The Comparison of Activation Energy between raw CSM and commercial CSM using TGA

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1. Introduction

The cable material is plastic or rubber. Chlorosulphonated polyethylene (CSM) in the rubber has been commonly used as a cable jacket for nuclear power plant cabling. CSM has a reasonable thermal life under thermal stress. The thermal life of different manufacturers' CSM varies depending on the compound [1].

The commercial CSM in Korean nuclear power plant was widely installed as the cable jacket material. Its activation energy in Elongation At Break (EAB) was about 96.3kJ/mol. We experimented with the raw and commercial CSMs and compared activation energies using ThermoGravimetric Analysis (TGA).

The objective of this study is to determine the thermal decomposition kinetics of two CSMs that has been subjected to pyrolysis under different operating conditions in TGA, and to compare their lifetimes.

2. Experimental Method

TGA is one of the most widely used techniques for composition analysis of polymer and rubber products. TGA methods are also used to predict the thermal and thermo-oxidative stability of polymeric materials [2,3].

The decomposition kinetic study was carried out using the TGA Q5000 IR (TA Instruments) in Fig. 1 and Table 1. It is a thermal weight-change analysis instrument, used in conjunction with a controller computer and associated software to make up a thermal analysis system. The samples were heated under a nitrogen atmosphere up to 1000°C. Four different heating rates were applied (1, 2, 5 and 10°C/min, respectively) for this study. We compared inorganic compounds of the two samples with Scanning Electron Microscope (SEM).

Fig. 1. Thermo Gravimetric Analyzer.

Table 1. Experimental conditions for TGA

Item	Condition
Scan temperature	100 ~ 1,000 °C
Heating rate	1, 2, 5, 10 °C/min
Purge gas	Nitrogen
Sample weight	3.5 ± 0.5 mg

3. Theoretical Background

The decomposition kinetic parameters of CSMs were evaluated by Ozawa techniques. Four single heating-rate techniques were taken into consideration in this study. The sample mass is recorded continuously as a function of temperature. The temperatures for constant conversion are determined from the resultant mass loss curves. The Arrhenius activation energy is then determined from a plot of the logarithm of heating rate versus the reciprocal of the absolute temperature at constant conversion level. This equation is as follows [4].

$$E = -(R/b) * \Delta(\log\beta)/\Delta(1/T) \quad (1)$$

Where E refined Arrhenius activation energy (J/mol), R is gas constant (8.314J/mol·K), b is approximation derivative from ASTM E 1641 table(use b=0.4567/K on the first iteration), β is heating rate (K/min), T is temperature (K) at constant conversion.

The activation energy may be used to calculate thermal endurance and an estimate of the lifetime of the material at a certain temperature.

4. Results and Discussion

The experimental materials are L's raw CSM and J's commercial CSM. SEM analysis on two types of CSM was performed at the magnification of 300 times. The SEM pictures are shown in Fig. 2. The raw CSM consists of C, Cl, O, Si, Mg and Ca. Since the commercial CSM was added with an antioxidant, flame retarded and etc., three additional compounds, Al, Sb and Pb, were found.

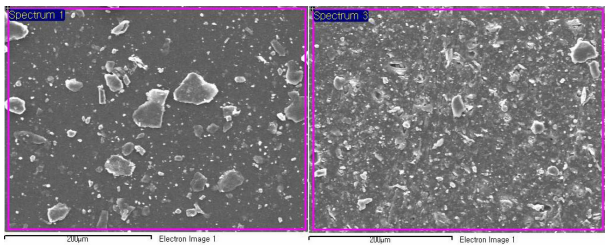

Fig. 2. The SEM Picture of raw and commercial CSM

To evaluate its activation energy, CSMs were tested at the same experimental conditions. The TGA experiments of CSMs were conducted at the heating rates 1, 2, 5 and 10°C/min in nitrogen atmosphere. Burning temperature of commercial CSM continued to the 1000°C because the weight was not dropped until the temperature to 500°C. Results of the thermal decomposition kinetics are shown in Fig. 3, 4, 5 and 6. The decomposition is due to the breakdown of polymer

chains. The activation energy values are increased from 124.5kJ/mol to 150.9kJ/mol as the conversion level increases from 5% to 20% (refer to table 2). The raw CSM shows higher values compared to the commercial CSM.

