermal degradation test were temperature, heating time, and degradation circumstances. The temperature was 110, 130, 150, 160, and 170°C. Two circumstances were investigated for each temperature and each heating time. One was an open system in which the bare resin was heated directly in the furnace. The other was a closed system in which the resin was enclosed in a vessel equipped with a check valve. The degradation product gas from the resin was released from the vessel, while oxygen intake from the air was suppressed in the closed system. The maximum heating time was 15000 hours. Six specimens were examined for each experimental condition.
The weight loss was ascribed to two reactions, namely thermal oxidation of the polymer and dehydration of aluminum hydroxide. In the open system, the oxidation and dehydration occurred freely. However, the oxidation in the closed system was suppressed after the oxygen in the vessel was consumed. The closed system simulated the actual circumstances in the metal cask.
Figure 1 indicates weight loss behavior of the resin at various temperatures. For both the open and closed systems, the resin weight increased at low temperatures because the resin polymer was coupled with oxygen. At low temperatures, oxidation products of the resin dissipated slowly, and the resin retained the increased weight. Because the dissipation rate of the degradation products increased temperature, the weight of the resin decreased with time at high temperatures. The weight loss of the resin in the closed system was smaller than that in the open system because oxidation of the polymer was suppressed.
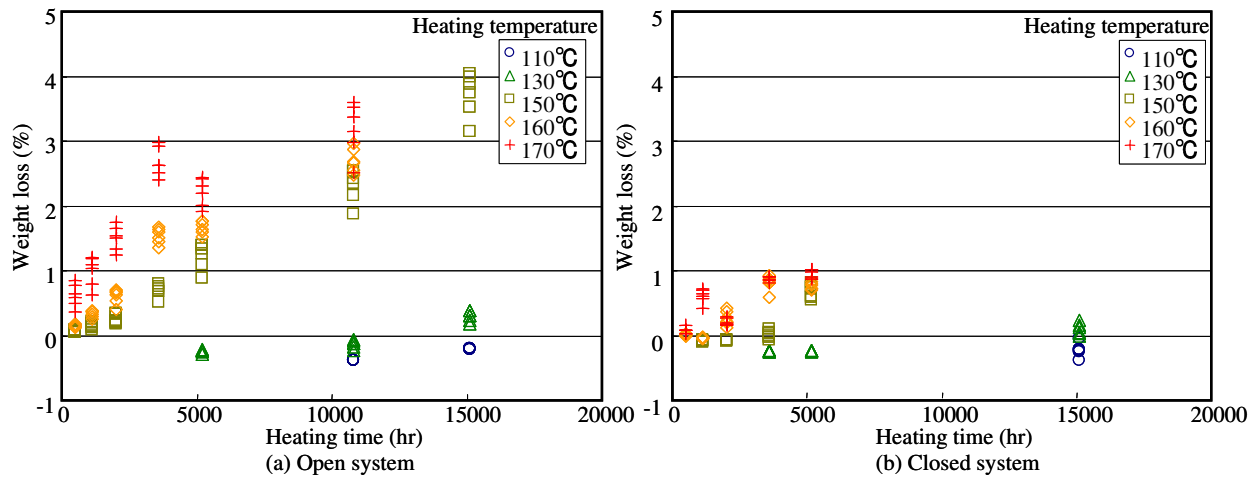
Figure 1. Thermal degradation behavior of our resin

The dependence of weight loss on time is expressed by the following empirical formula, which is the same as the one used with conventional resin[4].

$$\Delta w = a \cdot T \cdot (C + \ln t) + b \qquad \text{Eq. 1}$$

T: temperature (K), t: heating time (hr)
a, b, C: constants specific for the resin

Detail numerical values of a, b and C are indicated in Table 2.

Table 2. Numerical values of formula of Eq. 1

Circumstance	a	b	C
Open	2.01×10^{-3}	-25.5	23.0
Closed	0.83×10^{-3}	-11.1	24.2

The weight loss of the resin is also expressed by another formula, indicated below.

