Reduction in the flammability of polystyrene with the use of phosphonic acid derivatives

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Fires resulting from the ignition and combustion of polymeric materials annually do a great deal of damage and lead to loss of life. Data on the statistics of fires are presented in Table 1. Experience of fire safety measures indicates that up to 80% of fires arise from low-calorie sources of ignition (sparks, burning matches, cigarettes, etc.). Over 60% of fires occur on account of the ignition of polymeric materials and wooden articles.

Thermoplastic polymeric materials, in particular polystyrene (PS), are used in different sectors of the national economy for the manufacture of composite materials used in motor vehicles and in the home. In addition, the problem of lowering their flammability and smoking capacity and the toxicity of their combustion and pyrolysis products, determining the ecological impact, has not been fully tackled.

Lowering the flammability of PS is a complex task because the temperature of the start of its thermal degradation is 250°C, the temperature of its half-decomposition is 364°C, and at 450°C it is gasified entirely with the liberation of highly volatile, flammable products. The thermolysis of PS proceeds at a fairly high rate. During the combustion of polystyrene, black smoke containing soot particles is formed. The specific heat of combustion of polystyrene is 43 MJ/kg, which is similar to that of crude oil [1].

Investigations carried out earlier showed that, to lower the flammability of PS, most promising is the method of introducing combustion inhibitors (CIs) into the polymer melt during moulding [2]. CIs of different composition are used for this purpose.

The method of producing synthetic materials with lower flammability by introducing CIs into the polymer melt during moulding makes it possible to retain the existing technology for producing articles, is characterised by high economy, and creates the prerequisites for the development of ecologically clean processes, and it also ensures high resistance of the fireproofing effect to wet treatments.

In 2001, the demand for CIs amounted to 1.1 Mt. In the main, three types of CI are used: inorganic, halogen-containing, and phosphorus-containing.

In recent years, great attention has been paid to the development of ecologically clean, effective fire-retarding systems lowering the smoke and toxicity of thermolysis

<table>
<thead>
<tr>
<th>Table 1 Data on statistics of fires</th>
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<tbody>
<tr>
<td><strong>Year 2000</strong></td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>Fires</td>
</tr>
<tr>
<td>Loss (thousand roubles)</td>
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<td>Fatalities</td>
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products. In view of this, the application of previously widely used halogen-containing CIs has been discontinued, since when they are used it is possible for such harmful substances as HCl, HBr, and sometimes such highly toxic compounds as dioxins to be emitted [3].

Phosphorus-containing CIs are promising since they lower, along with flammability, the soot formation, which is particularly urgent for PS, the combustion of which is accompanied with the release of a large amount of smoke and soot.

Investigations carried out earlier in the faculty showed the highly efficient fireproofing action of phosphonic acid derivatives for such carbon-chain polymers as polyethylene and polypropylene [4]. The possibility of using phosphonic acid derivatives to lower the flammability of PS was investigated.

Phosphonic acid derivatives possess a higher heat stability compared with phosphoric acid derivatives, which is one of the requirements laid down for CIs introduced into the melt during moulding.

The phosphonic acid derivatives selected were ammonium salt of methylphosphonic acid amide, which is contained in fireproofing agent T-2, and ammonium salt of aminotrimethylene phosphonic acid (ASAMP) of the following formulae:

- T-2: \( \text{NH}_2 \text{CH}_3 \text{P} = \text{O} + 2\text{NH}_2\text{Cl} \)
- ASAMP: \( \text{N} \left( \text{CH}_3\text{P} = \text{ONH}_4 \right)_3 \)

The elemental composition and thermophysical characteristics of phosphorus- and nitrogen-containing CIs are presented in Table 2. The thermophysical characteristics were investigated by means of differential scanning calorimetry (DSC) and differential thermogravimetric analysis (DTA).

The CIs selected are characterised by a high content of phosphorus and nitrogen which are capable of inhibiting the process of thermolysis of the polymer.

The results of DTA of the CIs selected indicate that they break down with a considerable endothermic effect. It is known that, the higher the value of the endothermic effect, the more intensive will be the heat absorption during combustion of the polymer by breakdown of the CI.

The main differences in the CIs used is their behaviour at high temperatures. Data of thermogravimetric analysis (TGA) of the CIs selected are presented in Table 3.

From the data it follows that ASAMP breaks down at a maximum rate that is half that of fireproofing agent T-2 and in a higher temperature region. At 700°C, the carbonised residue (CR) of ASAMP is considerably higher than the CR of fireproofing agent T-2, which indicates the higher carbonisability of ASAMP which is a polyfunctional phosphorus- and nitrogen-containing compound.

