Characterization of Damaged Epoxy Resins on Steel Liners Originated in Operation of Nuclear Power Plant

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ABSTRACT

The property changes of epoxy coatings on steel plate in atomic reactor container have been analyzed in terms of thermal properties in the case of simple irradiation and designed accident conditions (DBA: design basis accident). Two kinds of the epoxy coating systems were selected in this work. The specimens were irradiated by two different dose rates, i.e., 1×10^6 and 5×10^5 rad. The total dosage was fixed at 2×10^8 rad. Two kinds of DBA conditions were applied in the specimens. Their effects have been surveyed in the context of the changes of glass transition temperature (T_g), the initial decomposition temperatures (T_{IDT}), and the maximum decomposed temperature (T_{max}). As a result, the different epoxy systems, irradiation rates, and DBA test conditions showed a significant change on the thermal properties of the specimens.

INTRODUCTION

In real nuclear applications, epoxy resins are largely coated on the steel liner plate in reactor container building. This epoxy resin coated on the liner should ensure their role of covering of the surface during a predetermined operating period. And it should also sustain at the emergency state, including designed accident conditions. Until now, there are very few results to attempt to analyze the damaged state of the epoxy resin at real conditions [1-5]. Our work is focused on the developing of an analytic tool to treat the damaged state of the epoxy resin coated on carbon steel A36.

The damaged states of the epoxy coatings are very difficult to define. Generally the appearance of the crack and the blistering have been mentioned as a criteria of the acceptance [6-8]. In a reactor building, the operator usually observes the color change, which darkens the yellowness during the operation period, etc. The observation by eye is frequently very erroneous and one cannot find the proper tool to analyze or quantify the effect of the applied conditions. Because of that there are little advance on the control and the acceptance criteria of the candidate materials in atomic reactor building and the surroundings.

The required sample quantity for thermal analyses is very small and the accuracy in thermal analysis is remarkable. The changed state of the epoxy resin by various treatments has been checked by the thermal analyses. Two different types of the epoxy coating systems, irradiation rates, and DBA (Design Basis LOCA) test conditions were chosen to understanding our work.

EXPERIMNTAL

Materials and Sample Preparation

The nearly white blast-cleaned steel liner plate by using steel ball has been coated by two times of IZ197 and then ET562 (case A), ET562/ET562 (case B) epoxy resin from Korea Chemical Co. The coating procedure has been done by air spraying method. The epoxy resin is directly applied to the surface without any primer. There was 5 day-drying time between the 1st and 2nd application of the coating. And the final drying time was 14 days. The final coating thickness was about 6~9 mils. The specimen size was 2"×4"×1/8".

Measurements

Irradiation test

To study the effect of irradiation on specimen, the irradiation exposure was executed according to the ANSI N512-74. And, to investigate the effect of dose rate, two dose rates were irradiated on the half of the specimens by a gamma source, i.e., 5×10^5 and 1×10^6 rad/h, respectively. The total integrated dosages was fixed at 2×10^8 rad/h and its value consists of the gamma contribution due to a Design Basis LOCA and the dose contribution due to 40 years of normal operation.

DBA test

The DBA test was executed according to the ANSI- N101.2. The temperature-pressure-versus-time curve for the containment atmosphere following DBA-LOCA shall meet the requirement indicated on Figure 1 (case A) and 2 (case B), respectively.

DSC and TGA analysis

To study the effect of irradiation and DBA experiments on glass transition temperature (T_g) and thermal properties of the specimen, DSC and TGA were executed at the heating rate of 10℃/min in a nitrogen environment, respectively.

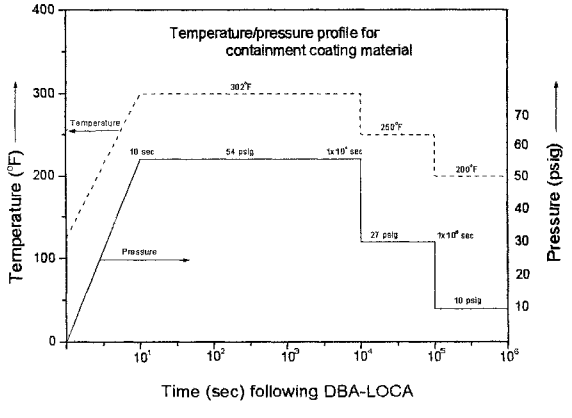

Fig. 1. DBA condition of case A.