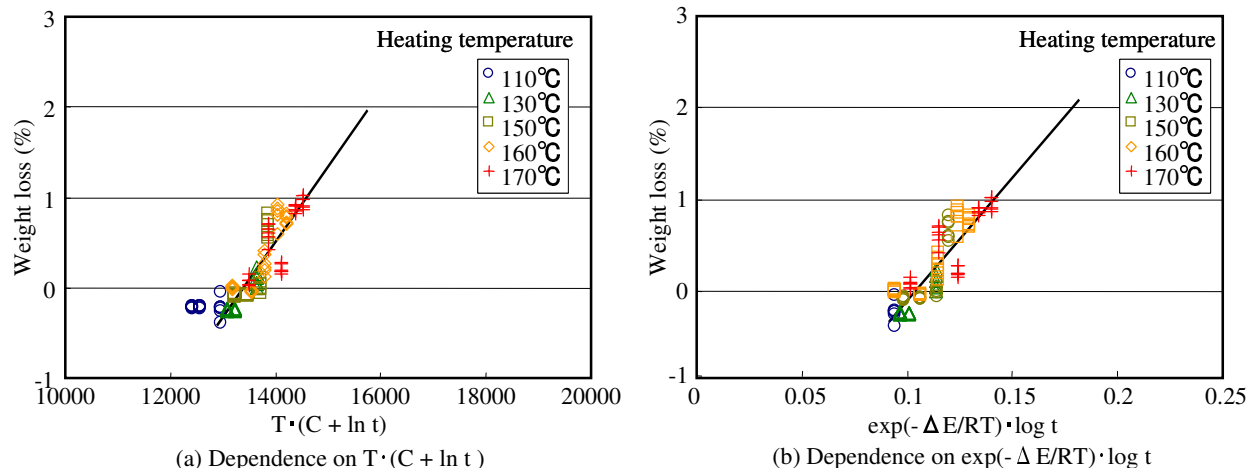$$\Delta w = C_1 \cdot \exp(-\Delta E/RT) \cdot \log t + C_2 \qquad \text{Eq. 2}$$

T: temperature (K), t: heating time (hr)
C_1, C_2, $\Delta E/R$: constants specific for the resin

Table 3. Numerical values of formula of Eq. 2

Circumstance	C_1	$-\Delta E/R$	C_2
Open	85.9	-1.62×10^3	-5.7
Closed	26.7	-1.45×10^3	-2.8

As shown in Fig. 2, the weight loss of the developed resin had a linear dependence on $T \cdot (C + \ln t)$ and $\exp(-\Delta E/RT) \cdot \log t$.

3

(a) Dependence on T·(C + ln t)　　　　(b) Dependence on exp(- Δ E/RT)·log t

Figure 2. Dependence of weight loss of our resin on heating time and temperature

The weight loss of our resin under desired conditions was calculated using the presented empirical formulas. In the closed system, the weight loss of the resin heated at 130°C for 50 years is about 1-2%. Thermo-gravimetric and differential thermal-analysis revealed that no significant chemical change or weight loss occurred in the developed resin even at 200°C. Thus, the developed resin was found to have high thermal durability, and it can be used at 150°C normally.

The decomposition products of our resin were determined using gas analysis. The main products were water vapor and carbon dioxide. No liquid water droplets were observed in the vessel used for the thermal degradation test. The oxygen supply in the resin part was suppressed in the metal cask. Thus, corrosion of metal surrounding the resin of the metal cask was limited.

Resin degradation due to irradiation was investigated using a ^{60}Co gamma-ray source. About 56 kGy of gamma rays were irradiated onto the resin heated at 140°C. The irradiation was found to have only a little influence on the heat degradation behavior.

FABRICATION PROCESS OF THE DEVELOPED RESIN

Fabrication process

The curing reaction of our resin was moderate. The liquid resin maintained a low enough viscosity for smooth pouring for more than 10 hours at room temperature. The curing reaction heat of epoxy and hardening reagents was small. Thus, a large amount of the resin, for example 500–2000 kg of resin, was treated at one time.

Increasing the amount of the resin treated at one time can reduce the frequency needed for mixing the components and pouring the resin into the shielding part of the metal cask. It was necessary that no significant voids or cracks occur in the resin when a large amount of it was cured at the same time. In general, no significant voids and cracks were observed when the curing reaction of the resin proceeded homogeneously. A chemical reaction simulation method was developed to optimize the fabrication conditions. The curing behavior of our resin was investigated using the simulation.

Simulation method of the curing reaction of the resin

The molar ratio of epoxy and anhydrous acid was unified in our resin system. The reaction of epoxy and anhydrous acid was assumed to be first order. The fraction of epoxy is expressed by the following formula.

$$C(t) = \exp(-k(T) \cdot t) \qquad\qquad \text{Eq. 3}$$

        t: reaction time(sec), T: reaction temperature(K)

        C(t): the quantity ratio of epoxy of unreaction at t and initial

        k(T): reaction rate constant at T

The reaction heat generation rate, q, was assumed to be proportional to the reaction rate.

$$q = Q \, dC(t)/dt = Q \, k(T)C(t) \qquad\qquad \text{Eq. 4}$$

        q(J/s/mol): reaction heat generation rate,

        Q: reaction heat (J/mol)

By heat conduction analysis, we calculated spatial distributions of temperature and the reacted fraction of epoxy in the resin from the beginning of the reaction to the completion. ANSYS ver. 9 was used for the calculation. Heat generation of each mesh of the resin was calculated applying Eq. 4 at every time step (1200 sec). The resin mixture had fluidity at the beginning of the reaction, and the fluidity decreased with the curing reaction. But the resin mixture was treated as a solid from the beginning of the reaction because its initial viscosity was much higher than that of an ordinary liquid.

