Analysis of Pyrolysis Kinetic Behaviors for CR/EPR Cable via TG analyzer

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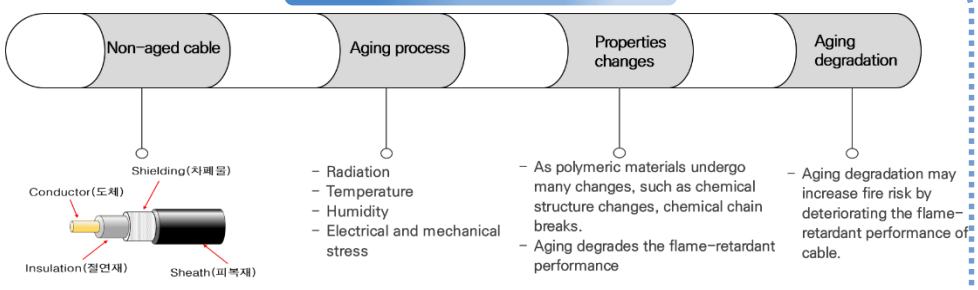
Abstract

Electrical cables are one of long life items that have not been considered for replacement during the life time of nuclear power plants. The cables are required to maintain their normal operating functions while they are exposed to harsh environmental conditions such as high temperature, humidity, and radiation. However, continuous exposure to these conditions causes the degradation of polymeric materials used in the cables. The aging of polymers affects different properties of materials at the physical, chemical, and mechanical level. Therefore, it is necessary to study on degradation aging properties of cables to accurately grasp the changes of properties for the aging cables. In this study, the pyrolysis properties of cables are investigated using thermogravimetric analyzer. In addition, pyrolysis parameters such as activation energy and pre-exponential factor are calculated by applying the kinetic models. These results will be used to determine the accurate thermal aging mechanism.

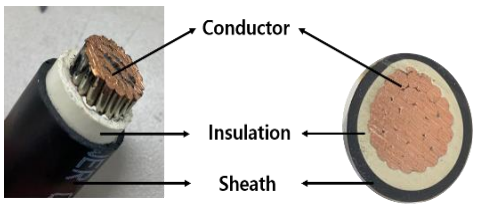
Introduction



- It is necessary to study on the aging degradation properties of cables to accurately grasp the change of properties for the aging cables.
- In this study, the pyrolysis properties of cable are investigated using thermogravimetric analysis (TGA). These results will be used to determine the accurate thermal aging mechanism.

Materials

- A non-class 1E cable used in NPPs was selected.
- The cable is used application of power supply and consist of a CR based sheath and an EPR based insulation.
- Test specimens were prepared with same weight ratio in order to consider the pyrolysis properties of polymeric sheath and insulation at the same time.



Division		Detail
Power capacity [V]		600
Material properties	Sheath	Polychloroprene rubber (CR)
	Insulation	Ethylene propylene rubber (EPR)
	Conductor	Copper

Kinetic models

- The kinetic models were used to determine the pyrolysis parameter activation energy(E_a).
- The pyrolysis parameters of non-isothermal solid phase reaction can be effectively calculated based on the conversion rate $d\alpha/dt$(Eq.1).
- Conversion(α) and rate constant(k) are given by Eqs. 2-3.
- For non-isothermal dynamics, the heating rate b=dT/dt is introduced into the equation and the conversion rate can be obtained in the Eq. 4.
- In this study, three model-free methods Ozawa-Flynn-Wall(OFW) method, Kissinger method and Kissinger-Akahira-Sunose(KAS) method were used.
- The model-free calculate the reaction E_a without modelistic assumptions which is usually done by grouping the terms such as the pre-exponential factor(A) and model into the intercept of a linear equation and using the slope of that equation to calculate the E_a.

$$\frac{d\alpha}{dt} = kf(\alpha) \quad \text{(Eq.1)}$$

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f} \quad \text{(Eq.2)} \qquad k = A\ \exp\left(\frac{-E_a}{RT}\right) \quad \text{(Eq.3)}$$

$$\frac{d\alpha}{dT} = \left(\frac{A}{\beta}\right)\exp\left(\frac{-E_a}{RT}\right)f(\alpha) \quad \text{(Eq.4)}$$

Eq. No.	Method	Expressions	Plots
(5)	OFW	$\log\beta = log\left(\frac{AE_a}{Rg(\alpha)}\right) - 2.135 - \frac{0.4567E_a}{RT}$	$\log\beta$ versus $1/T$
(6)	Kissinger	$\ln\left(\frac{\beta}{T_m^2}\right) = ln\left(\frac{AR}{E_a g(\alpha)}\right) - \frac{E_a}{RT_m}$	$\ln(\beta/T_m^2)$ versus $1/T_m$
(7)	KAS	$\ln\left(\frac{\beta}{T^2}\right) = ln\left(\frac{AR}{E_a g(\alpha)}\right) - \frac{E_a}{RT}$	$\ln(\beta/T^2)$ versus $1/T$

TG Analyzer

- TG analyzer is a useful tool to analyze the thermal decomposition and the pyrolysis of materials by using TG analysis and differential thermal analysis(DTA).
- Sample masses were approximately 10 mg (sheath 5 mg + Insulation 5 mg)
- Samples are heated from 25 °C to 600 °C in nitrogen atmosphere with a flow 100 ml/min.
- Four different heating rates of 5, 10, 15, 20 °C/min were adopted.

