Thermal degradation behaviours of flame-retardant polycarbonate containing potassium diphenyl sulfonate and polymethylphenylsilsesquioxane

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Abstract: Potassium diphenyl sulfonate (KSS) and polymethylphenyl silsesquioxane (PMPSQ) were proved to be effective flame retardants for PC by the LOI test and UL-94 measurements. The thermal degradation behaviours were investigated by TGA and flame-retardant mechanism of KSS/PMPSQ/PC system was studied by the kinetic analysis methods including Kissinger method and Flynn-Wall-Ozawa method. The results showed that the activation energies of flame-retardant PC (FRPC) were lower than that of pure PC at lower degree of conversion, which indicated that the KSS and PMPSQ both promoted the thermal degradation of PC in the early and middle stages. Flynn-Wall-Ozawa method further revealed that the addition of the flame retardant PMPSQ increased the activation energy of FRPC thermal degradation in the final stage, which illustrated that the PMPSQ stabilized the char residues and improved the flame retardancy of FRPC in the thermal degradation. Therefore, the improved flame-retardant behaviours of KSS and PMPSQ on PC were achieved.

Introduction

Polycarbonate (PC) is widely used in automotive, rail and aircraft, office equipment, data recording media, medical equipment and glazing, due to its excellent transparency, flame retardancy, electrical and mechanical properties [1, 2]. However, the flame retardancy of PC cannot meet the demand for electron and electric applications, yet [3]. To make it possible, various halogen flame retardants have been used, such as brominated aromatic compounds. But in recent years, the use of halogen flame retardants is being restricted because of environmental problems [4, 5].

The addition of alkali or alkaline earth metal salts of inorganic sulphur compounds in very low levels (well below 1wt%) has been found to be effective in flame-retardant PC. The investigations show that when present in catalytic amounts, aromatic sulfonates are capable of increasing the thermal degradation rate of PC and accelerating the formation of a carbon layer at the burning surface [6, 7]. However, the use of these materials alone is not satisfactory especially in thin walled articles. A series of publications and patents indicate the combinations between the sulfonate salts and other flame retardants are effective [8-10]. The beneficial effect of polysilsesquioxanes, especially branched polymethylphenylsilsesquioxane (PMPSQ), in combination with metal salts of organosulfonic acid has been discovered. In view of the halogen-free approach taking more attention, branched PMPSQ was recently
reexamined and studied in detail [11-13]. Liu S M, et al. [14] has reported the flame retardancy of PC containing KSS, polyaminopropylphenylsilsesquioxane (PAPSQ), and found that the combination decreased the activation energy of PC degradation and elevated the thermal degradation rate of PC to ensure the formation of an insulating carbon layer. Since PAPSQ from the hydrolytic condensation of APS and PTMS is a reactive-type flame retardant, it cannot present the common polysilsesquioxanes, which are additive-type flame retardants and have been proved more efficient and convenient in flame-retardant PC [15, 16]. Moreover, the present researches concentrate on the combination effect of the sulfonate salts and PMPSQ, paying little attention to the thermal degradation behaviours of flame-retardant process.

In this paper, we will study the effect of KSS and PMPSQ on flame retardancy of PC and try to reveal the thermal degradation behaviours and flame-retardant mechanism of KSS/PMPSQ/PC system through the TGA measurement and kinetics analysis methods.

**Results and discussion**

**Flammability**

The LOI test and UL-94 measurement are both direct and practical methods and widely used to evaluate the flame retardancy of materials, especially for flame-retardant polymer. The influence of KSS content on the LOI value of PC is shown in Tab. 1. It can be seen that the LOI of pure PC (S₀) is about 26.3 and a small addition of KSS (0.4 wt%, S₀.₄) causes a sensible LOI increment of PC. When the content of KSS arrives at 0.7 wt%, the LOI value of the PC seems to reach the maximum 34.4, implying perhaps a specific chemical interaction with the polymeric substrate. When the content of KSS is increased, the flame-retardant character of the mixtures containing KSS beyond 1.0 wt% becomes poor, which indicates that a further increment of the LOI value of PC cannot be achieved by increasing the content of KSS. This behaviour of KSS is similar to that of other organic metal salts although the concentration is different. It has been confirmed that KSS promotes the char layer on the surface by quickly degrading PC in lower temperature, and the thermal degradation rate of this expanded char is responsible for the increase of the flame retardancy of PC. When the KSS loading level is less than 0.7 wt% (optimum value), the rate of the degradation process is matching to the crosslinking char formation. Therefore, the flame retardancy of PC was improved. In contrast, it is possible that the LOI values of S₁.₀ and S₁.₆ become low. In that case, quickly degrading PC cannot form more amount of charring layers to improve the flame retardancy and the formed charring layers was destroyed by the excessive rate of thermal degradation process.

