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

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1. Introduction

Electrical cables are one of the long life items that have not been considered for replacement during the life time of nuclear power plants (NPPs) [1]. 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 [2,3]. However, continuous exposure to these conditions causes the degradation of polymeric materials used in the cables. The aging of polymers affects different properties of the materials at the physical, chemical, and mechanical level [4]. Therefore, it is necessary to study on the degradation aging properties of the cables to accurately grasp the changes of properties for the aging cables. In this study, the pyrolysis properties of the cables are investigated using thermogravimetric (TG) analyzer. In addition, the pyrolysis parameters such as activation energy (E_a) and pre-exponential factor (*A*) are calculated by applying the kinetic models. These results will be used to determine the accurate thermal aging mechanism.

2. Material and Methods

2.1 Material

In other to analyze, the pyrolysis properties of cables, a non-class 1E cable used in NPPs was selected. The cable is used the application of power supply and consists of a polychloroprene rubber (CR)-based sheath, an ethylene propylene rubber (EPR)-based insulation. In this study, test specimens were prepared with the same weight ratio in order to consider the pyrolysis properties of the polymeric sheath and insulation at the same time.

2.2 TG experiment

The TG analyzer is a useful tool to analyze the thermal decomposition and the pyrolysis of materials by using TG analysis (TGA) and differential thermal analysis (DTA) according to the controlled heating rate. In this experiment, sample masses were about 10mg (Sheath 5 mg + Insulation 5 mg) and they are heated from room temperature to 600℃ in nitrogen atmosphere with a flow 100 ml/min. Four different heating rates of 5, 10, 15, and 20 ℃/min were adopted.

2.3 Kinetic models

The kinetic models were used to determine the pyrolysis parameter E_a, which can deepen our understanding of the whole reaction [5].

The pyrolysis parameters of non-isothermal solid phase reaction can be effectively calculated based on the conversion rate $d\alpha/dt$;

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

where k is the rate constant and f(α) is the reaction model. Conversion α and rate constant are given by Eqs. (2) and (3)

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f} \quad (2)$$

$$k = A \exp\left(\frac{-E_a}{RT}\right) \quad (3)$$

where m_0, m_t, and m_f refer to the mass of sample at begin, time t, and final respectively, E_a is the activation energy, A is the pre-exponential factor, R is the gas constant (=8.314 J/mol K).

For non-isothermal dynamics, the heating rate $\beta = dT/dt$ is introduced into the equation and the conversion rate can be obtained in the Eq. (4);

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

In this study, three model-free methods Ozawa-Flynn-Wall (OFW) method [6], Kissinger Method [7], Kissinger-Akahira-Sunose (KAS) method [8] were used. The model-free calculate the reaction activation energy without modelistic assumptions which is usually done by grouping the terms such as the *A* and model into the intercept of a linear equation and using the slope of that equation to calculate the activation energy [9]. All their expressions are described using Eqs. (5) - (7) in Table I.

Table I: Methods used to determine the E_a

Eq. No.	Method	Expressions	Plots
(5)	OFW	$\ln\beta = log\left(\frac{AE_a}{Rg(\alpha)}\right) - 2.135 - \frac{0.4567E_a}{RT}$	$\ln\beta$ 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 $1/T$

3. Results and discussions

3.1 TGA/DTA

The TG curves and corresponding DTG (differential thermogravimetric) curves of the cable under different heating rate conditions (5, 10, 15 and 20 ℃/min) were represented Fig. 1. Similar plots are obtained at different rates, the initial temperature at which thermal conversion reaction begins is approximately 200℃. The pyrolysis processes could be distinguished into two stages. The first stage, from about 300℃ to 390℃, was decomposition of insulation (EPR). And then the second stage took place in the temperature range of 400-500℃, which was caused by the decomposition of sheath (CR). For the sheath containing Cl (Chlorine), the dehydrochlorination reaction occurs in the range of 300-500℃ [5]. This is useful for understanding the pyrolysis process of the cable considering the properties of sheath and insulation.