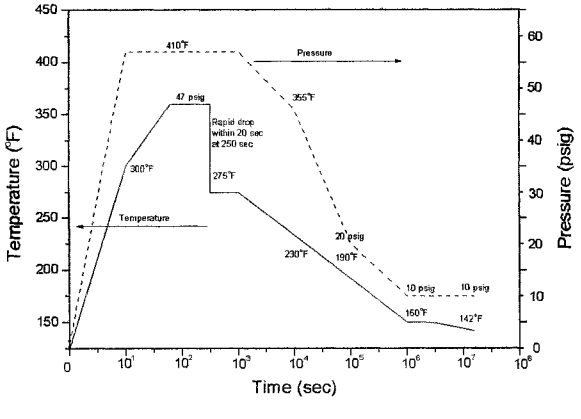

Fig. 2. DBA condition of case B.

RESULTS AND DISCUSSION

It is generally accepted that reliable degradation temperature and kinetic parameters, such as the initial decomposed temperature (IDT), the temperature of maximum rate of weight loss (T_{max}), the integral procedural decomposition temperature (IPDT) and the activation energy for decomposition (E_t), can be used to assess material's lifetime [9].

Figure 3 shows the schematic diagram of the TGA for determining the IPDT of a major factor of thermal stability of the specimen based on the C. D. Doyle's proposition [9], and then the IPDT is calculated as follows;

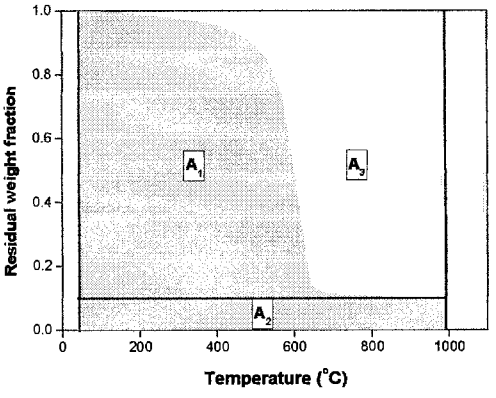

Fig. 3. TGA thermogram area of A_1, A_2, and A_3 for determining A^* and K^*.

$$IPDT\ (^{\circ}C) = A^* \cdot K^* (T_f - T_i) + T_i \quad (1)$$

where, A^* is the area ratio of total experimental curve divided by total TGA thermogram $[(A_1 + A_2)/(A_1 + A_2 + A_3)]$, K^* the coefficient of A^* $[(A_1 + A_2)/A_1]$, T_i the initial experimental temperature (40 ℃, in this work), and T_f the final experimental temperature (840 ℃).

Also, the connected thermal degradation kinetics is possible to measure the energy of activation for decomposition, E_t, of the specimens. The E_t of cured specimens is calculated from TGA curves by the integral method of Horowitz and Metzger [10] according to the following equation;

$$ln[ln(1-\alpha)^{-1}] = E_t\theta/RT^2_{max} \quad (2)$$

where, α is the decomposed fraction, E_t the activation energy for decomposition, T_{max} the temperature at maximum rate of weight loss, $\theta = T - T_{max}$, and R the gas constant.

Case A

Figure 4 and 5 show the TGA thermograms of the different dose rate, i.e., 5×10^5 and 1×10^6 rad/h irradiated specimens in a nitrogen atmosphere, respectively. From the Figure 4and 5, all thermal stability parameters are calculated and listed in Table 1. These results indicate that the thermal stability parameters of specimen, including IDT, $A^* \cdot K^*$, and IPDT increase with treatment of DBA test compared to the specimen without treatment, due to have high glass transition temperature (T_g) of DBA specimen, as shown in Table 1. However, the irradiated specimen decreases in thermal stabilities. This result is probably due to the fact that the relaxation of the epoxy resins by irradiation is very significant and it makes in the remarkable decrease of T_g, whereas the DBA treatment induces high thermal energy application resulting in the increasing of T_g, owing to the influence of post-curing of the epoxy resins. And, the higher dose rate also accelerates the relaxation of the epoxy resins by irradiation resulting in the decreasing of T_g, however, the DBA specimen is a little increased in T_g according to the higher dose rate due to the recovery of the relaxation. Consequently, the higher dose rate seems to partly make an influence on the thermal energy of the specimen.