**Tab. 1.** Flame retardancy of KSS/PC mixture with different contents of KSS.

<table>
<thead>
<tr>
<th>Samples</th>
<th>S₀</th>
<th>S₀.₄</th>
<th>S₀.₇</th>
<th>S₁.₀</th>
<th>S₁.₃</th>
<th>S₁.₆</th>
<th>S₂.₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>LOI</td>
<td>26.3</td>
<td>33.5</td>
<td>34.4</td>
<td>33.7</td>
<td>32.1</td>
<td>30.6</td>
<td>29.7</td>
</tr>
<tr>
<td>UL-94(rating)</td>
<td>V-2</td>
<td>V-0</td>
<td>V-0</td>
<td>V-0</td>
<td>V-0</td>
<td>V-1</td>
<td>V-1</td>
</tr>
</tbody>
</table>

Sₙ, The subscript numbers are the content of KSS added to the PC.
The influence of the PMPSQ content on the LOI value of PC is shown in Tab. 2. It can be obtained that the LOI values of PC increased with the increasing of PMPSQ content and enhanced up to 30.4 from 26.3 when the content of PMPSQ reaches 2.0 wt%.

**Tab. 2.** Flame retardancy of PMPSQ/PC mixture with different contents of PMPSQ.

<table>
<thead>
<tr>
<th>Samples</th>
<th>S₀+0</th>
<th>S₀+0.4</th>
<th>S₀+0.7</th>
<th>S₀+1.0</th>
<th>S₀+1.3</th>
<th>S₀+1.6</th>
<th>S₀+2.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>LOI</td>
<td>26.3</td>
<td>27.2</td>
<td>27.9</td>
<td>28.6</td>
<td>29.2</td>
<td>29.7</td>
<td>30.4</td>
</tr>
<tr>
<td>UL-94 (rating)</td>
<td>V-2</td>
<td>V-2</td>
<td>V-2</td>
<td>V-2</td>
<td>V-1</td>
<td>V-1</td>
<td>V-1</td>
</tr>
</tbody>
</table>

Sₙ, The subscript numbers are the content of PMPSQ added to the PC.

The flame retardancy of PC containing KSS and PMPSQ is also investigated (Tab. 3), where the total content of these two flame retardants is kept at 2.0 wt%. Whatever the KSS concentration is, the LOI of PC containing KSS and PMPSQ is higher than the sample using equivalent KSS alone. When 0.7 wt% KSS and 1.3 wt% PMPSQ are added to the PC, the LOI value of PC arrives at 35.6. It is illustrated that the effect of two flame retardants (KSS and PMPSQ) adding into PC is greater than the effect of each flame retardant individually, which means that KSS and PMPSQ have a combined effect on the flame retardancy of PC.

**Tab. 3.** Flame retardancy of KSS/PMPSQ/PC mixture with different contents of KSS and PMPSQ.

<table>
<thead>
<tr>
<th>Samples</th>
<th>S₀+2.0</th>
<th>S₀.4+1.6</th>
<th>S₀.7+1.3</th>
<th>S₁.0+1.0</th>
<th>S₁.3+0.7</th>
<th>S₁.6+0.4</th>
<th>S₂+0.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>LOI</td>
<td>30.4</td>
<td>34.8</td>
<td>35.6</td>
<td>34.2</td>
<td>32.4</td>
<td>30.9</td>
<td>29.7</td>
</tr>
<tr>
<td>UL-94 (rating)</td>
<td>V-1</td>
<td>V-0</td>
<td>V-0</td>
<td>V-0</td>
<td>V-0</td>
<td>V-1</td>
<td>V-1</td>
</tr>
</tbody>
</table>

Sₙ₊ₘ, The subscript numbers are the content of KSS and PMPSQ added to the PC, respectively.

