# A Thermal Degradation Study of Insulation Materials Extruded Polystyrene

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## Abstract

This paper presents a research on the thermal degradation of typical polymer insulation materials extruded polystyrene (XPS) under both oxidizing gas air and non-oxidizing gas nitrogen. The Kissinger-Akahira-Sunose method was employed to calculate the activation energy values according to thermogravimetic analysis (TGA) results. Thermal degradation characteristics of XPS were studied by using thermogravimetry and differential scanning calorimetry (TG-DSC) hyphenated technique. XPS follows a two-stage and three-stage weight loss during the entire process under nitrogen and air, respectively. Evolved products of XPS and the degradation mechanism in helium were investigated with pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) method. The results reveal that styrene monomers are the dominate products of XPS degradation. Methylbenzene, α-methyl styrene, dimer and some other oligmers of styrene are also detected.

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*Keywords*: Extruded polystyrene, Thermogravimetic analysis, Pyrolysis-gas chromatography, Mass spectrometry

## 1. Introdution

Polystyrenes (PS) are a typical class of high polymers that widely used in our daily life. PS products can be produced from the polymerization reaction of styrene monomers and other additives. In particularly, extruded polystyrene (XPS) has been commonly used as the insulation material in building insulation system because of its excellent performance [1]. However, XPS insulation materials bring serious fire risks due to their flammability and low thermal stability. More and more building fires were caused by the ignition of XPS. The fire disaster happened in China Central Television (CCTV) new site building, in February 9, 2009, leaded to 4 billion RMB economic losses, due to the applications of XPS as the insulation material for building facade. Thermal decomposition is always the initial step of solid combustion processes and the degradation products that contain gaseous fuel support the combustion [2]. Hence, investigation on thermal degradation behavior and evolved products of XPS are very necessary.

Many researchers conducted relative studies on thermal degradation of PS [3-6] or expanded polystyrene [7-8]. The kinetics and volatile products were investigated in detail under different environments. However, few of them pay attention to XPS materials, especially for insulation applications. Thermogravimetry and differential scanning calorimetry (TG-DSC) hyphenated technique is an efficient method for studying thermal decomposition characteristics and changes of heat. The objective of this work is to obtain more details with regard to evolution of gaseous products and attempt to research degradation mechanism of XPS insulation material. In our study, pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) was employed, which is an important mean to detect the evolution of decomposition products on-line [9].

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## 2. Experimental

### 2.1. Materials

The XPS materials were produced by Anhui Jurong insulation materials co., LTD in China. And the formula was typical for building insulation materials in market. The samples were cut to fine particles for all the experiments.

### 2.2. Thermal behavior experiment

Thermal behavior experiment parts were performed under both inert gas $N_2$ and oxidizing gas air environments. Thermogravimetric analysis were conducted with a TGA Q5000 analyzer from TA Instruments at the heating rates (5, 10, 20, 30 °C/min) to 700 °C, while the sample gas flow was 75 mL/min. TG-DSC hyphenated technique measurements were carried out with a SDT Q600 from TA Instruments. The sample weights about 4 mg, heated up to 700 °C at a heating rate of 10 °C/min. And the flow rate of was 100 mL/min.

### 2.3. Py-GC-MS experiment

Identification of the volatile products was performed on a Perkin Elmer Pyris 1 TGA coupled with a Clarus 680 gas chromatographic analyzer and Clarus SQ 8T mass spectrometer (Py-GC-MS). The material sample was heated from room temperature up to 700 °C at a heating rate of 10 °C/min. And the environment gas was helium gaseous atmosphere with a flow rate 75 mL/min. Connections for gas transportation between the apparatuses were set at 190 °C to allow the decomposition products in a gaseous state.

## 3. Results and discussion

### 3.1. Thermogravimetic analysis

The TG and DTG results of XPS at different heating rates (5, 10, 20, 30 °C/min) under nitrogen and air are shown in Figs. 1 and 2. There are many integral isoconversional methods suitable for calculating non-isothermal kinetic parameters. In this study, the Kissinger-Akahira-Sunose (KAS) method which improves significantly in the accuracy was utilized to obtain the activation energy $E$.

