

## THERMAL DEGRADATION PROCESS OF POLYSULFONE ARAMID FIBER

by

**Fang-Long ZHU<sup>a,b\*</sup>, Qian-Qian FENG<sup>a</sup>, Qun XIN<sup>a</sup> and Yu ZHOU<sup>a</sup>**

<sup>a</sup> College of Clothing, Zhongyuan University of Technology, Zhengzhou, China

<sup>b</sup> The Chinese People's Armed Police Forces Academy, Lanfang, China

Original scientific paper  
DOI: 10.2298/TSCI1405637Z

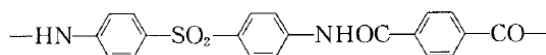
*Polysulfone aramid fiber is one kind of high temperature fibers. In the paper, thermal degradation behavior and kinetics of polysulfone aramid fiber were investigated by thermogravimetric analysis and differential thermogravimetric at different heating rates under nitrogen and air, respectively. The experimental results show that its initial degradation temperature is 375 °C in nitrogen and 410 °C in air at heating rate of 10 K/min. When temperature went to 800 °C, the fiber loses all mass in air. The mass losses in the stage showed that degradation of polysulfone aramid occurs in two-step process as could be concluded by the presence of two distinct exothermic peaks in differential thermogravimetric curves.*

**Key words:** polysulfone aramid fiber, thermal degradation, heating rate

### Introduction

In fire, firefighters, who assume the task of fire rescue, may encounter post flash fire. Clothing materials worn by firefighters will be ignited and then thermally pyrolyzed. Therefore the flame resistant characteristics of firefighters' protective clothing fabric are directly related to the rescue work and their own lives in a terrible fire field [1].

At present the most frequently used flame-resistant protective fiber materials used in firefighters' protective clothing in the Europe and America is Aramid 1313. Its market is mainly controlled by DuPont company in the United States and Japan Teijin company. Polysulfone aramid (PSA) fiber developed by Chinese researchers has been changed the situation that the dependence on import for high temperature resistant protective fiber materials in China. Polysulphonamide fiber is also called as aromatic polysulfonamide and polystyrene sulfone amide of dimethyl benzene amide fibers [2]. For PSA short fiber, the chemical structure of its polymer monomer can be specified as:



The electron cloud density on the amide nitrogen atoms significantly decreases because of strong electron withdrawing from sulfone groups (-SO<sub>2</sub>) existing in the backbone of PSA and benzene ring double bond conjugate. Also, it is difficult to oxidate for PSA fiber due to high oxidation rate of sulfur atoms in the backbone of aromatic sulfone molecules and the inertia of aromatic ring. Therefore the PSA fiber has rather excellent performance of flame retardant.

\* Corresponding author; e-mail: zhufanglong\_168@163.com

Much work on thermal behaviors of PSA fiber, has been reported in the domestic [3-5]. However, more attentions have been paid on the understanding of thermal stability of PSA fiber. The analysis of thermal degradation was also imperfect. Therefore, in this article we applied thermal analysis technique to analyze the thermal degradation process of PSA fiber in N<sub>2</sub> and air atmosphere.

## Experimental

Fiber samples consisting of PSA short fibers, which were provided by Shanghai Tanlon fiber Co. Ltd., were used in the paper. No pretreatments for the samples were conducted prior to testing. Thermogravimetric (TG) analysis/differential thermogravimetric (DTG) measurements were carried out on a Netzsch STA209F1 thermalgravimetric analyzer in dynamic nitrogen and air environment from room temperature to 900 °C. Flow rate was fixed at 20 ml/min and the kinetics experiments in N<sub>2</sub> were performed at several heating rates of 5, 10, 15, and 20 K/min. In air environment, the heating rate of 10 K/min was selected air flow with flow rate was 20 mL/min.

## Results and discussion

### Thermal decomposition

TGA is one of the most commonly used techniques to study the primary reactions of decomposition of solids. The kinetics of such reactions can be described by various equations by considering the special features of their mechanisms. The results of thermogravimetric experiments were expressed as conversion  $\alpha$ , defined as:

$$\alpha = \frac{m_i - m_t}{m_i - m_f} \quad (1)$$

where  $m_i$ ,  $m_t$ , and  $m_f$  are the initial mass of the sample, the mass of pyrolyzed sample, and the final residual mass, respectively.