Results and Discussion

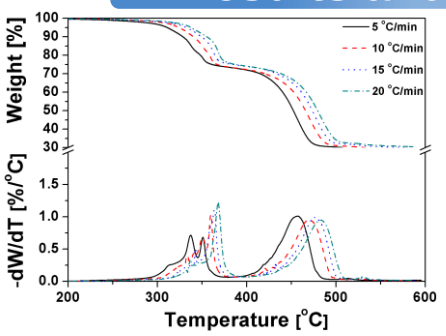


Fig. 1. TG-DTG analysis of cable samples

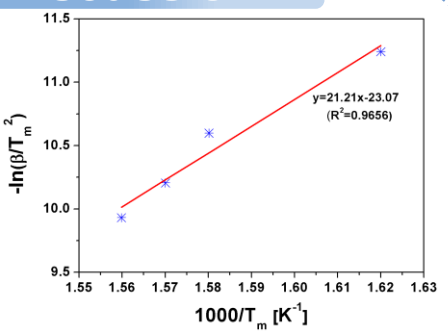


Fig. 2. Kissinger plot of cable samples

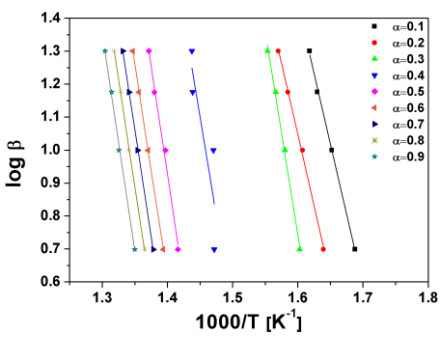


Fig. 3. OFW method plot of cable samples

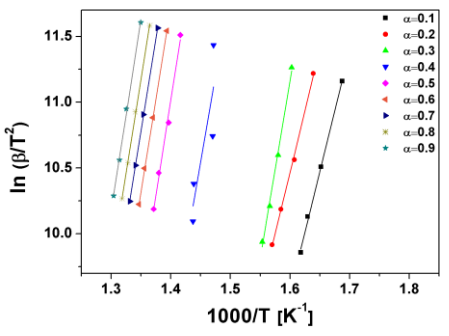


Fig. 4. KAS method plot of cable samples

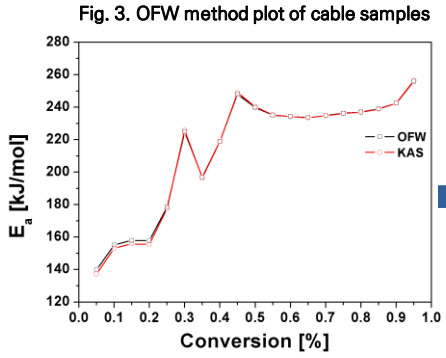


Fig. 5. Activation energies variation calculated via OFW and KAS methods

Conversion (α)	KAS [kJ/mol]	OFW [kJ/mol]
0.1	153.06	155.11
0.2	155.50	157.72
0.3	225.79	224.73
0.4	218.87	219.00
0.5	240.22	239.78
0.6	234.15	234.19
0.7	234.72	234.87
0.8	236.92	237.08
0.9	242.51	242.52
Avg.	215.75	216.11

- Initial temperature at which thermal conversion reaction begins is approximately 200 °C.
- Pyrolysis processes could be divided two stages. The first stage, from 300 °C to 390 °C, was decomposition of insulation(EPR). And then, the second stage took place in the temperature range of 400-500 °C, which was caused by the decomposition of sheath(CR).
- Plots of the three methods are shown in Figs. 2-4. The slopes of graph represent the E_a in form of "y=ax+b" and calculate the E_a.
- The Kissinger method shows a linear plot according to first decomposition peak temperature and the E_a is calculated 176.36 kJ/mol.
- The activation energies obtained from OFW and KAS methods significantly increased at α=0.3 and α=0.5 , which are polymers with a higher thermal stability participate in the reaction.
- The average activation energies calculated via the KAS and OFW methods are 215.75 kJ/mol and 216.11 kJ/mol, which is approximately 40 kJ/mol higher than that of the Kissinger method.

∴ Therefore, it is necessary to consider the conversion in terms of analyzing the pyrolysis properties of the cable.

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