The reaction rate constant k(T) was assumed to obey Arrhenius' law.

$$k(T) = A \cdot \exp(-\Delta Ec/RT) \qquad\qquad \text{Eq. 5}$$

        A: frequency factor

        ΔEc: activation energy of the curing reaction (J/mol)

        R: gas constant (J/(K$\cdot$mol))

The basic data for the simulation was obtained as follows. The activation energy of the curing reaction was determined from the Arrhenius plot of the viscosity increase rate of the resin. The frequency factor, A, and reaction heat, Q, were determined using benchmark tests in which the dependence on time of the temperature distribution in the specimen was measured. Thermal conductivity and specific heat were analyzed for the developed resin and used in the heat conduction analysis.

Results of simulation of curing reaction of resin

We simulated the temperature at the desired point and time of the resin of various shapes using the simulation method. Table 4 shows the highest temperature of the resin in the mock-up specimen depicted in Fig. 4 during the curing reaction. Even when a large quantity of resin was cured at one time, the temperature was homogeneous, which meant that the curing reaction of the resin proceeded homogeneously. Next, we carried out a mock-up test to determine the validity of the fabrication process.

Table 4 Simulation of maximum temperature of curing resin

Position	Maximum temperature (°C)
Surface of the center section	27
Center of the center section	28
Bottom of the center section	31
Room temperature	25

FABRICATION MOCK-UP TEST

A fabrication mock-up test was conducted using the full-scale specimen depicted in Fig. 4. The specimen simulated the side shielding part of the metal cask. To prevent the cracking caused by

volume shrinkage of the resin with the curing reaction, we spread the mold lubricant inside the specimen prior to molding the resin. About 1 ton of resin was molded into the mock-up specimen and cured at about 25-30°C.
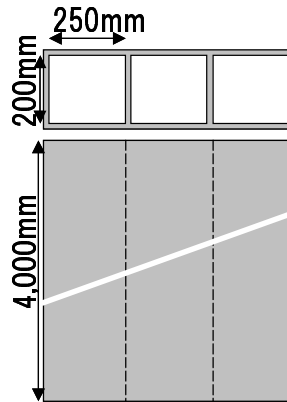
Figure 4. Specimen of mock-up test

The temperature of the resin was measured in the center section. The difference in resin temperature and room temperature was at most 5°C. This agreed well with the results of the simulation. The simulation method was effective in predicting the curing behavior of the resin. The curing reaction was found to proceed homogeneously. The specimen was disassembled after the curing reaction was completed, and the resin was analyzed. The concentrations of aluminum and boron were homogenous, as shown in Table 4. Significant cracks or voids were not found in the cured resin.

The curing behavior of our resin in the actual metal cask was investigated using the simulation method. The temperature of the resin during the curing reaction was homogeneous. Thus, our resin is suitable for use in a metal cask.

Table 4. Concentration of main elements

Sampling point	Concentration (g/cm^3)		
	H	**Al**	**B$_4$C**
Top	0.103	0.786	0.0226
Middle	0.103	0.786	0.0229
Bottom	0.103	0.786	0.0224

CONCLUSIONS

A new type of neutron shielding resin was developed for a dual-purpose metal cask.
The resin was found to have long-term stability in a thermal degradation test. The estimated weight loss of the resin during storage was about 1–2%.
A chemical reaction simulation and mock-up tests were used to determine the validity of a fabrication method for our resin. A large volume of resin can be treated at one time. The results of the mock-up test showed no significant voids or cracks in the resin, and the elemental composition was uniform. Our simulation method was found to be effective for predicting the curing behavior of the resin and is suitable for optimizing the fabrication conditions of the resin in the metal cask.

REFERENCES

1) N. Kumagai, et al., "Full-Scale Prototyping of the Hitachi Dual-Purpose Metal Cask and Verification of Its Heat Transfer Characteristics", 14th International Symposium on the Packaging and Transportation of Radioactive Materials, PATRAM 2004, Berlin, Germany, September 20–24, 2004

2) N. Kumagai et al., "Development of High Performance Metal Casks for Transportation and Storage of Spent Nuclear Fuels", Global 2005, Tsukuba, Japan, October 9–13, 2005

3) M. Kamoshida, et al., "DEVELOPMENT OF HEAT-RESISTANT NEUTRON SHIELDING RESIN FOR HIGH PAYLOAD METAL CASK", 15th International Conference on Nuclear Engineering, Nagoya, Japan, April 22–26, 2006

4) N. Yamada, et al., "Thermal Behavior of Neutron Shielding Material, NS-4-FR, under Long Term Storage Conditions", 14th International Symposium on the Packaging and Transportation of Radioactive Materials, PATRAM 2004, Berlin, Germany, September 20–24, 2004