### Thermal degradation of PSA fiber in N<sub>2</sub>

Thermogravimetric and DTG curve of PSA fiber at heating rate of 5, 10, 15, and 20 K/min. are shown in fig. 1. The pyrolysis of PSA in N<sub>2</sub> atmosphere can be roughly divided into four stages. In the first stage, mass loss rate was tiny prior to 100 °C. This was due to the release of physically adsorbed water. No significant mass change was found in the second

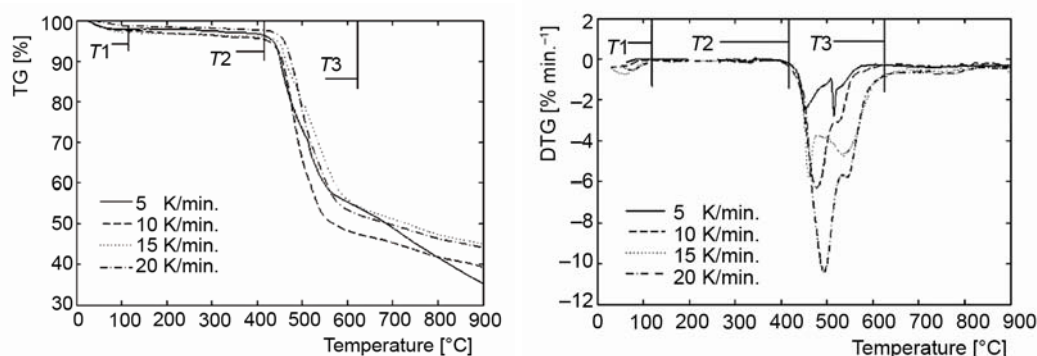


Figure 1. TG and DTG curve of PSA degradation in N<sub>2</sub> atmosphere

stage considered as transition one in the temperature range of  $T_1$  and  $T_2$ . Therefore, a mass loss rate platform was observed in the stage. The third one is the fast pyrolysis stage. There were two obvious mass loss peaks observed in this stage. This phenomenon can be explained by two reasons. One reason is that two peaks are caused by amide linkage and sulfone base fracture of PSA, respectively. The characteristics of sulfone groups ( $-\text{SO}_2$ ) in the backbone of PSA fiber is strongly electron-withdrawing, and its structure is quite stable. Only when temperature is rather high, the sulfone will rupture. A large number of amide group rupture can result in the largest mass loss peak. Another possible reason is that there are impurities or chain branched in the PSA pyrolysis process. The fourth stage for carbonization phase mainly is the slow decomposition process of residue after the temperature  $T_3$ . At this moment, the DTG curve changed slowly and TG curve was relatively flat.

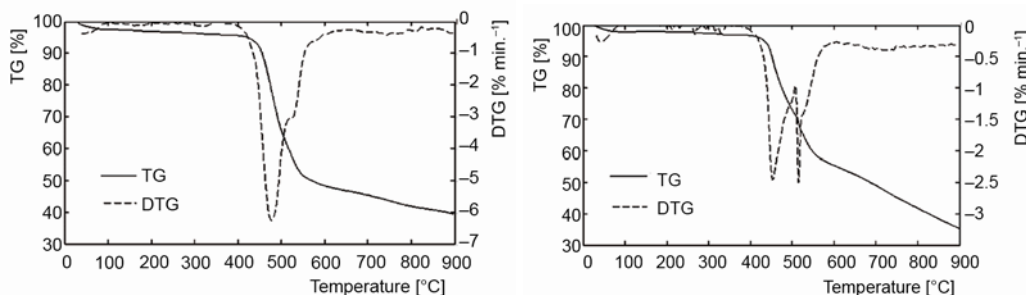
Generally speaking, the heating rate exerts both positive and negative influence on thermal degradation process. The response time of pyrolysis temperature for sample particles will shorter when the heating rate increases. High heating rate will benefit thermal degradation. However, the total reaction time will decrease and the conversion degree will also reduce. Simultaneously, thermal lag occurs due to the increased temperature difference between inside and outside of particle. Moreover, the outer particles diffused without in time will prevent the internal decomposition.