The equation is as follows:

$$\ln\left(\frac{\beta_i}{T_{\alpha,i}^2}\right) = Const - \frac{E_\alpha}{RT_\alpha} \tag{1}$$

In equation (1), $\beta_i$, $E_\alpha$ and $T_{\alpha,i}$ represent heating rate, activation energy and absolute temperature, respectively. The index $i$ here is to indicate different heating rates, and $R$ is the gas constant.
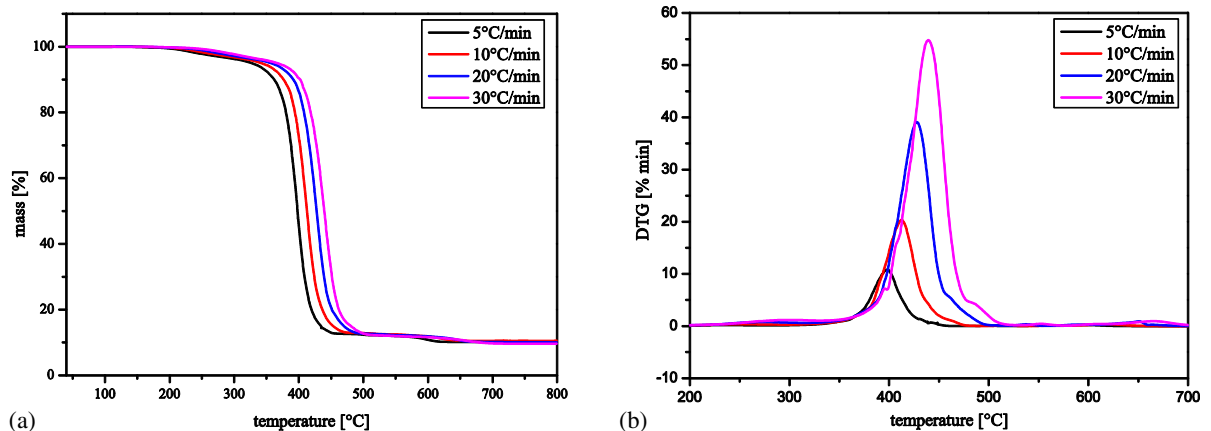


(a)                                                                 (b)

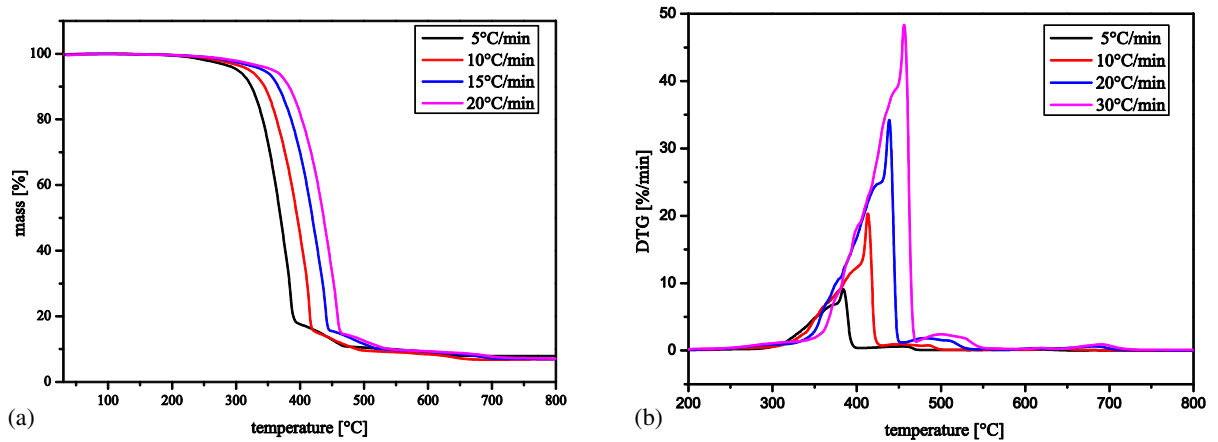Fig. 1. The (a) TG and (b) DTG results of XPS at different heating rates (5, 10, 20, 30°C/min) under nitrogen.



