Thermal Degradation of Flame Retarded Polyvinylchloride Cable Sheath in Air Atmosphere

Jiaqing Zhang, Liufang Wang, Minghao Fan, Hui Xie, Wei Li and Shuping Wang
State Grid Anhui Electric Power Research Institute, Hefei 230601, China
Email: dkyzjq@163.com

Abstract. A series of thermogravimetric experiments from 10 K/min to 50 K/min was performed to analyse the pyrolysis behaviours and reaction kinetics of typical old flame-retarded PVC cable sheath in air atmosphere. Two model-free methods of Flynn-Wall-Ozawa (FWO) method and Kissinger-Akahira-Sunose (KAS) method were used to estimate the activation energy, as well as the model-fitting method called Coats-Redfern (CR) method. Three peaks can be observed in mass loss rate profiles and the first peak value is much larger than the other two. Due to the oxidation of carbon or others, the first and third peak values in air atmosphere are significantly larger, and the final residue mass fraction in air atmosphere is around 62% the one in Nitrogen atmosphere. FWO method predicts the activation energy of 223.1kJ/mol while KAS model estimates the one of 223.7kJ/mol in air atmosphere, and both have the deviation of 0.27%. By CR method, the most probable reaction mechanism is $[1 - (1 - \alpha)^{-2}] / (-2)$ for current fire retarded PVC cable sheath. Moreover, it estimates the activation energy of 237.6 kJ/mol, which is well agreeable with those from FWO and KAS methods.

1. Introduction
With rapid development of China modernization construction, electrical cables with over kilo voltage have been extensively applied in industries. The outer sheath of electrical cable is still combustible even it is designed to be flame-retarded. Therefore the potential hazards of these cable sheaths in fires are a matter of great account. So the fire safety issues of electrical cables deserve more attentions.

Since the outer sheath is the main combustible part of the cable, its pyrolysis and combustion processes of the cable sheath is significantly important to the focus of fire detection and protection of cables. For example, the cable combustion is significantly dependent on its pyrolysis kinetics; the detector design is also related to the pyrolysis gas components and their physical and chemical characteristics. On the cable outer sheath, Ma et al. [1], Henrist et al. [2], Cheng et al. [3], and Gao [4] have studied the thermal degradation characteristics of typical PVC cable widely used in China. Xie et al. [5] carried out TG and FTIR experiments to focus on the pyrolysis behaviours of both the old and new cable outer sheath. These studies is most on the pyrolysis in Nitrogen atmospheres and little work is carried out in air atmospheres since both pyrolysis and oxidation are significantly important to the cable fire. Moreover, no more work was done to analyse its characteristics of the old flame-retarded cable pyrolysis kinetics. Therefore, in current study, TG experimental runs in both Nitrogen and air atmospheres were carried out.
2. Materials
The samples used in this study were the outer sheath of flame retarded cables from Baosheng S&T Innovation Co. Ltd. The main components are polyvinylchloride (PVC) and flame retarded additives. Before the thermogravimetric measurement runs, the samples were cut into very small particles with the diameter of less than 0.25 mm and furthermore all samples had been dried for about 24 h at 80 °C for removing the moisture in it.

3. Experimental details
The thermogravimetric experiments were performed on a TA Instrument SDT Q600 thermal analyser from 300 K to 1000 K with five heating rates (10, 20, 30, 40 and 50 K/min). The cable sample powder with about 6.0 mg was kept in an Alumina cup without a lid. The flow rate of the carrier gas (N2: purity 99.9% or air: purity 99.99%) was 100 mL/min, which was high enough to sweep the produced gas away from the sample to keep the nitrogen or air atmosphere around it.

4. Pyrolysis Kinetics method
For obtaining the Pyrolysis kinetic parameters such as the activation Energy and the pre-exponential factor etc, two common iso-conversational methods of Flynn-Wall-Ozawa (FWO) [6-7] and Kissinger-Akahria-Sunose (KAS) [8-9] were employed. These two methods are model-free, which means they can be used to calculate the activation energy value without the choice of reaction mechanism that avoids the error caused by the assumption of different reaction mechanism. In current study, the model-fitting method called Coats-Redfern (CR) method [10] is also employ to obtain reaction mechanism of current flame-retarded PVC cable sheath.