**Thermal analysis**

![TGA and DTG curves of PC under air and N₂.](image)

**Fig. 1.** TGA and DTG curves of PC under air and N₂.
The TGA and DTG curves of PC under a nitrogen and air atmosphere at the rate of 10 °C/min are shown in Fig. 1. In comparison with degradation in nitrogen, weight loss in air begins at 400 °C, which is about 50 °C earlier than in nitrogen. The end of the main degradation step of PC occurs at about 510 °C in nitrogen, leaving a residual weight of about 20%. In air atmosphere, there exist two peaks in thermal weight loss rate curve, one emerges at 485 °C and the other is at 600 °C. It has been noted that the weight loss rate in air is slower than that in nitrogen in the main weight loss region. The residue remains constant up from 540 °C to 700 °C in nitrogen, but it continues to degrade in air, eventually going to zero.

![Fig. 2. TGA and DTG curves of PMPSQ and KSS under N₂.](image)

The thermal degradation of single PMPSQ and KSS at a heating rate of 10 °C/min in nitrogen atmosphere is depicted in Fig. 2. KSS shows rarely no weight loss up to 400 °C and decomposition occurs in multiple regions with the maximum rate of degradation around 512 °C.

![Fig. 3. TGA and DTG curves of KSS/PC mixture.](image)
According to the TGA result, the temperature range of the main degradation process before 700 °C is 460-600 °C and the residue of KSS at 700 °C is 63.8%. To the contrary, the TGA and DTG curves for PMPSQ reveal that a slow weight loss occurs at 200 °C mainly due to the condensation of residual silanols groups, followed by a rapid weight loss due to the degradation of phenyl and methyl groups [17], and the temperature of maximum weight loss rate emerges at 524 °C, resulting in 58.3% residue at 700 °C. From the DTG curves, it can be obtained that the major degradation of KSS and PMPSQ is almost in the same temperature range as pure PC, and higher residue amounts are exhibited by KSS and PMPSQ.

The influence of concentrations of KSS on thermal degradation of PC is examined. The TGA and DTG curves of PC with various amounts of added KSS are shown in Fig. 3. The flame retardant KSS has high decomposition temperature (>400 °C). As evidenced from the curves, KSS causes thermal destabilization of polycarbonate and the maximum rate of weight loss decreases as the amount of flame retardant additives increases. The residues of PC with various amounts of added KSS at 700 °C are similar to these of pure PC.

![Fig. 3. TGA and DTG curves of KSS/PMPSQ/PC mixture.](image)

The TGA and DTG curves of PC containing KSS or both KSS and PMPSQ are shown in Fig. 4. It can be found from the DTG curves that the thermal degradation temperature and the maximum thermal decomposition rate of sample $S_{0.7+1.3}$ are both lowest in the all samples, which should be relative to the flame retardancy of the samples. On the other hand, it also can be observed that the residues of the systems with various amounts of added KSS and PMPSQ at 700 °C are different. In a comparison of $S_{0.7}$ with $S_{0.7+1.3}$, there is 1.75% more residue amount of the latter than of the former. The same case can be observed between $S_{1.3}$ and $S_{1.3+0.7}$. This result suggests that the PMPSQ with methyl and phenyl could induce crosslinking reactions of PC during the thermal degradation process, and promote the formation of the char which might play an important role for the flame retardancy of KSS/PMPSQ/PC system. In fact, the LOI values of $S_{0.7+1.3}$ and $S_{1.3+0.7}$ are higher than those of $S_{0.7}$ and $S_{1.3}$, respectively. It seems that the higher LOI values are relative to the larger residues. It is apparent that the residue at 700 °C is the result of charring, which
further confirms that the addition of PMPSQ can cause the quantitative increase of the carbon layer, even if present in a small amount.

**Thermal degradation kinetics**

The TGA and DTG curves of samples for PC (S<sub>0</sub>) and FRPC (S<sub>0.7</sub>, S<sub>0.7+1.3</sub>) at different heating rates in a nitrogen flow are shown in Fig.s 5-7. All curves indicate that samples exhibit a thermal decomposition in one step, resulting in a residue of approximately 20 wt% at a heating rate of 10 °C/min, only but the sample of S<sub>0.7+1.3</sub> whose residue reaches 22% at 700 °C. Furthermore, it also can be seen that the onset decomposition temperature enhances with the increasing of heating rates.

**Fig. 5.** TGA and DTG curves of PC at different heating rates.

**Fig. 6.** TGA and DTG curves of PC with 0. wt% KSS at different heating rates.

The combustion is a sequence of complex physical and chemical process; for polymer it is a kind of thermal degradation process. Thus, the kinetic parameters of thermal degradation can be used to characterize the thermal stability of polymer, and
the activation energy \((E)\) can be considered as a semiquantitative factor. To study the thermal degradation processes of PC and FRPC, the Kissinger method and Flynn-Wall-Ozawa method are both used to deal with their TGA and DTG curves.