(a)　　　　　　　　　　　　　　　　　　　　　　　　　　　　(b)

Fig. 2. The (a) TG and (b) DTG results of XPS at different heating rates (5, 10, 20 , 30°C/min) under air.

At each extent of conversion $\alpha$, the activation energy $E_\alpha$ can be calculated from the slope of the straight line $\ln(\beta_i / T_{\alpha,i}^2)$ vs. $1/T_\alpha$. Based on the data obtained by TG analysis in $N_2$ and air, the activation energies of XPS were obtained and the dependence of E on $\alpha$ is presented in Table 1.

Table 1. The dependence of activation energy values $E$ on the extent of conversion α for XPS in $N_2$ and air.

| Gas environment | Degree of conversion | $E_a$/kJ/mol | Standard Error | Gas environment | Degree of conversion | $E_a$/kJ/mol | Standard Error |
|---|---|---|---|---|---|---|---|
| | 0.02 | 82.21 | 6.97 | | 0.02 | 96.65 | 5.08 |
| | 0.05 | 133.56 | 0.72 | | 0.05 | 89.17 | 2.21 |
| | 0.1 | 147.43 | 1.75 | | 0.1 | 89.06 | 2.72 |
| | 0.15 | 160.26 | 3.00 | | 0.15 | 90.44 | 2.91 |
| | 0.2 | 164.64 | 5.18 | | 0.2 | 90.66 | 2.42 |
| | 0.25 | 165.36 | 5.90 | | 0.25 | 90.58 | 1.94 |
| | 0.3 | 165.02 | 6.67 | | 0.3 | 90.04 | 1.94 |
| | 0.35 | 164.36 | 5.91 | | 0.35 | 89.68 | 1.96 |
| Nitrogen | 0.4 | 164.06 | 6.79 | Air | 0.4 | 89.79 | 2.25 |
| | 0.45 | 163.40 | 6.18 | | 0.45 | 89.82 | 2.46 |
| | 0.5 | 163.31 | 6.74 | | 0.5 | 90.4 | 2.69 |
| | 0.55 | 162.46 | 6.75 | | 0.55 | 90.75 | 3.14 |
| | 0.6 | 161.80 | 6.96 | | 0.6 | 91.26 | 3.42 |
| | 0.65 | 161.21 | 6.72 | | 0.65 | 91.59 | 3.53 |
| | 0.7 | 161.14 | 6.99 | | 0.7 | 92.18 | 3.73 |
| | 0.75 | 162.27 | 7.20 | | 0.75 | 92.07 | 3.52 |
| | 0.8 | 164.07 | 7.41 | | 0.8 | 91.26 | 3.12 |
| | 0.85 | 165.84 | 6.95 | | 0.85 | 91.36 | 2.32 |
| | 0.9 | 164.52 | 1.66 | | 0.9 | 120.98 | 15.63 |
| | 0.95 | 149.24 | 5.59 | | 0.95 | 128.34 | 12.44 |

At the beginning of XPS degradation under $N_2$, the activation energy value is only 82.21 kJ/mol. It indicates that the degradation reaction is easy to start when material subjected to heat. Then the *E* value increases rapidly and maintain an approximate constant 165 kJ/mol between the conversion range α=0.15-0.9, corresponding to the main thermal weight loss stage. In the end (α>0.9), the value decreases to 149.24 kJ/mol. In air environment, the activation energy value can be distinguished into three stages along with the conversion rate α. The *E* value first shows a slight decline and then stabilize around 90 kJ/mol from α= 0.05. It requires a relatively lower activation energy value at the primary weight loss stage. However, the value in air increase quickly up to 120 kJ/mol after α= 0.85.