According to tab. 1, the initial decomposition temperature of PSA fiber was above  $400\text{ }^\circ\text{C}$ , and the pyrolysis rate was approximate to zero below  $400\text{ }^\circ\text{C}$ , as are shown in figs. 2 and 3. The PSA fiber kept relatively good stability, and mass loss was greater than 10% when the temperature is about  $460\text{ }^\circ\text{C}$ .

**Table 1. TG and DTG data of PSA**

Heating rate [ $\text{Kmin}^{-1}$ ]	$T_{5\%}$ [ $^\circ\text{C}$ ]	$T_{10\%}$ [ $^\circ\text{C}$ ]	$T_{50\%}$ [ $^\circ\text{C}$ ]	$T_{\text{max}}$ [ $^\circ\text{C}$ ]	$\text{CR}_{800\text{ }^\circ\text{C}}$ [%]
5	434.6	451.7	687.6	515.3	41.8
10	423.9	455.8	570.2	477.2	41.9
15	444.4	463.1	733.9	459.9	47.4
20	459.4	475.4	692.0	493.9	46.4

$T_{5\%}$ ,  $T_{10\%}$ ,  $T_{50\%}$ , respectively, the temperature when the mass loss rate was 5%, 10%, and 50%;  $T_{\text{max}}$  denote the temperature of the maximum weight loss rate;  $\text{CR}_{800\text{ }^\circ\text{C}}$  denote residue under  $800\text{ }^\circ\text{C}$ .



**Figure 2. TG and DTG curves at heating rate of 5 K/min, 10 K/min**

It was seen from these figures that its complete pyrolysis occurred when temperature reached  $800\text{ }^\circ\text{C}$  and at the end of the degradation more than 40% residual remained. The benzene ring structure is too stable to broken, and the residual contain a lot of carbon element at this moment. The PSA fiber have very excellent thermal stability and the thermal decomposition temperature was above  $400\text{ }^\circ\text{C}$ . These results indicated that PSA fibers could be used as fire protective clothing materials.

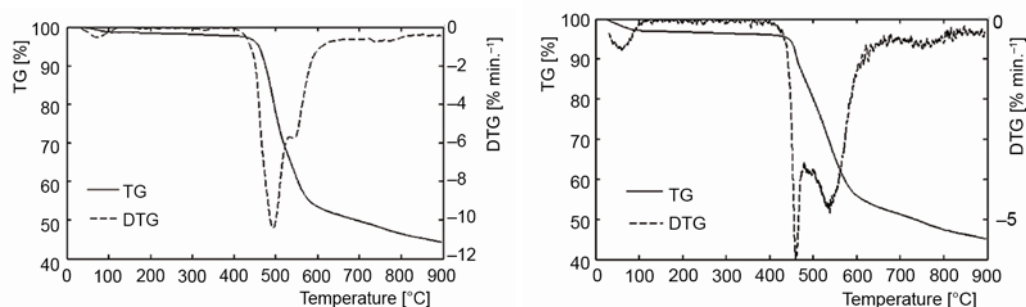


Figure 3. TG and DTG curves at heating rate of 15 K/min, 20 K/min

#### Thermal degradation of PSA fiber in air atmosphere

Figure 4 shows the mass loss rate of PSA fiber under air atmosphere. It is observed that the DTG curve was fluctuated greatly with the temperature. This is because of the participation of the other gases besides oxygen in the pyrolyzed reaction. In order to make the trend of the weight loss rate of PSA fiber under air atmosphere more clear, the Matlab software was used to reduce the noise for the DTG curve, as was shown in fig. 5.

