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Measurement of Activation energy for Nuclear power plant cable using TGA and DMA

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1. Introduction

The extension life of in service nuclear power plant is one of the most important concerns in the world nuclear industry. The components of nuclear power plant have been considered to be replaced during the design life of nuclear power plant. Qualification of the polymer which should be used as main cable materials of nuclear system is very important for safety of nuclear power plant. Commonly, Aging test of polymer is to measure activation energy from UTM (Universal Test Machine) after inserting a lot of specimens into electrical furnace. But, this method require lots of labor and time. So we will perform qualification of polymer by inducing activation energy using TGA(Thermo-Gravimetric Analyzer) and DMA(Dynamic Mechanical Analyzer) equipment in KIMM.

2. Method

2.1 Arrhenius Equation

Arrhenius equation is a simple, but remarkably accurate, formula for the temperature dependence of a chemical reaction rate. Also, it can take activation energy from the reaction rate by time and temperature. Arrhenius equation is as follows.

$$k = A\exp(-\frac{E_a}{RT})$$

It convert in terms of aging temperature and time.

$$\ln\frac{t_o}{t_a} = -\frac{E_a}{R}(\frac{1}{T_o} - \frac{1}{T_a})$$

Arrhenius equation is used to calculate thermal endurance and estimate the lifetime of the material through accelerated thermal aging.

2.2 TGA theory

TGA provides method for determining weight of the material as a function of temperature or time by changing heating rates of material.

The Arrhenius activation energy is then determined from a plot of the logarithm of heating rate versus the inverse of absolute temperature at constant conversion level, using Ozawa method or ASTM Kinetics method. Ozawa method is as follows.

$$E_a \approx -4.35\frac{d\log\beta}{dT^{-1}}$$

ASTM Kinetics method used in this case is as follows.

$$E_a = -\left(\frac{R}{b}\right) \times \Delta(\log\beta) / \Delta\left(\frac{1}{T}\right)$$

2.3 DMA theory

DMA provides a method for determining elastic and loss modulus of material as a function of temperature, frequency or time, or both. A plot of storage elastic modulus or viscous modulus (loss elastic modulus) versus temperature gives a graphical representation of elasticity and damping as a function of temperature or frequency. The mechanical behaviors of polymeric materials have been well established by WLF(Williams-Landel-Ferry) equation. Shift factor is of importance in studying the physical and mechanical properties of viscoelastic materials. Time-based shift factor was measured using multi frequency sweep analysis (MFSA). The amount of shifting along the horizontal (x) axis in a typical time-temperature superposition (TTS) is generally described using both the WLF equation and Arrhenius equation.

WLF equation is

$$\log\alpha_T = \frac{-C_1(T - T_o)}{C_2 + (T - T_o)}$$

and Arrhenius equation(convert as frequency) is

$$\ln\alpha_T = \ln\frac{f}{f_o} = \ln\frac{t_o}{t} = \frac{E_a}{R}(\frac{1}{T} - \frac{1}{T_o})$$

Activation energy can be taken plot of $\log\alpha_T$ versus $(1/T-1/T_o)$.

3. Experiment

3.1 Materials

There are various Class 1E cables for nuclear power plants. We choose as specimen EPR (Ethylene Propylene Rubber), CR (Chloroprene Rubber) and CSP (Chloro-Sulfonated Polyethylene Rubber) placed at the part of cable sheath. Specification of test specimens are given in Table 1.

	Model	Performance	Manufacture Year
EPR	0210LBN6	600V, 10AWG	1997
CR	0306LRN8	600V, 3/C, 6AWG	2001
CSP	718L2325	300V, 10P, 16AWG	1997

Table 1. Specification of test specimens

3.2 Thermo-gravimetric analysis

We used TGA Q500 of TA Instrument as TGA system. And performed experiment based on ASTM E 1131-98 and E1641-99. The samples were heated from room temperature(25℃) to 800℃ at heating rates of 5, 10, 15 and 20℃/min. About 20 mg of sample was used, and supplied nitrogen gas 99.99%(inert gas) by flow rate 50mL/min. Purge Time was 2 minutes. Experimental method is to measure weight changes of the material depending on various heating rates. Activation energy is measured when weight loss of 5% is reached on thermal degradation curve as shown in Figure 1.