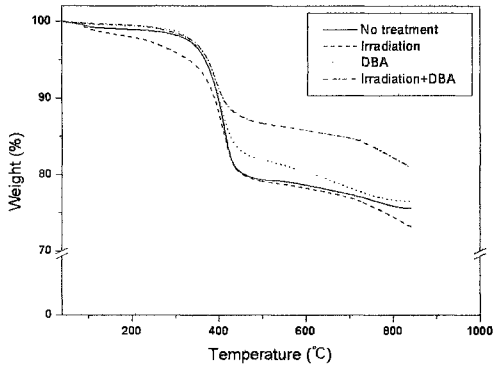

Fig. 4. TGA thermograms of 5×10^5 rad/h dose rate irradiated specimens.

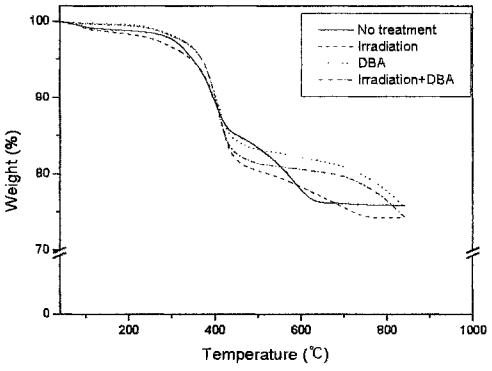

Fig. 5. TGA thermograms of 1×10^6 rad/h dose rate irradiated specimens.

Also, to evaluate the effect of irradiation and DBA treatment on specimen, the activation energy for decomposition is given by the straight line corresponding to the $ln[ln(1-\alpha)^{-1}]$ *vs.* θ, according to the equation (2). As a result, it is observed that the E_t increases with treatment of DBA test, as seen in Table 1, resulting in presenting the similar behaviors with those of IPDT.

Table 1. Thermal analysis of case A

Specimen	Dose rate (5×10^5 rad/h)					Dose rate (1×10^6 rad/h)				
	IDT (℃)	T_{max} (℃)	$A^*\cdot K^*$	IPDT (℃)	E_t (kJ/mol)	IDT (℃)	T_{max} (℃)	$A^*\cdot K^*$	IPDT (℃)	E_t (kJ/mol)
NO[1]	390	414	4.95	3996	78	390	414	4.95	3996	78
IRA[2]	362	408	4.62	3736	71	297	408	4.53	3664	66
DBA[3]	394	412	4.99	4032	94	352	400	4.84	3912	87
ALL[4]	395	390	4.65	3760	86	333	394	4.57	3696	81

[1]NO: no treatment, [2]IRA: irradiation treatment, [3]DBA: DBA treatment, [4]ALL:irradiation and DBA treatment

Case B

To study the effect of DBA experimental conditions on epoxy resins coating system, we also execute the thermal analysis of different dose rate irradiated specimens. Figure 6 and 7 show the TGA thermograms of the same dose rate above. The T_g and thermal stability parameters of case B are arrayed in Table 2. As a result, the IDT, $A^*\cdot K^*$, IPDT, and E_t exhibit the same tendency, as studied in case A. However, the relaxation of the epoxy resins by irradiation is much smaller than that of case A. Therefore, the T_g of DBA specimen is little decreased by over application of longer and higher thermal energy treatment. This is probably due to the effect of lower pressure over all experimental steps in spite of higher temperature and longer tests time than case A. However, the dose rate has a little influence on T_g. Because the higher dose rate reveals a strong change of the network system of the cured epoxy coating resins.

Consequently, the thermal properties of specimens are largely affected on irradiation rate per hour and thermal application by DBA test conditions. This is probably due to the network rearrangement and scission of the epoxy resin during the DBA and irradiation treatment.

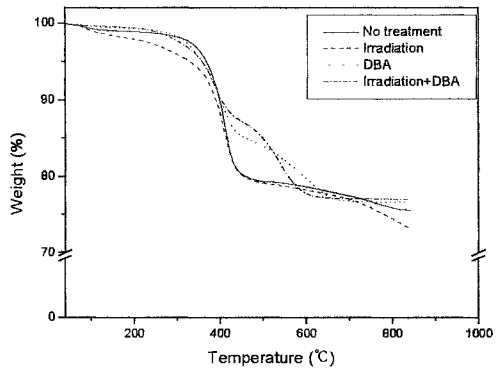

Fig. 6. TGA thermograms of 5×10^5 rad/h dose rate irradiated specimens.