4.1. Flynn-Wall-Ozawa (FWO) method
The FWO method can be expressed as:

$$\ln \beta = \ln \left( \frac{AE_a}{R G(\alpha)} \right) - 5.331 - 1.052 \left( \frac{E_a}{RT} \right)$$

where $\beta = dT / dt$ is the heating rate (K/s); $A$ is the pre-exponential factor (s$^{-1}$); $E_a$ is the activation energy of the reaction; $R$ is the universal gas constant (8.314 JK$^{-1}$mol$^{-1}$) and $T$ is the absolute temperature. $G(\alpha)$ is an integral function of the conversion it can be written as:

$$G(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T \exp\left(-\frac{E_a}{RT}\right) dT$$

where $\alpha$ is the conversion rate.

The plot of $\ln \beta$ versus $1/T$ gives a straight line whose slope can be used to calculate $E_a$. If $G(\alpha)$ is given, $A$ can be calculated from the intercept.

4.2. Kissinger-Akahira-Sunose (KAS) method
The KAS method presents an isoconversional linear integral to determine $E_a$ :

$$\ln \frac{\beta}{T^2} = \ln \left( \frac{AE_a}{RG(\alpha)} \right) - \frac{E_a}{RT}$$

It is similar to FWO method, $E_a$ can be calculated from the slope of the straight line between $\ln (\beta / T^2)$ and $1/T$.

4.3. Coats-Redfern (CR) method
The CR method can be expressed as:

$$\ln \frac{G(\alpha)}{T^2} = \ln \left( \frac{AR}{BE_a} \right) - \frac{E_a}{RT}$$

CR method can reflect the pyrolysis reaction mechanism well and has been widely used in solid reaction kinetics analysis. $E_a$ can be derived by the slope of the straight line between $\ln G(\alpha)/T^2$ and $1/T$ if $G(\alpha)$ is given.

5. Thermogravimetric analysis
Fig. 1 presents the mass loss (TG) and mass loss rate (DTG) of cable sheath in air atmosphere, as a function of temperature under varying heat rates of 10K, 20K, 30K, 40K and 50K. In DTG curves, three peaks can be observed, and moreover the first one is much dominant, which locates at the temperature between 544K to 620K. With the increase of the heating rate, the DTG peak locations are shifted towards higher temperature. Furthermore, the peak values of $\frac{dm}{dn} \times 1000$ range from 12 to 15. The locations of the second peak are in the range from 705K to 870K, and the peak values are around 1/(5~6) the ones of the first peak, but larger than the third peak ones. The third peak locates around 1000K and only shows some fluctuations with relatively small amplitude. Subsequently, the mass loss rate demonstrates a slow decrease and eventually decays to zero. The average value of final residue is about 16% in all thermogravimetric runs.

Fig. 1. Total mass loss (TG) and mass loss rate at different heating rates in air atmosphere

Fig. 2 presents the mass loss (TG) and mass loss rate (DTG) of cable sheath in Nitrogen atmosphere. By comparison with Fig. 1 and Fig. 2, three significant differences can be found. Firstly, the first peak values are around 11~13.5 in Nitrogen atmosphere, which are smaller than in air atmosphere. Secondly, the final residue mass fraction is about 26%, which shows that the one in air atmosphere is around 62% the one in Nitrogen atmosphere. Thirdly, the third peaks are flatter in Nitrogen atmosphere.

For cable sheath pyrolysis of polyvinylchloride(PVC) and flame retarded additives in Nitrogen atmosphere, the first peak should be caused by the fast volatilization of hydrogen chloride by the reactions of chlorine free radical formation, and hydrogen chloride removal from the cable sheath surface, which leads to about 43% mass loss in this process. Then, the cleavage of conjugated polyene chain and structural reorganization between PVC and additives results in the second peak with mass loss of 20%. The third one with around 3% mass loss is caused by slow pyrolysis of remained residue.