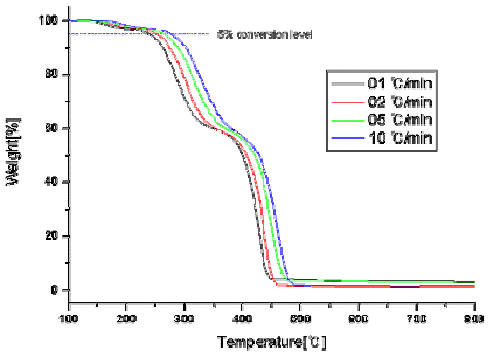

Fig. 3. Mass loss curves in raw CSM

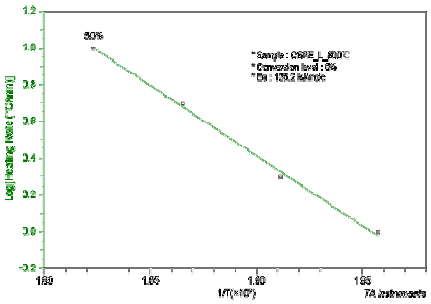

Fig. 4. Arrhenius plot of heating rate, temperature of constant conversion date in raw CSM

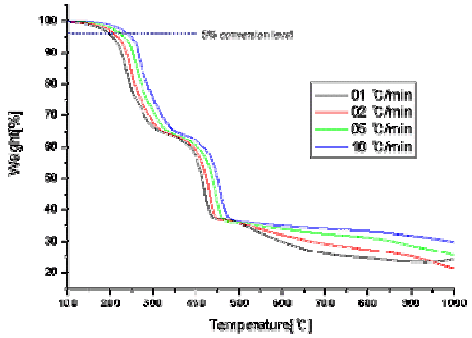

Fig. 5. Mass loss curves in commercial CSM

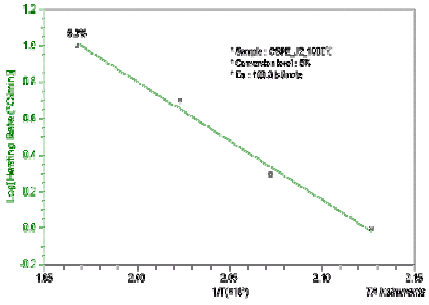

Fig. 6. Arrhenius plot of heating rate, temperature of constant conversion date in commercial CSM

Table 2. Activation energy of conversion level

Sample Type	Activation energy of Conversion level (kJ/mol)			
	5%	10%	15%	20%
Raw CSM	136.2	140.8	145.5	148.0
Commercial CSM	124.5	132.7	144.7	150.9

The deviation of activation energy values of raw and commercial CSMs was 11.47kJ/mol. This deviation affects 12 years of lifetimes.

The activation energy values experimented until 500°C were 134.9kJ/mol for raw CSM and 96.6kJ/mol for commercial CSM. The activation energy value of commercial CSM was similar to the value of EAB.

5. Conclusions

The thermal degradation of two types of CSM has been studied using an isothermal thermogravimetric technique in a flowing nitrogen atmosphere at several heating rates between 1, 2, 5 and 10°C/min. The dynamic thermogravimetric analysis curve has been analyzed using Ozawa methods to obtain information of the activation energies. Ozawa methods showed values of 124.5~150.9kJ/mol upon fractional weight loss. TGA showed the shifting of thermograms towards the higher temperature region with the increase of heating rate.

The activation value of raw CSM was 11.47kJ/mol higher than that of commercial CSM. 11.47kJ/mol of deviation corresponded to 12 years. As the result of this experiment, it was found that the activation energy of cable should be calculated by using real cable.

Since burning temperature of commercial CSM is higher than that of raw CSM, due to addictive material of oxidant resistance. The experiment for commercial CSM should be continued until the temperature goes to 1000°C.

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