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Investigation on smoke toxicity of the novel intumescent flame retardant LDPE composites based on the mice experiment

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Abstract: The smoke toxicity of the novel flame retardant low-density polyethylene (LDPE) composites with good flame retardant properties and excellent water resistance was studied by mice experiments, and the upper limit of the no death smoke concentration of the smoke was assessed. Furthermore, different heating temperatures were selected to research the smoke toxicity for the flame and flameless combustion. The results show that the smoke toxicity of the flame retardant LDPE composites with flame combustion is much smaller than that with the flameless combustion. Meanwhile, fire risk assessment of flame retardant LDPE composites is achieved by fire performance index and fire development index. The work provides some experimental data for preparing environment-friendly flame retardant LDPE composites with excellent properties.

Key words: low-density polyethylene (LDPE); flame retardancy; smoke toxicity; mice test

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研究快报

基于小白鼠实验的新型膨胀阻燃低密度聚乙烯复合材料烟气毒性研究

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摘要:利用小白鼠试验来研究新型阻燃低密度聚乙烯(LDPE)复合材料的烟气毒性,探寻材料烟气毒性最大

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不至死浓度,根据相关标准判断材料毒性所属级别,并比较研究不同燃烧状况下阻燃 LDPE 复合材料产烟毒性.从烟气毒性实验可知,有焰燃烧比无焰燃烧具有较小的烟气毒性.同时利用火灾性能指数和火灾发展指数对阻燃 LDPE 复合材料的火灾安全性进行评价.研究结果有助于优化设计环境友好、综合性能优良的阻燃低密度聚乙烯复合材料.

关键词:低密度聚乙烯;阻燃;烟气毒性;小白鼠实验

Low-density polyethylene (LDPE) has broad applications due to its excellent properties, such as electrical insulation properties, easy processability, etc. However, flammable property limits its applications. So preparing LDPE composites with good flame retardant properties is necessary. Until now, many methods for improving fire retardancy of LDPE have been investigated, and intumescent flame retardant method is one of the most promising methods[1-4].

In order to prepare flame retardant LDPE composites with good flame retardant properties and excellent water resistance, a char forming agent (CFA)[5-6] and silica-gel microencapsulated APP (MCAPP)[7] were selected to form novel intumescent flame retardant system (IFRs), and then the influence of the novel intumescent flame retardants on the thermal and flame retardant properties of LDPE were studied. The results of cone calorimetry show that the flame retardant properties of LDPE have been improved remarkably. The heat release rate peak and total heat release with 30% (mass fraction) novel intumescent flame retardant (CFA/MCAPP=1:3) decrease respectively from 1 479.6 to 273.5 $kW \cdot m^{-2}$ and from 108.0 to 80.5 $MJ \cdot m^{-2}$[8].

With the improvement of the people's living standards, the requirement for intumescent flame retardant materials is getting increasing attention. The intumescent flame retardant materials should satisfy the flame retardant requests and usage requirements, so the smoke toxicity of flame retardant materials should be within an acceptable range. So far, the smoke toxicity of intumescent flame retardant materials has remained insufficiently studied, especially by animal experiment.

In this work, the mice experiment was used to study the smoke toxicity of the novel flame retardant LDPE composites. The smoke concentration and the products are different for flameless and flame combustion conditions, leading to some differences in the smoke toxicity. So the smoke toxicity of the novel flame retardant LDPE composites was studied based on two conditions — flame or flameless combustion. The upper limit of the no death smoke concentration of the smoke was assessed.

The flame retardant LDPE composites was prepared by the following steps. Firstly, LDPE, MCAPP and CFA were dried in a vacuum oven at 80 ℃ overnight before use. Then LDPE (mass fraction 70.0%), MCAPP (mass fraction 22.5%) and CFA (mass fraction 7.5%) were melt-mixed in a twin-roller mill (KX-160, Jiangsu, China) for 10 min. The temperature of the mill was maintained at 160 ℃ and the roller speed was 60 r/min. The prepared composites was hot-pressed into sheets with a suitable thickness of 3 mm, and was cut into 400 mm long uniform stripes for the mice experiment.