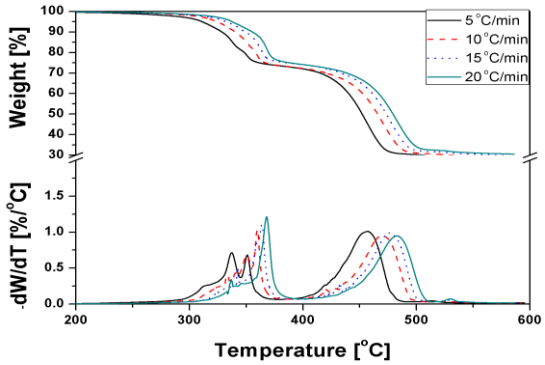

Fig. 1. TG-DTG analysis of cable samples.

3.2 Kinetic parameter

In general, the chemical kinetic parameters are of great importance in understanding the materials thermal conversion microscopic reaction mechanism [10]. Therefore, in this study, the activation energy was calculated by using the methods presented in Table I.

Fig. 2 shows the linear plot of $-\ln(\beta/T_m^2)$ versus 1000/T according to the Kissinger method. The slope of line equals E_a/R. The activation energy was calculated by Eq. (6) where T_m is the first decomposition peak temperature. The activation energy obtained from Kissinger method is 176.36 kJ/mol.

The variation of E_a against the conversion rate (α) is plotted in Fig. 3, as can be seen that the distributions of the activation energies obtained from OFW and KAS methods are similar on the whole. All the calculated values of E_a for the cable are summarized in Table II. The activation energies obtained from OFW and KAS methods significantly increased at α=0.3, which is polymer with a higher thermal stability participate in the reaction. Afterwards, the activation energy increased until α=0.5, and the maximum activation energies are calculated 240.22 kJ/mol and 239.78 kJ/mol respectively. The average activation energy obtained from OFW and KAS methods is about 216 kJ/mol, which is about 40 kJ/mol higher than that of the Kissinger method.

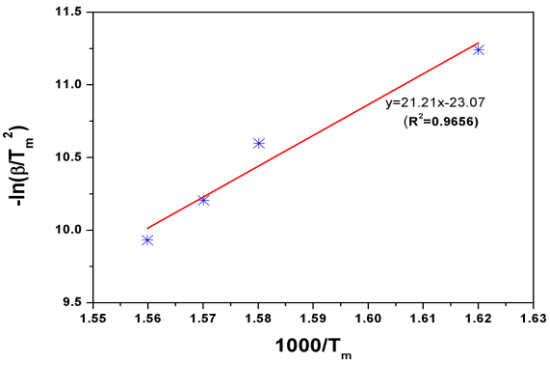

Fig. 2. Kissinger plot of cable samples.

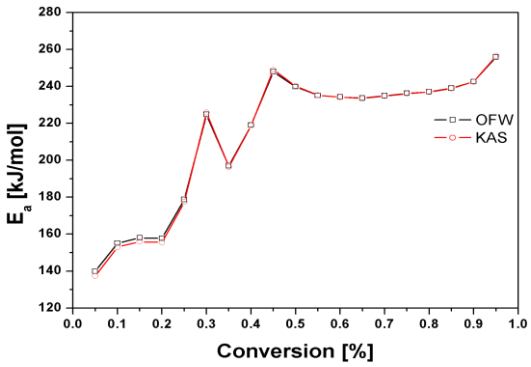

Fig. 3. Activation energies variation calculated via OFW and KAS method.

Table II: The activation energy of the cable at different conversion rates.

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
average	215.75	216.11

4. Conclusions

Pyrolysis kinetic parameters are important in determining the thermal aging degradation mechanism. In this study, the activation energy of non-class 1E cable is calculated by applying model-free methods, and is intended to be used as foundational data for the pyrolysis properties of the cable. For the Kissinger method, it is confirmed that the heating rates (β) shape a linear plot

with respect to the first decomposition temperature (T_m). The activation energy obtained from Kissinger method is about 176 kJ/mol. OFW and KAS methods are similar on the whole, and the activation energy for the pyrolysis reaction of the cable is calculated in the range α=0.3-0.5. The average activation energy obtained from OFW and KAS methods is about 216 kJ/mol, which is about 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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