In air atmosphere, three peaks values with mass loss of about 45%, 25% and 13% are significantly larger than those in Nitrogen atmosphere. This provides the information of occurrence of oxidation reaction. Due to carbon formation in the process of cable sheath pyrolysis, we can deduce the existence of carbon oxidation. But we cannot determine how much it contributes to mass loss of cable sheath pyrolysis. Maybe other oxidation reactions also exist in this complicated pyrolysis process.
6. Pyrolysis kinetics
For obtaining the activation energy using KAS and FWO methods, the conversion rate was chosen between 0.1 and 0.8 at five heating rates. Fig.3(a) plots the relationship between $\ln\beta$ and $1000/T$ for FWO method while Fig.3(b) shows $\ln\frac{\beta}{T^2}$ as a function of $1000/T$ for KAS method. Calculated from the slopes of the fitting lines at various conversion rates, $-\frac{1.052E_a}{R}$ for FWO and $-\frac{E_a}{R}$ for KAS can be estimated and further $E_a$ values are computed, as listed in Table. 1. It is found that, with increasing the conversion rate, the activation energy first increases and then decreases. For FWO, the activation energy ranges from 128.1 kJ/mol to 385.7 kJ/mol with the average value of 223.1kJ/mol and the maximum value of 385.7 kJ/mol at the conversion rate of 0.7. For KAS, the activation energy falls in the range of 120.8 kJ/mol to 393.0 kJ/mol, and has the average value of 223.7kJ/mol and the maxima of 393.0 kJ/mol at the conversion rate of 0.7. This shows that both FWO and KAS gives the maximum activation energy at the same conversion rate of 0.7 and the nearly identical average value with the deviation of 0.27%.

Figure 2. Total mass loss (TG) and mass loss rate (DTG) at different heating rates in Nitrogen atmospheres

Figure 3. FWO and KAS plots for different conversion rates
The CR method for thermogravimetric data was used for the estimation of reaction mechanism. Table 2 presents the activation energy predicted by CR method. It should be noted that 4 reaction order models, 4 diffusional models and two contracting geometry models are taken into account to first calculate the values at different heating rate and then obtain the average ones. By comparison between these average values and the ones from FWO and KAS methods, one can find that the activation energy predicted by reaction order model is 237.6 kJ/mol, which is most close to 223.1kJ/mol from FWO and 223.7kJ/mol from KAS. So the most probable reaction mechanism is \(1-(1-\alpha)^{-2}/(-2)\) for current fire retarded PVC cable sheath.

### Table 1. Pyrolysis parameters of PVC cable sheath by FWO and KAS methods

| α   | FWO      | KAS      |
|-----|----------|----------|
|     | Ea (kJ/mol) | LnA (s^{-1}) | R² | Ea (kJ/mol) | LnA (s^{-1}) | R² |
| 0.1 | 159.7    | 31.40    | 0.8008 | 158.6    | 11.41    | 0.8829 |
| 0.2 | 172.6    | 34.64    | 0.9636 | 172.1    | 14.63    | 0.9407 |
| 0.3 | 176.8    | 35.48    | 0.9869 | 176.4    | 15.44    | 0.9801 |
| 0.4 | 172.2    | 34.19    | 0.9903 | 171.4    | 14.11    | 0.9855 |
| 0.5 | 282.8    | /        | 0.5696 | 287.0    | /        | 0.4023 |
| 0.6 | 306.6    | /        | 0.9390 | 310.5    | /        | 0.9128 |
| 0.7 | 385.7    | /        | 0.7451 | 393.0    | /        | 0.6436 |
| 0.8 | 128.1    | /        | 0.9034 | 120.8    | /        | 0.8429 |

### Table 2. Ea values for cable sheath by CR method

| Reaction model | 10K/min | 20K/min | 30K/min | 40K/min | 50K/min | Average value |
|---------------|---------|---------|---------|---------|---------|---------------|
| G(\alpha)     | Ea      | R²      | Ea      | R²      | Ea      | R²           | Ea      | R²         |
| α             | 141.9   | 0.89    | 172.0   | 0.83    | 177.9   | 0.84         | 160.4   | 0.85       | 156.6   | 0.86       |
| −\ln(1−\alpha)| 163.7   | 0.91    | 198.8   | 0.86    | 205.6   | 0.86         | 185.3   | 0.88       | 151.3   | 0.88       |
| [1−(1−\alpha)^{-1}/(-1)] | 188.0   | 0.93    | 228.7   | 0.88    | 236.4   | 0.88         | 213.0   | 0.90       | 174.1   | 0.90       |
| [1−(1−\alpha)^{-2}/(-2)] | 214.6   | 0.94    | 260.6   | 0.89    | 270.3   | 0.90         | 243.5   | 0.91       | 199.2   | 0.92       |
| α²           | 293.1   | 0.90    | 353.5   | 0.84    | 365.5   | 0.84         | 330.4   | 0.86       | 271.3   | 0.87       |
| −(−1−\alpha)\ln(1−\alpha)+\alpha | 306.9   | 0.90    | 370.5   | 0.85    | 383.0   | 0.85         | 346.2   | 0.87       | 284.3   | 0.88       |
| [1−(1−\alpha)^{1/2}] | 73.4    | 0.90    | 90.0    | 0.83    | 93.2    | 0.84         | 83.5    | 0.86       | 67.2    | 0.86       |
| 1−2\alpha^3−(1−\alpha)^{2/3} | 311.8   | 0.915   | 376.5   | 0.85    | 389.2   | 0.85         | 351.8   | 0.87       | 288.9   | 0.88       |
| Contracting geometry | 1−(1−\alpha)^{1/2} | 152.2   | 0.90    | 185.0   | 0.84    | 191.4   | 0.85         | 172.5   | 0.87       |
| 1−(1−\alpha)^{1/3} | 156.2   | 0.91    | 189.6   | 0.85    | 196.0   | 0.85         | 176.7   | 0.87       | 144.2   | 0.88       |