Comparing the results under two circumstances, the activation energy value *E* in $N_2$ is almost twice times of that in air. This reveals that under air environment, the thermal degradation of XPS is much easier.
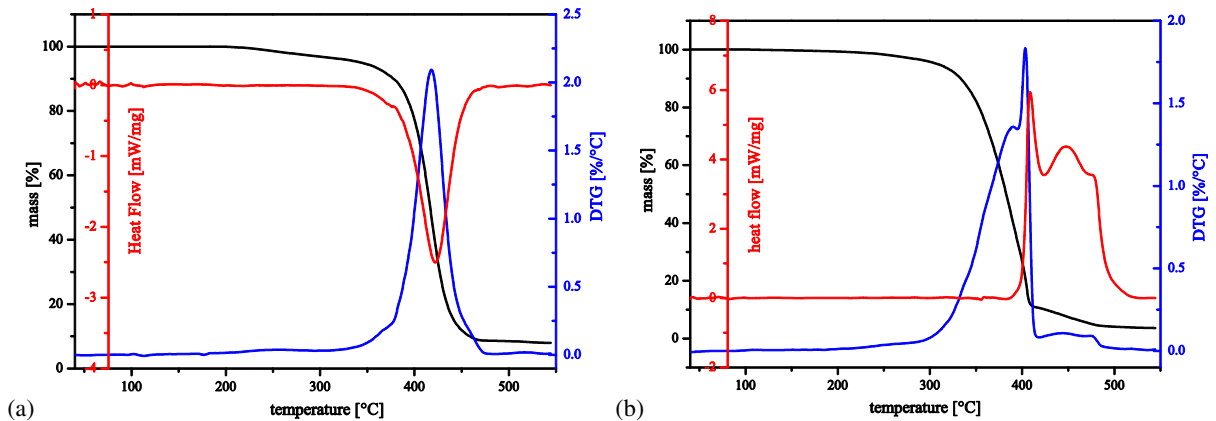
## 3.2. TG-DSC results



Fig. 3. TG-DTG and DSC curves of XPS in (a) nitrogen and (b) air atmospheres at 10 °C/min.

Figure 3 (a) and (b) illustrates the TG-DTG and DSC results in nitrogen and air at a heating rate 10 °C/min. Thermal degradation parameters obtained from TG and DSC results of XPS are listed in Table 2.

Two obviously weight loss stages of XPS degradation under nitrogen are observed from the TG results in Fig.3 (a). The initial stage starts at around 215 ℃ and the corresponding weight loss is very small. The second degradation stage in 330-470 ℃ is the main stage with a significantly weight loss ratio of 87%. According to the TG and DTG curves in Fig. 3 (b), XPS follows a three-stage weight loss during the entire process in air. Similar to the condition under $N_2$, a small amount of weight loss is found between 200 ℃ and 280 ℃, while the temperature range is less than that in nitrogen. It suggests that some small molecule products remaining in the materials or additives volatilize in this stage.

The second and third stages are the main degradation stages in air. Both DTG and DSC results of XPS show an overlap of peaks, while the peak at the third stage is very sharp. Since the existence of oxygen, the degradation reaction in air becomes more rapidly and violent with a complicated mechanism. The release of heat starts after the main weight loss is almost finished. This special phenomenon demonstrates that thermal degradation of XPS in air, the main weight loss stage before 400 ℃ is dominated by a physical process, such as volatilization of products. And Most of the bonds in material haven't begun to fracture. Only when most of XPS material volatilize into gas products, severe chemical reactions occur to release heat. During the whole process in air, the total heat release reach up to 2107.97 J/g. Nevertheless, XPS shows only one apparent endothermic peak in $N_2$, corresponding to the main thermal weight loss stage with a heat absorption of 639.8 J/g. At the final stage in 410-480 ℃, the remaining residues continue to decompose to volatile products.