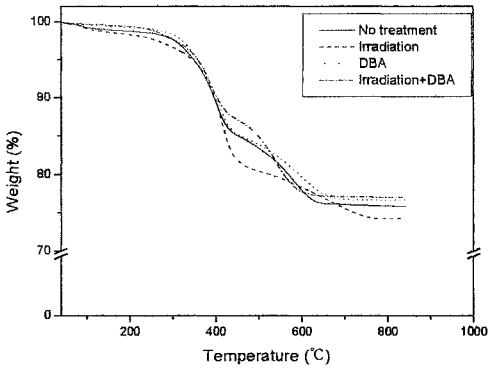

Fig. 7. TGA thermograms of 1×10^6 rad/h dose rate irradiated specimens.

Table 2. Thermal analysis of case B

Specimen	Dose rate (5×10^5 rad/h)					Dose rate (1×10^6 rad/h)				
	IDT (℃)	T_{max} (℃)	$A^*\cdot K^*$	IPDT (℃)	E_t (kJ/mol)	IDT (℃)	T_{max} (℃)	$A^*\cdot K^*$	IPDT (℃)	E_t (kJ/mol)
NO[1]	380	405	4.97	4016	79	380	405	4.97	4016	82
IRA[2]	354	402	4.71	3808	73	279	399	4.65	3760	70
DBA[3]	382	411	4.99	4032	95	312	392	4.85	3920	90
ALL[4]	390	407	4.84	3912	87	290	383	4.80	3880	85

[1]NO: no treatment, [2]IRA: irradiation treatment, [3]DBA: DBA treatment, [4]ALL:irradiation and DBA treatment

CONCLUSION

The irradiation induced the relaxation in cured epoxy network system resulting in the significant decrease of T_g. The DBA test gave a main role as thermal energy application in epoxy systems. This could accelerate the partly cured epoxy resin and harden the network system of epoxy resin owing to the increasing of T_g. The higher dose rate made a relaxation of epoxy resin to reduce the hardening of the network system. Therefore, we can conclude that the irradiation doses rate, and DBA test condition exhibited significant effects on thermal properties of epoxy coating system.

REFERENCES

1. Ohta, H., Byon, O., Uemura, M., and Kudo, A., "Weatherbility of flexural properties of FRP materials under steady flexural load", *J. Reinforced Plastics in Japan,* Vol. 32, 1986, 145-152.
2. Chateauminois, A., Chabert, B., Soulier, J. P., and Vincent, L., "Hydrothermal Aging Effects on Viscoelastic and Fatigue Behavior of Glass/Epoxy Composites", *Proc. Of the 8th International Conference of Composites Materials (ICCM-8),* 16-E, Honolulu, USA, July 1991.
3. Pafitis, D. G., and Hull, D., "Environmental Effects on the Progressive Crushing of Composites", *Proc. Of the 8th International Conference of Composites Materials (ICCM-8),* 16-L, Honolulu, USA, July 1991.

4. Bouadiand, H., and Sun, C. T., "Hydrothermal Effects on Structural Properties of Unidirectional Glass-Epoxy Composites", *Proc. Of seventh International Conference on Composites Materials (ICCM-7),* pp 212-217, Guangzhou, China, Nov., 1989.
5. Bulmanis, V. N., Sarzhenetskaya, T. A., and Popov, N. S., "Effect of Moisture and Low Temperature on Physical and Mechanical Characteristics of Glass-Fibre Reinforced Plastics and Organic Plastics", *Proc. of seventh International Conference on Composite Materials (ICCM-7),* pp 218-225, Guangzhou, China, Nov., 1989.
6. Albertsson, A. C., and Karlsson, S., "Environmental Interaction of Polymers-Natural Metabolites as Opposed to Degradation of Synthetic Polymers", *36th IUPAC International Symposium on Macromolecules,* pp 564, Seoul, Korea, Aug., 1996.
7. Clough, R. L., Polymer Durability, Degradation, Stabilization, and Lifetime Prediction, American Chem. Soc., Washington DC, 1996.
8. Prian, L., Pollard, R., Shan, R., Mastropietro, C. W., Gently, T. R. Bank, L. C. and Barkatt, A., "Use of thermogravimetric analysis of develop accelerated test methods to investigate long-term environmental efects on fiber-reinforced plastics", pp 206-222, *High Temperature and Environmental Effects on Polymer Composites.*, 2nd Vol., ASTM STP, 1977.
9. Doyle, C. D., *Analytical Chemistry,* Vol. 33, 1961, 77.
10. Horowitz, H. H., and Metzger, G., *Analytical Chemistry,* Vol. 35, 1963, 1464.