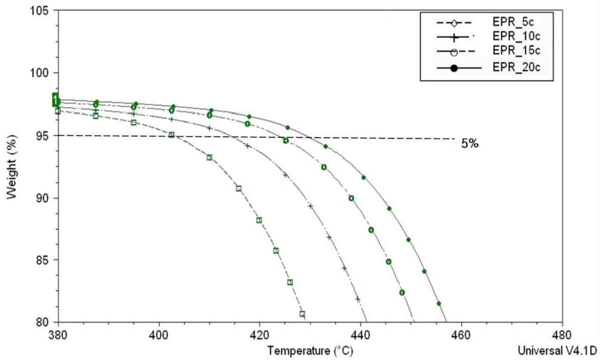

Figure 1. Thermal degradation curve of EPR

3.3 Dynamic mechanical analysis

DMA system (Pyris Diamond DMA of Perkin Elmer Instrument) was use satilized to measure activation energy based on ASTM D4065-01, E2254-03 and E1867-01. A specimen size is 1.5(t)×10(b)×50(L) mm as the standard size of ASTM D 4065-01. Experimental Temperature is room temperature(25℃) to 300℃ and frequency is 0.5~20 Hz. Experimental method to measure modulus depending on various frequency under specific temperature. Figure 2 shows that the storage elastic modulus decreases as a temperature, and increases as a frequency. To get the activation energy, these data are modified as plot of ln α_T vs. $(1/T - 1/T_o)$ for specific modulus as shown in Figure 3.

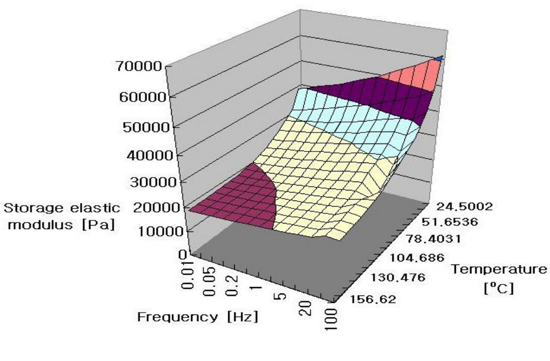

Figure 2. Modulus as a function of temperature and frequency

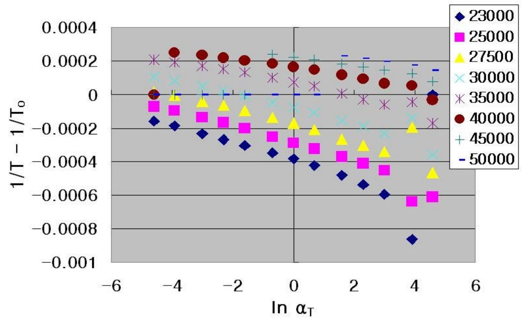

Figure 3. Plot of ln α_T vs. $(1/T - 1/T_o)$ under specific modulus

4. Results and Conclusion

Activation energy obtained from TGA and DMA is given in Table 2. and fairly closed to those of Wyle Lab. Activation energy with DMA was newly develop method are measured as well as TGA. DMA data of Wyle Lab is absent. So there is no comparison data. If it carries out the examination by thermal aging test, it takes the enormous time. But if it executes the one by the only TGA and DMA, it takes the opportunity that is able to reduce the examination time and it will be able to secure the trust on the repeat test for the many polymer materials.

[eV]

	KIMM		Wyle Lab.	
	TGA	DMA	UTM	TGA
EPR	1.30	1.27	1.23	-
CR	0.74	1.72	-	0.65
CSP	0.99	1.03	-	1.07

Table 2. Activation energy of power cable

Nomenclature

k : rate constant , A : pre-exponential factor
E_a : activation energy [eV], [J/mol] R: gas constant
t_o : normal service time T_o : normal service temperature
t_a : aging time T_a : aging temperature
α_T : shift factor [f/f$_o$] β : heating rate [^{o}C/min],
C : empirically determined constants f$_o$: reference frequency,
b : approximation derivative taken from ASTM E 1641-99 table 1.

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