Smoke toxicity test device (YD-1, Jiangning Analysis Instrument Company, China) was used for the mice experiment. In the experiment, the sample was heated stably using the hoop-stove by scanning way. The carrier gas was uniform, and the hoop-stove moved at a constant speed. The mice experiment was carried out when the smoke was fully generated. The detailed experiment was carried out according to the standards[9-10]. The mice aged 6～8 weeks were obtained from Anhui Medical University. There were eight mice for each group, with four females and four males. The average weight of the mice was about 23 g.

In the mice experiment, the heating

temperature of the material should be determined firstly and the relevant smoke production rate also should be calculated. So 300 ℃, 400 ℃, 500 ℃ and 600 ℃ were selected as the heating temperatures. The experiment shows that at 300 ℃ the sample is under the flameless combustion condition, and above 400 ℃ the sample is under the flame combustion condition. The smoke production rate can be calculated, and the change in smoke production rate with temperature is shown in Fig. 1. The smoke production rate of flame retardant LDPE composites increases with the increase in temperature. From 300 ℃ to 400 ℃ the smoke production rate increases from 28.0% to 77.2%, and increases to 82.8% at 500 ℃. From 500 ℃ to 600 ℃, the smoke production rate increases from 82.8% to 83.2%, and a rising rate of 0.4%. This indicates that the smoke production rate changes little if the heating temperature continues to increase. As the smoke concentration and the products are different for flameless and flame combustion conditions, which leads to some differences in the smoke toxicity, it is necessary to study the smoke toxicity of the two conditions. So 300 ℃ and 600 ℃ were selected as the heating temperatures to study the smoke toxicity of the flame retardant LDPE composites.

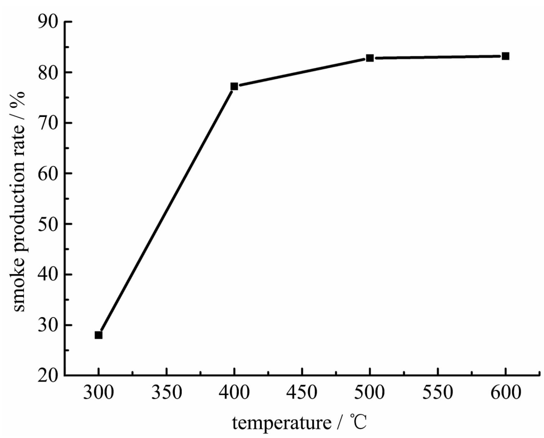
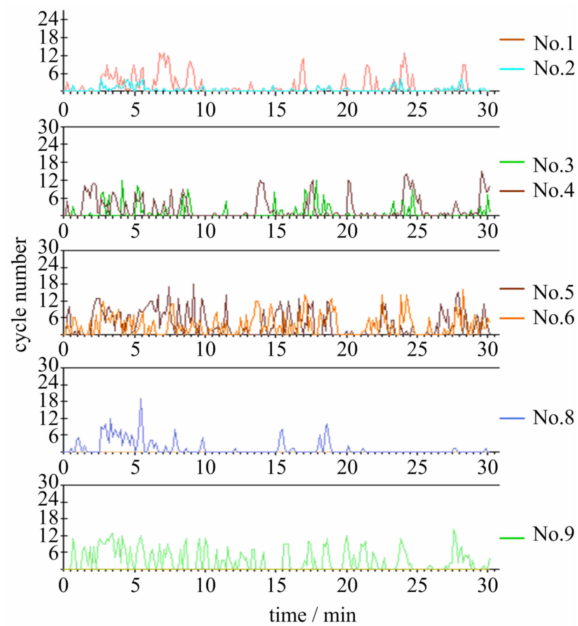