Table 2. Parameters obtained from TG and DSC results of XPS thermal degradation.

| Gas environmet | Temperature range/ ℃ | Weight loss/ % | $T_{max}$ (from DSC curve) / ℃ | Heat (J/g) |
|---|---|---|---|---|
| Nitrogen | 215-330 | 4.2 | 421.7 | -639.8 (absorption) |
|  | 330-470 | 87 |  |  |
| Air | 200-280 | 3 | 408, 448.5 | +2107.97 (release) |
|  | 280-410 | 85.6 |  |  |
|  | 410-480 | 7.1 |  |  |

### 3.3. Py-GC-MS

Py-GC-MS analysis experiment was carried out in helium. Gas chromatogram of the volatile products during XPS thermal degradation in helium is shown in Fig. 4. It shows that various compounds are detected. The four peaks of GC result in Fig. 4 are assigned to toluene, styrene, α-methyl styrene and styrene dimers, respectively.
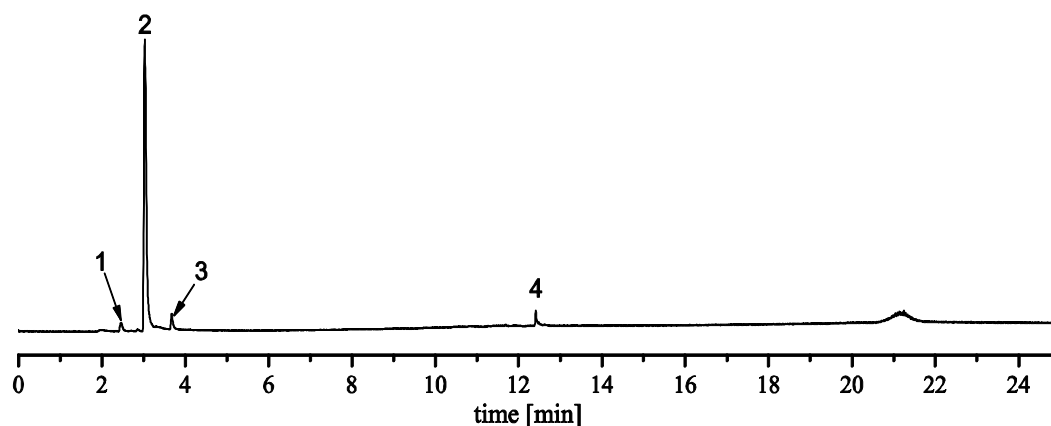


Fig. 4. Gas chromatogram of the volatile products during XPS thermal degradation in helium.

The m/z signals of volatile products evolution of XPS at different temperature regions are displayed in Figs. 5 to 8. Linear chain product 1, 3-butadiene, which gives a strong m/z 54 signal, shows a two-stage release at 220-300 ℃ and 350-500 ℃ in Fig. 5. As the MS results displayed in Fig. 6, signals at m/z 104, 103, 78, 51 and 77 are observed with high intensity. Meanwhile, the No.2 peak which represents styrene monomers is also the maximum height of peak in gas chromatogram. It reveals that styrene monomers are the dominant volatile gases in the range of 350-500 ℃. And depolymerization reaction predominate the thermal degradation of XPS material at this stage. Methylbenzene and α-methyl styrene [10] are also detected by GC-MS from about 370 ℃.
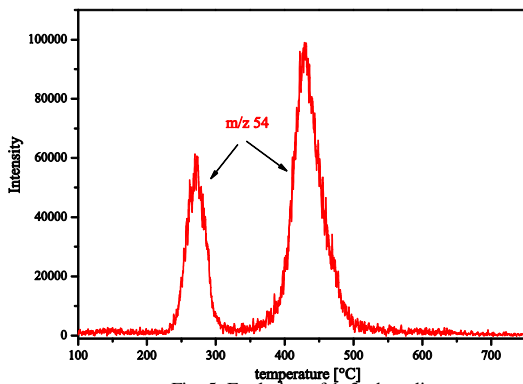
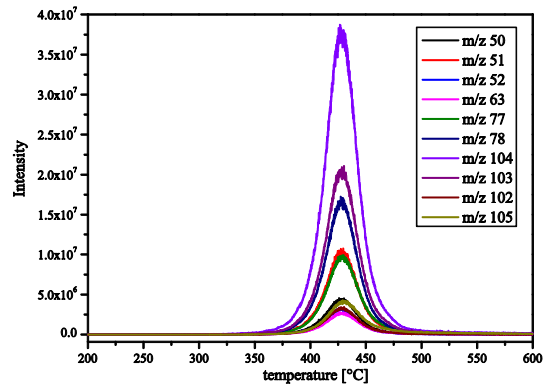Fig. 5. Evolution of 1, 3 - butadiene.
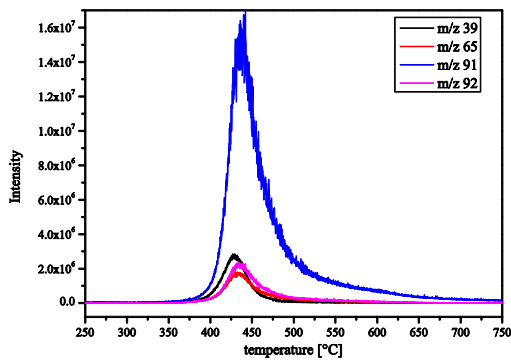