### 7. Conclusions

A series of thermogravimetric experiments from 10 K/min to 50 K/min was performed to analyse the pyrolysis behaviours and reaction kinetics of typical old flame-retarded PVC cable sheath. Two model-free methods of FWO and KAS were used to estimate the activation energy, as well as the model-fitting method called CR method. The latter was also applied to determine the reaction mechanism of current cable sheath. Main conclusions are drawn as follows.

1. Based on thermogravimetric analysis, with the increase of the heating rate, the peak locations of mass loss rates are shifted towards higher temperature. Three peaks can be observed and the first peak value is much larger than the other two.
(2) By comparison of TG and DTG in Nitrogen and air atmospheres, due to the oxidation of carbon or others, the first and third peak values are significantly larger in air atmosphere, and the final residue mass fraction in air atmosphere is around 62% the one in Nitrogen atmosphere.

(3) With increasing the conversion rate, the activation energy first increases and then decreases. FWO and KAS predicts the maximum activation energy at the same conversion rate of 0.7 and the nearly identical average values of 223.1kJ/mol and 223.7kJ/mol with the deviation of 0.27%.

(4) By CR method, the most probable reaction mechanism is \( \frac{1 - (1 - \alpha)^2}{\alpha(1 - \alpha)} \) for current fire retarded PVC cable sheath. Moreover, it estimates the activation energy of 237.6 kJ/mol, which most matches those from FWO and KAS methods.

References

[1] R.H. Ma, Y.C. Lin, C.P. Kuo, The study of thermal pyrolysis mechanisms for chloro organic compounds in electric cable and medical wastes, J. Anal. Appl. Pyrolysis 75 (2) (2006) 245–251.

[2] C. Henrist, A. Rulmont, R. Cloots, et al., Toward the understanding of the thermal degradation of commercially available fire-resistant cable, Mater. Lett. 46 (2–3) (2000) 160–168.

[3] J.Q. Cheng, W.N. Jia, Z.J. Shu, et al., Experimental research on rules of releasing of the halogen gas of PVC cable under hydrogenation condition, Fire Sci. Tech. 26 (4) (2007) 383–386.

[4] Y.P. Gao, Study on pyrolysis characteristics of insulative PVC material used for fire retardant cable, Eng. Plast Appl. 35 (3) (2007) 44–47.

[5] Qiyuan Xie, Heping Zhang, Lin Tong. Experimental study on the fire protection properties of PVC sheath for old and new cables. Journal of Hazardous Materials 179 (2010) 373–381

[6] Kissinger HE. Variation of peak temperature with heating rate in differential thermal analysis. J Res Nat Bur Stand 1956;57:217–21.

[7] Akahira T, Sunose T. Joint convention of four electrical institutes. Res Rep Chiba Inst Technol 1971;16:22–31.

[8] Flynn JH, Wall LA. A quick, direct method for the determination of activation energy from thermogravimetric data. J Polym Sci, Part C: Polym Lett1966;4:323–8.

[9] Ozawa T. A new method of analyzing thermogravimetric data. Bull Chem Soc Jpn 1965, 38:1881–6.

[10] Coats A, Redfern J. Kinetic parameters from thermogravimetric data. Nature 1964;201:68–9.