Fig. 1 Changes in smoke production rate with temperature

Choosing the smoke concentrations of 37.86, 33.93 and 28.7 mg/L as the research object with the heating temperature at 600 ℃, the needed quality of the materials (7 573.0, 6 787.3 and 5 736.0 mg) can be calculated. During the experiment, the mice ran to avoid the smoke. Later, occular and respiratory abnormalities appeared, with mucus increasing in their oral and nasal cavities. During the experiment that lasted 30 minutes, six of the eight mice died at the smoke concentration of 37.86 mg/L, and the two that survived lived on within 1 h, but were weak and anorexic. At the smoke concentration of 33.93 mg/L, two of the eight mice died. The remaining mice were weak and anorexic and ran slowly. At the smoke concentration of 28.7 mg/L, no mice died during the experiment or within 1 h after the experiment. The changes in movement cycle number of the mouse cages with time are shown in Fig. 2, and the mice almost always ran during the experiment. For all of the three smoke concentrations, the weight of the mice that survived recovered in 3 d. From the above results it can be known that the upper limit of the no death smoke concentration is 28.7 mg/L.



No. means the serial number of cage

Fig. 2 Changes in movement cycle number with time at the smoke concentration of 28.7 mg/L at 600 ℃

According to the result of smoke toxicity obtained at 600 ℃, the smoke concentration 28.7

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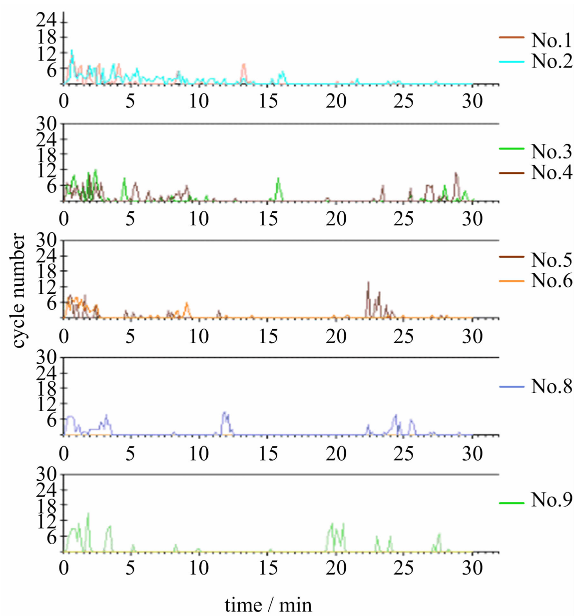
mg/L was chosen to investigate smoke toxicity at 300 ℃. The mice ran to avoid the smoke, There were no mice dead during the experiment or within 1 hour after the experiment. The changes of movement cycle number of the mouse cages with time are shown in Fig. 3. The weight of the mice recovered in 3 d.



No. means the serial number of cage

Fig. 3　Changes in movement cycle number with time at the smoke concentration of 28.7 mg/L at 300 ℃

To judge the smoke toxicity under different combustion conditions, the total movement cycle number of the mouse cages at different heating temperatures (600 and 300 ℃) with the same smoke concentration (28.7 mg/L) is studied.

There were no mice dead at the smoke concentration of 28.7 mg/L at 600 ℃ or 300 ℃. However, from Fig. 4, it can be seen that the movement cycle number of the mouse cages at the heating temperature of 600 ℃ is greater than that at 300 ℃, meaning that the smoke toxicity at 600 ℃ with the flame combustion is much smaller than that at 300 ℃ with the flameless combustion. This phenomenon can be seen directly from the digital photos of the smoke chamber (Fig. 5). The composites are under flameless combustion when the heating temperature is 300 ℃. The white foggy smoke in the smoke chamber is heavy. The smoke concentration is much higher than that at the heating temperature of 600 ℃. The main reasons for this is that part of the pyrolysis products is fully burned at the high temperature by flame combustion, so the smoke and poisonous products are relatively less and shows lower toxicity when compared with the insufficient flameless combustion. There is some deviation in No. 2, and it is mainly due to the mice' individual differences.