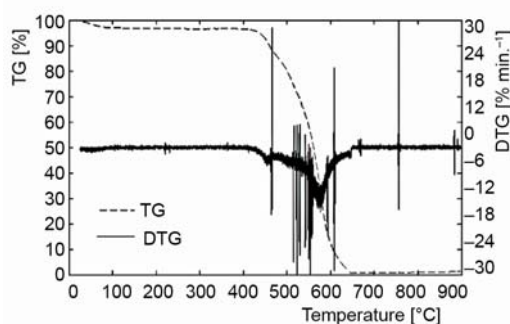


Figure 4. TG and DTG curves in the air before being processed

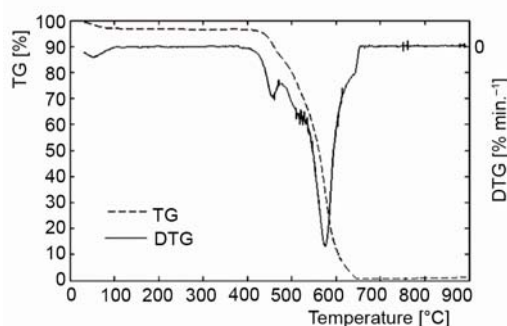


Figure 5. TG and DTG curves in the air after being processed

Table 2. TG and DTG data of PSA in air atmosphere

Heating rate [Kmin <sup>-1</sup> ]	$T_{5\%}$ [°C]	$T_{10\%}$ [°C]	$T_{50\%}$ [°C]	$T_{\max}$ [°C]	CR <sub>800 °C</sub> [%]
10	437.28	459.43	480.63	587.3	0.90377

$T_{5\%}$ ,  $T_{10\%}$ ,  $T_{50\%}$ , respectively, the temperature when the weightlessness rate was 5%, 5 % and 50%;  $T_{\max}$  denote the temperature of the maximum weight loss rate; CR<sub>800 °C</sub> denote residue under 800 °C.

When the mass loss rate was 5% and 10% at the heating rate of 10 K/min., there was little difference between the two environments. However, it was very different under the condition that the mass loss rate was 50% (tab 2.). The temperature is 480.6 °C in air atmosphere and 570.2 °C in N<sub>2</sub>. According to the reaction rate, it can be found that PSA decomposition reaction is more intense in oxygen than that in N<sub>2</sub>. The complete reaction occurred in air environment. This can be validated by the residual percentage of 0.9%. Similar with pyrolysis in N<sub>2</sub>, PSA degradation in the air could be also divided into four stages. But little carbonaceous residual remained compared with that in N<sub>2</sub> due to benzene fracture resulting in small molecules in the final decomposition stage.

## Conclusions

The initial decomposition temperature of PSA located between 423.9-459.4 °C and PSA stabled up in the range of 620-650 °C. At the end of the degradation almost 35-45% residual remained. The thermal degradation process can be divided into drying stage, transition stage, fast pyrolysis and carbonization stage. In air environment, this process was also made up of four stages. But little carbonaceous residual remained compared with that in N<sub>2</sub> due to benzene fracture resulting in small molecules in the final decomposition stage.

## Acknowledgments

The work is supported financially by the joint project from the Henan – Provincial and the China – National Natural Science Foundations under Grant No. U1304513 and Rescuing Technology Foundation of the Ministry of Public Security of China under Grant No. KF201301.

## References

- [1] David, A. T., George, V. H., Research in Protective Clothing for Firefighters: State of the Art and Future Direction, *Fire Technology*, 35 (1999), 2, pp. 111-130
- [2] Wang, J. M., Development Survey and Market Prospect of Polysulphonamide Fiber, *Hi-Tech Fiber & Application*, 33 (2008), 6, pp. 39-45
- [3] Xin, B. J., *et al.*, Study on the Thermal Behavior of Polysulfonamide/Multi-Wall Carbon Nanotube Composite, *Journal of Industrial Textile*, 42 (2012), 4, pp. 434-445
- [4] Wang, Z. H., Shen, H. G., Tensile Behavior of Polysulfonamide Fiber after Chemical Treatment, *Energy Procedia, Part A*, 16 (2012), pp. 432-437
- [5] Ye, J. Q., *et al.*, Thermal Stability Analysis of PSA Fiber, *Journal of Donghua University*, 31 (2005), 2, pp. 13-16