Fig. 6. Evolution of styrene monomers.
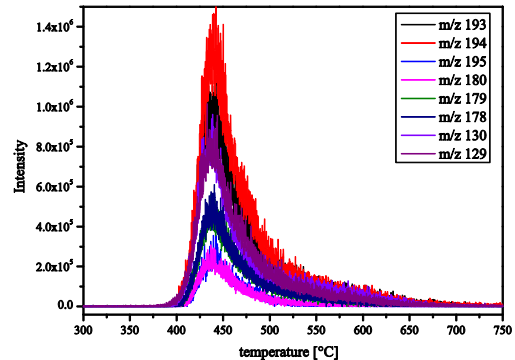

Fig. 7. Evolution of methylbenzene.


Fig. 8. Evolution of Styrene dimers.

Mass signals from m/z 194, 193, 130, 179 and 195 with respect to temperature are illustrated in Fig. 8, which confirm the evolution of styrene dimers. At higher temperature stage from about 400 ℃ to 650 ℃, dimer and some other oligmers of styrene are formed in the evolved products. At the meantime, the products start to react with each other and make the thermal degradation more complicated. Identification of the evolving products during thermal degradation of XPS by Py-GC-MS analysis is listed in Table 3.
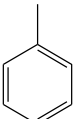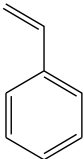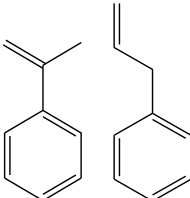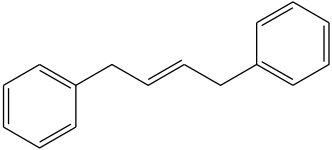
## 4. Conclusions

Comparing the results under two circumstances, the activation energy value E in N2 is almost twice times of that in air. It is confirmed that the thermal degradation of XPS is much easier under air. The E value maintains an approximate constant 165 kJ/mol in N2, while it stabilizes around 90 kJ/mol in air.

XPS follows a two-stage and three-stage weight loss during the entire process under nitrogen and air, respectively. Some small molecule products remaining in the materials or additives volatilize in the initial stage. Since the existence of oxygen, the degradation reaction in air becomes more rapidly and violent with a complicated mechanism. The total heat release reach up to 2107.97 J/g with only one apparent endothermic peak in N2.

On the basis of Py-GC-MS technique, it is demonstrated that depolymerization reaction predominate the thermal degradation of XPS in helium and styrene monomers are the dominant volatile gases. Methylbenzene, α-methyl styrene, dimer and some other oligmers of styrene are also detected.

Table 3. Identification of evolving products during the degradation of XPS by GC-MS.

| Peak | Corresponding compound | m/z | Temperature range / °C | Retention / min |
|------|------------------------|-----|------------------------|-----------------|
| 1 |  | 91<br>92<br>65<br>39 | 375-550 | 2.5 |
| 2 |  | 104<br>103<br>78<br>51<br>77<br>50<br>105<br>52<br>102<br>63 | 350-500 | 3.03 |
| 3 |  | 118<br>129<br>117<br>103<br>78<br>77<br>91<br>115 | 370-600 | 3.68 |
| 4 |  | 194<br>193<br>130<br>179<br>195<br>180<br>129<br>130 | 400-650 | 12.42 |

## Acknowledgements

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