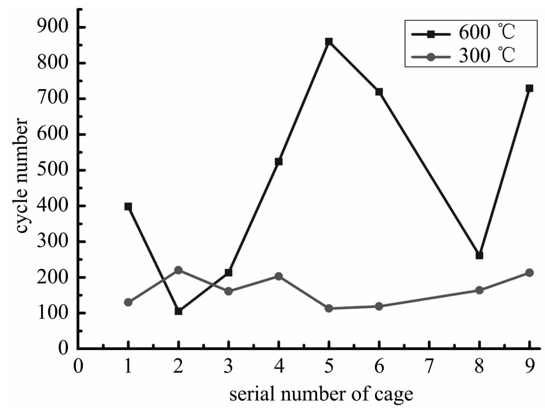
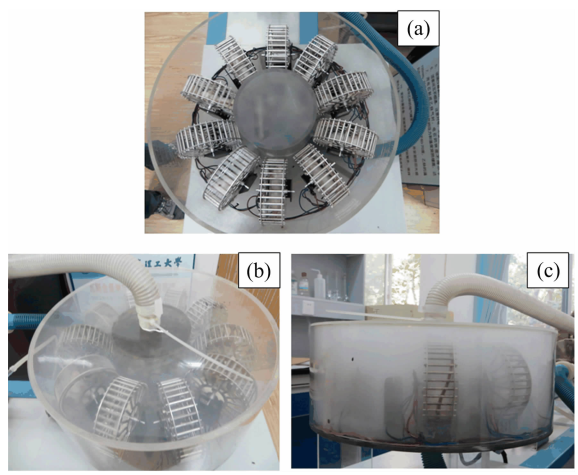


Fig. 4　The movement cycle number of the mouse cages at different heating temperatures



(a) before experiment, (b) experiment at 600 ℃, (c) experiment at 300 ℃

Fig. 5　The digital photos of the smoke chamber

According to the results of the smoke toxicity experiment and the standard[9], the smoke toxicity of the flame retardant LDPE composites is judged as "stimulus", and the level of the smoke toxicity risk is ZA1(≥25.0 mg/L) belonging to quasi safety.

In order to get a full understanding of the flame retardant LDPE composites, the fire risk assessment of flame retardant LDPE composites is achieved by the derivative index of fire performance index and fire development index[11].

Fire performance index FPI=TTI/pHRR

Fire development index FGI=pHRR/t_p

The value of TTI (time to ignition), pHRR (peak heat release rate) and t_p (the time to reach the peak) were obtained by cone calerimetry, and the value is shown in Tab. 1.

Tab. 1 The FPI and FGI of the pure LDPE and flame retardant LDPE composites

sample	TTI	t_p	pHRR	THR	FPI	FGI
LDPE	85	180	1479.6	108.0	0.057	8.22
flame retardant LDPE	75	87	273.5	80.5	0.274	3.14

From Tab. 1 it can be seen that the FPI of the pure LDPE is 0.057, and FGI is 8.22. The FPI of the flame retardant LDPE is 0.274, and FGI is 3.14. The FPI of the flame retardant LDPE composites is 4.8 times as much as that of pure LDPE, and FGI is only 0.38 time as much as that of pure LDPE. It is well known that the smaller the FPI, the smaller the fire risk, and the larger the FPI, the greater the fire risk. So the prepared novel intumescent flame retardant LDPE composites have a low fire risk.

In summary, the smoke toxicity of the flame retardant LDPE composites at the heating temperature of 600 ℃ under flame combustion condition is much smaller than that at 300 ℃ with the flameless combustion. According to the results of the smoke toxicity experiment, the smoke toxicity of the flame retardant LDPE composites is judged as “stimulus”, and the level of the smoke toxicity risk belongs to quasi safety. Meanwhile, the study of the fire performance index and the fire development index shows that the flame retardant LDPE composites have a much lower fire risk compared with that of pure LDPE. This work provides some experimental data for preparing environment-friendly flame retardant LDPE composites with excellent properties, and is benefitial to fully understand the smoke toxicity of intumescent flame retardant composites at low and high temperatures.

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