1) Kissinger method

The Kissinger expression is as follows [18]:

\[
\ln\left(\frac{\beta}{T_{\text{max}}^2}\right) = \left\{ \ln \frac{AR}{E} + \ln \left[ n(1-a_{\text{max}})^{n-1} \right] \right\} - \frac{E}{RT_{\text{max}}}
\]

Where \(\beta\) is the heating rate, \(T_{\text{max}}\) is the temperature of the peak rate, \(A\) is the absorbance, \(R\) is a gas constant, \(\alpha\) is the conversion rate and \(n\) is the empirical order of reaction.

![Fig. 7. TGA and DTG curves of PC with 0.7 wt% KSS and 1.3 wt% PMPSQ at different heating rates.](image)

The peak rate temperatures determined at different heating rates allow the activation energy to be calculated by the Kissinger method. Plotting the natural logarithm of \(\ln(\beta/T_{\text{max}}^2)\) against the reciprocal of the absolute temperature \((1/T_{\text{max}})\), the slope of the resulting line is given by \(-E/R\), which allows the activation energy \(E\) to be obtained.

**Tab. 4.** Kinetic data for degradation of PC and FRPC by Kissinger method.

<table>
<thead>
<tr>
<th>Samples</th>
<th>(T_{\text{max}}) /(^\circ\text{C})</th>
<th>(E)/kJ•mol(^{-1})</th>
<th>(\ln A)/min(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>S(_0)</td>
<td>484 502 520 537</td>
<td>186.54</td>
<td>21.07</td>
</tr>
<tr>
<td>S(_{0.7})</td>
<td>460 474 491 514</td>
<td>171.41</td>
<td>19.64</td>
</tr>
<tr>
<td>S(_{0.7+1.3})</td>
<td>435 449 471 494</td>
<td>143.68</td>
<td>15.82</td>
</tr>
</tbody>
</table>
The activation energies for the thermal degradation processes of PC and FRPC, predicted by Kissinger kinetics theory are displayed in Tab. 4. Note that the activation energies for FRPC (171.41 kJ•mol⁻¹, 143.68 kJ•mol⁻¹) are lower than that for PC (186.54 kJ•mol⁻¹). This means that the flame retardant additives are effective to promote the degradation process of PC. Also, the activation energy of S₀.₇+₁.₃ is lowest in these three PC systems. It may be concluded that activation energy of thermal degradation of PC is largely decreased by the combined effect of KSS and PMPSQ, resulting in an accelerated thermal degradation to promote the formation of an insulating carbon layer, and improved flame-retardant behaviours of PC compositions is obtained.

2) Flynn-Wall-Ozawa method

Because of the relative limitation of the Kissinger method, its data can only provide information at the peak rates. To make it possible, the TGA data are further studied by Flynn-Wall-Ozawa kinetic analysis method. Flynn–Wall–Ozawa method is one of the integral methods that can determine the activation energy without knowledge of reaction order and differential data of TGA [19-20]. With the application of that method, more informative kinetic parameters can be obtained. The equation of decomposition can be expressed as follows:

\[
\lg(\beta) = \lg \frac{AE}{g(a)}R - 2.315 - 0.457 \frac{E}{RT}
\]  

(2)

The above equation shows that \( \lg(\beta) \) is linearly proportional to \( 1/T \). The activation energy for any particular degree of decomposition can then be determined by a calculation of the slope from the \( \lg(\beta) - 1/T \) plots. These data for the activation energies are summarized in Tab. 5 and the conversion values (\( a \)) of 0.02, 0.05, 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80, 0.90 and 0.95 are selected in this study.

Tab. 5. Kinetic data for degradation of PC and FRPC by Flynn-Wall-Ozawa method.

| \( a \) | \( E/\text{kJ•mol}^{-1} \) |
| --- | --- | --- |
|  | PC | PC+0.7%KSS | PC+0.7%KSS+1.3%PMPSQ |
| Early stage | | | |
| 0.02 | 161.39 | 156.86 | 125.25 |
| 0.05 | 158.39 | 155.50 | 136.18 |
| 0.10 | 175.67 | 158.83 | 144.73 |
| 0.20 | 183.85 | 162.75 | 148.69 |
| 0.30 | 186.25 | 167.51 | 150.89 |
| 0.40 | 191.81 | 170.89 | 154.76 |
| Middle stage | | | |
| 0.50 | 197.05 | 173.55 | 158.82 |
| 0.60 | 201.65 | 175.98 | 163.75 |
| 0.70 | 207.51 | 179.90 | 171.20 |
| 0.80 | 215.66 | 183.75 | 184.83 |
| Final stage | | | |
| 0.90 | 234.36 | 194.18 | 290.38 |
| 0.95 | 266.52 | 260.94 | 399.62 |

