Preparation and Properties of Paraffin/Polyurethane Foams Composite with Flame Retardant as Thermal Energy Storage Materials
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Abstract-Thermal energy storage plays an important role in energy conservation, and can be applied in many areas. Paraffin/polyurethane foams composite with flame retardant as thermal energy storage materials were prepared by absorbing paraffin in honeycomb structure of polyurethane rigid foams. These composites provide a new energy saving materials, which can be used for building heating/cooling systems, and the composites can also enhance the thermal comfort for residents. The attempt of polyurethane’s heat absorption capacity. They are also trapped within the honeycomb like structure developing insulation materials, they are highly competitive. The air insulation as the ultimate energy savers. Compared with other Polyurethane rigid foams have been widely used for thermal energy storage materials were prepared by absorbing paraffin/polyurethane foams composite. The compositions of paraffin, polyurethane (PU), and flame retardant in the composites are listed in Table I. Four kinds of paraffin/polyurethane foams composite were prepared, denoted PCM-1, PCM-2, PCM-3, and PCM-4. The compositions of paraffin, PU, and flame retardant in the composites are listed in Table 1.

TABLE 1 THE COMPOSITIONS OF PARAFFIN, PU AND FLAME RETARDANT IN THE COMPOSITES

<table>
<thead>
<tr>
<th>Samples</th>
<th>Compositions (in mass portions)</th>
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<tbody>
<tr>
<td>PCM-1</td>
<td>50g PU</td>
</tr>
<tr>
<td>PCM-2</td>
<td>50g PU + 10g Paraffin</td>
</tr>
<tr>
<td>PCM-3</td>
<td>50g PU + 10g Paraffin + 12g nano-CC</td>
</tr>
<tr>
<td>PCM-4</td>
<td>50g PU + 10g Paraffin + 12g nano-CC + 3g RP</td>
</tr>
</tbody>
</table>

EXPERIMENTAL
A. Materials
Polyurethane foam mixed materials (stuff A: mixture of polyether polyol, foaming agent and so on. Stuff B: isocyanate) were purchased from Yantai Wanhua Co. Ltd., Shandong Province, China. The producer proposed weight ratio: stuff A:stuff B = 100:50, stuff temperature: 20-25°C, mold temperature: 55°C. The nano structured calcium carbonate (nano-CC) and red phosphorus (RP) were supplied by Jiangxi Huaming Co. Ltd., Jiangxi Province, China. Paraffin was made in FRIPP with the paraffin melting point 80-86°C, melting latent heat of 174.4kJ/kg.

B. Fabrication of Paraffin/Polyurethane Foams Composite with Flame Retardant
The predetermined masses of stuff A, paraffin and flame retardant were added in a beaker and mixed vigorously with strong stirring for 30s to obtain a formulated mixture. The predetermined masses of stuff B were then added into the same beaker with strong stirring for 60s. The resulted mixture was kept until the formation and growth of the foam. Then it was moved and kept in an oven at 50°C. Four kinds of paraffin/polyurethane foams composite were obtained, denoted PCM-1, PCM-2, PCM-3, and PCM-4.
C. Characterization of Paraffin/Polyurethane Foams Composite with Flame Retardant

The thermal properties of composites was obtained by using a differential scanning calorimeter (STA 449C Netzsch) at 5 °C/min under a constant stream of nitrogen at a flow rate of 20 ml/min. The structural analysis of composites was carried out using a FT-IR spectrometer. The FT-IR Spectra were recorded on a Nicolet 6700 from 500 to 4000 cm⁻¹ with a resolution of 2 cm⁻¹ using KBr pellets. Microstructures of the PU and composites were observed by using a SEM (Jeol 7500F, Japan) at room temperature. The flame retardant properties of composites was determined by limited oxygen index tester (JF-3, Jiangning Analysis Instrument Factory, China).

III. RESULTS AND DISCUSSION

A. FT-IR Analysis of Paraffin/Polyurethane Foams Composite

FT-IR spectra of the synthesized foams, namely PCM-1, PCM-2 and paraffin are presented in Fig. 1. The spectrum of PCM-1 presents all the distinctive bands of the polyurethane foams. The spectra of experimental groups are compared with that of PCM-1 and paraffin. The band of –OH stretching vibration at 3435-3352 cm⁻¹ is associated with the free H2O, -OH groups of non-bonded polyol or -OH groups within the foams structure. Peaks related to –CN and –C=O at 2271 and 1708 cm⁻¹ observed in the spectrum of PCM-1 disappear in the spectrum of PCM-2. This indicates incompleteness of PU chain arising from the addition of a secondary material into the structure. The intensity increases in peaks for –CH2 at 2955.9 and 2917.8 cm⁻¹ of PCM-2 is associated with capturing paraffin.

These characterized peaks are the evidence of a successful paraffin trapping in PU foams [16, 17]. It is meanwhile found that there is no shift in the absorption peaks of composites when compared with the spectra of paraffin. This result indicates that there is no chemical interaction between the functional groups of paraffin and PU.

B. SEM Photos of Paraffin/Polyurethane Foams Composite

SEM photos of PU foams and composites are shown in Fig. 2. Fig.2 (b) clearly illustrates some paraffin micelles distributing in PU foams. The excellent honeycomb structure obtained during foam formation made considerable amount of still air trapping possible, and effectively prevented the leakage possibility of paraffin [18,19].

C. The Thermal Properties of Paraffin/Polyurethane Foams Composite

Fig. 3 illustrates DSC curves of PU foams with paraffin and flame retardant. Compared with the pure PU foams, paraffin/PU foams composite has endothermic peak in the process of heating in the point of 80.3 °C, melting latent heat of 25.8kJ/kg. As shown in Table II, flame retardant has no significant influence to the latent heat. After the addition of paraffin with different melting temperatures, different paraffin/PU foams composite with various phase change temperatures can be gained.
The enhanced fire resistance of the flame retardant composites could be explained by the fire suppression mechanism of nano-CC and RP. The thermal decomposition of CC is an endothermic process, which can release CO2 to decrease temperature and dilute oxygen and flammable gases concentrated near the flame.[20] The decomposition product CaO is a fine flame material used as a retardant. The incorporation of RP into composites also improves the thermo-oxidative stability [21]. In a word, nano-CC and RP give a synergetic flame retarding effect to the composites.

IV. CONCLUSIONS

The preparation and properties of paraffin/PU foams composite with flame retardant are reported. Paraffin was used as PCM for thermal energy storage, and PU foams acted as the supporting material for improving the thermal stability of the composites. Nano-CC and RP were added in the composites in order to decrease the flammability of the composites. Paraffin was well dispersed in the honeycomb structure of the PU foams by capillary and surface tension forces, and the leakage of melted paraffin from the composites can be prevented even when it was heated above the melting temperature of the paraffin. As the mass percentage of paraffin in the composites was 16.7%, the composites melt at 80.3°C with a latent heat of 25.8kJ/kg. The addition of nano-CC and RP in the composites improved the thermal stability and increased the LOI values from 16% to 27%.

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