The given CIs and also their mixture (in a 1:1 ratio) were introduced into the polymer melt during moulding.

The fireproofing indices of the modified PS are presented in Table 4.

PS formed with the addition of a mixture of CIs is characterised by the highest fireproofing indices (OI = 28.4%). Consequently, the process of thermolysis, which is accompanied with the release of volatile flammable compounds, slows down.

The selected phosphorus-containing compounds alter the direction of thermolysis in condensed phase. In this connection, an investigation was made of the process of carbonisation of the selected fireproofing systems and PS modified with them at 350, 400, and 450°C, and the magnitude, composition, and structure of the CR formed during pyrolysis were analysed. The effect of the CIs on the yield of CR formed during the thermolysis of modified PS at different temperatures is given in Figure 1.

### Table 2: Elemental composition and thermophysical characteristics of phosphorus- and nitrogen-containing CIs

<table>
<thead>
<tr>
<th>CI</th>
<th>( T_{\text{mol}} ) °C</th>
<th>( \Delta H_{\text{mol}} ) kJ/kg</th>
<th>( \Delta H_{\text{endo}} ) kJ/kg</th>
<th>P</th>
<th>N</th>
<th>C</th>
<th>H</th>
<th>( E_{\text{act}} ) kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASAMP</td>
<td>231</td>
<td>131</td>
<td>1890</td>
<td>26.6</td>
<td>16.0</td>
<td>10.3</td>
<td>5.9</td>
<td>118</td>
</tr>
<tr>
<td>T-2</td>
<td>202</td>
<td>148</td>
<td>2120</td>
<td>13.6</td>
<td>21.1</td>
<td>5.9</td>
<td>7.8</td>
<td>69</td>
</tr>
</tbody>
</table>

### Table 3: Data of TGA of phosphorus- and nitrogen-containing CIs

<table>
<thead>
<tr>
<th>CI</th>
<th>( T_{\text{start breakdow}} ) °C</th>
<th>( T_{\text{max breakdow}} ) °C</th>
<th>( V_{\text{max}} ) mg/min</th>
<th>CR, % at 700°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-2</td>
<td>210</td>
<td>350</td>
<td>8.6</td>
<td>14</td>
</tr>
<tr>
<td>ASAMP</td>
<td>250</td>
<td>390</td>
<td>4.2</td>
<td>54</td>
</tr>
</tbody>
</table>
It was shown that the initial PS is gasified almost entirely at 450°C, whereas PS containing ASAMP forms the carbonised residue of greatest mass — 15.2%. PS modified with a mixture of CIs forms a carbonised residue of lower mass during thermolysis but has greater density and strength, which governs its high protective properties.

An investigation of the phosphorus content in the CR of PS composites showed that the greatest amount of phosphorus is contained in the CR produced during the thermolysis of a polymer modified with a mixture of the given CIs at a temperature of 450°C (Figure 2).

It is known that, during thermal oxidation, phosphorus-containing substances form meta- or polyphosphonic acids. The retention of phosphorus in the CR at 450°C indicates the formation of polyphosphonic acids which are noted for low volatility and are effective catalysts for the formation of graphite-like substances on the surface of the burning polymer.

An investigation of the content of phosphonic acid groups in the CR of PS composites showed that at 450°C the amount of the indicated groups in the CR of PS containing a mixture of CIs amounts to 10%, which is lower than in the CR of PS modified with ASAMP (Figure 3). Consequently, during thermolysis, polyphosphonic acids of greater molecular weight are formed, since more phosphorus remains in the CR.

It was established that, when CIs are used to modify PS, synergy if observed, consisting in an increase in the CR yield during the thermolysis of the composites produced (Figure 4). This was confirmed by subtracting from the CR of the composite the CR formed during thermolysis of the CIs, and the greatest synergism is characteristic of a PS composite containing a mixture of CIs. This behaviour pattern can be explained by the fact that the CI mixture inhibits the thermolysis of PS in a fairly wide temperature range (from 250 to 400°C) within which the selected CIs break down.

The introduction into PS of a mixture of CIs (15 wt.% of the polymer) makes it possible to produce a material of flame resistance class V-1. The given flame-retarding system can be recommended for practical use.
Figure 4 Influence of type of combustion inhibitor on carbonisation of polystyrene: □ CR of composites; ■ CR minus CR of CI

REFERENCES

2. V. V. Kopylov et al., Polymeric materials of reduced flammability (Ed. A. N. Pravednikov), Khimiya, Moscow, 1986, 250 pp.

(No date given)