It can be observed that the PC and FRPC all tend to exhibit three stages of activation energies in decomposition process. In the early stage, the loss of the light degradation compounds occurs such as carbon dioxide and the PC completes this stage before 10% weight loss generally [21,22]. After the early stage, the activation
energy values of FRPC rise as degradation proceeds, and then remain constant up to 80%, which means the stabilities of the intermediate products are rather similar. It can be seen that the activation energies of the FRPC are lower than that of pure PC at lower degree of degradation. The resulting data, together with the analysis of the activation energies, indicate that the pure PC has better thermal stability than FRPC in this stage. In other words, the additives KSS and PMPSQ both cause faster degradation of the FRPC in the early and middle stages.

But in the final stage (>80%), the PC systems of S₀, S₀.7 and S₀.7+1.3 are different in degradation process. With the different components of the flame-retardant additives, the addition of flame retardant PMPSQ quickly increases the activation energy of FRPC thermal degradation and has been greater than the PC systems of S₀ and S₀.7. It indicates that the flame retardant PMPSQ decreases the degradation behaviours of FRPC, which further reveals that the PMPSQ has the function of stabilizing the char residue and improving the flame retardancy of FRPC in the final period of thermal decomposition process. So it can be concluded from the kinetic analysis that the flame-retardant behaviours of KSS and PMPSQ on FRPC have been achieved.

Conclusions

KSS and PMPSQ have been proved to be effective flame retardants for PC by the LOI and UL-94 measurements. The kinetics analysis shows that the activation energies of FRPC are lower than that of pure PC at lower degree of degradation, which indicates that the additives KSS and PMPSQ both accelerate thermal degradation of FRPC in the early and middle stages. The Flynn-Wall-Ozawa method indicates that the addition of the flame retardant PMPSQ further increases the activation energy of FRPC in the final stage of thermal degradation, revealing that the flame retardant PMPSQ also stabilizes the char residue and improves the flame retardancy of FRPC in the final period of thermal degradation process, and improved flame-retardant behaviours of KSS and PMPSQ on FRPC are achieved.

Experimental part

Materials

The polycarbonate (PC) used was obtained from General Electric Company, China (Lexan-141). Potassium diphenylsulfone sulfonate (KSS) and polytetrafluoroethylene (PTFE) applied in this study were both supplied by Taiwan Chembridge International Corporation. The polymethylphenylsilsesquioxane (PMPSQ) synthesized by hydrolysis and condensation reaction of methylphenyldimethoxysilane (MPDS) and phenyltrimethoxysilane (PTMS), consisted of 82 mol% PTMS and 18 mol% MPDS units. Its end groups were mainly methyl’s with a few hydroxyls and molecular weight was 3.774e+4. The ratio of organic groups to silicon atoms (R/Si) which was used to indicate the branched extent of a polysilsesquioxane structure was 1.18.

Preparation

The PC pellets, anti-dripping agent PTFE and flame-retardant agents (fine dried PMPSQ, KSS, or both of them) were mixed in a high-speed mixer for 5 min and the content of PTFE was kept 0.3 wt%. Then the mixture was extruded by a MAPRE 2.83.0 41 twin-screw extruder through a strand die and palletized, where cylinder temperature was controlled at 290 °C and screw speed was 120 rpm. The resulting
pellets were dried at 120 °C for 12 h, and then moulded into test specimens at an injection temperature of 310 °C by a CJ-80E injection-molding machine.

Characterization

The limiting oxygen index (LOI) was measured on an oxygen index instrument JF-3 produced by Jiangning Analysis Instrument Factory and performed according to GB2406-93 of “Plastics-Determination of flammability by oxygen index” and the precision of this method is 0.2. Flame retardancy of test specimens was examined in accordance with UL94 method. Thermogravimetric analysis (TGA) was performed on a TA Q600 thermal analyzer. Around 10 mg sample was heated from 50 °C up to 700 °C at a heating rate of 10 °C /min (or 5, 20, 40 °C /min) under a nitrogen flow at a rate of 50 ml/min.

References