Synergistic effect of phosphorus-containing nanosponge on the intumescent flame retardant polypropylene

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Introduction

Intumescent flame retardant (IFR) has attracted more and more attentions in recent years because of its being halogen-free, low smoke and anti-dripping. However, its relatively low flame retardant efficiency limits its actual commercial applications. To overcome this disadvantage, many synergists including resorcinol bis(diphenyl phosphate) (RDP) [1] and beta-cyclodextrin (β-CD) [2] have been introduced to improve the flame retardant efficiency of IFR. However, as a liquid flame retardant, RDP is difficult to be incorporated and retained in solid polymers.

β-CD is a kind of cyclic oligosaccharides consisting of seven glucopyranose units, which is well-known for forming an inclusion complex with various guest molecules due to its special molecular structures---hydrophobic internal cavity and hydrophilic external surface [3]. By reacting β-CD with suitable cross-linking agents, a novel nanostructure material named nanosponge (NS) can be obtained. Due to its outstanding encapsulate capacity, the nanosponge can adsorb a great variety of substances [4]. As a result, they could be used as an efficient carrier for RDP. We proposed that the phosphorus-containing nanosponge (NS-RDP) would show a good synergistic effect with IFR in flame retardant PP.

Experimental

Materials

β-cyclodextrin (β-CD) was obtained from Shanghai Bio Science & Technology Co. Ltd. Epoxy resin (E-51, epoxy value=0.51) was supplied by Guangzhou Dongfeng Chemical Industrial Co., Ltd. Resorcinol di(phenyl phosphate) (RDP), was provided by Jiangsu Yoke Technology Co. Ltd. Polypropylene (PP), melamine pyrophosphate (MPP) and pentaerythritol (PER) were commercial products.

0.3 mol β-CD and 0.3 mol NaOH were added in a 500 mL round bottom flask containing 200 mL distilled water and stirred at 70 ^{o}C till a transparent mixture was formed. 0.3 mol E-51 was dissolved into 100 mL ethanol, and the mixture was added dropwise into the β-CD solution. The mixture was stirred at 70 ^{o}C for 8 h, and then the obtained slurry was moved into a 500 mL beaker and dried in a vacuum oven at 100 ^{o}C for 24 h. The NS was obtained. The reaction scheme and structure of NS was shown in Fig.1.

NS-RDP was prepared by mechanical grinding, and the chosen ratio between NS and RDP compound was 2:1. The obtained NS-RDP was compounded with PP, MPP and PER on a two-roll mill at 170 ^{o}C for 15 min, with the content of PP kept at 75 wt.%., the content of NS-RDP was 3.0 wt% and the weight ratio between MPP and PER was 3:1. The prepared composites were hot-pressed into sheets of suitable thickness and size for corresponding tests.

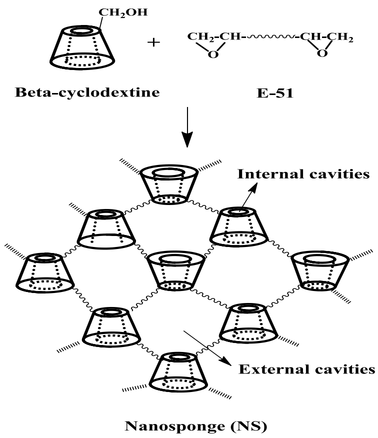

Fig. 1. Reaction scheme and the structure of NS

Apparatus and Procedures

The FTIR spectra were recorded on a Bruker TENSOR27 FTIR spectrometer (Bruker Co., Germany).

The limiting oxygen index (LOI) was carried out using an oxygen index meter (HC-2, Jiangning Analysis Instrument Co., China) according to ASTM D2863. The vertical burning test (UL-94) was conducted on a vertical burn instrument (CFZ-3, Jiangning Analysis Instrument Co., China) according to ASTM D635. The cone calorimeter test (CCT) was carried out using a cone calorimeter (Fire Testing Technology Co., UK) according to ISO5660.

Results and Discussion

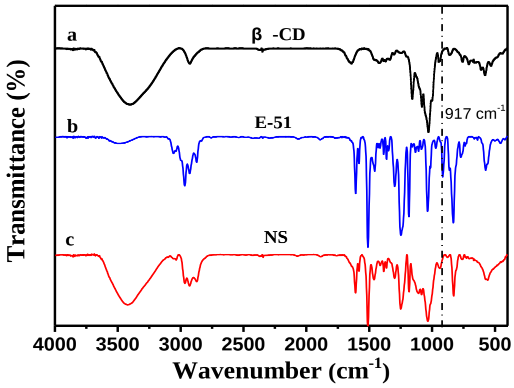

Fig. 2 FTIR spectra of β-CD, E-51 and NS

The FTIR spectra of β-CD, E-51 and NS are shown in Fig. 2. As can be seen, some of the characteristic absorption peaks of β-CD and E-51 were found in the FTIR spectrum of NS (see Fig. 2c). Meanwhile, the epoxy group at 917 cm^{-1} has disappeared, implying that all epoxy group had reacted with β-CD.

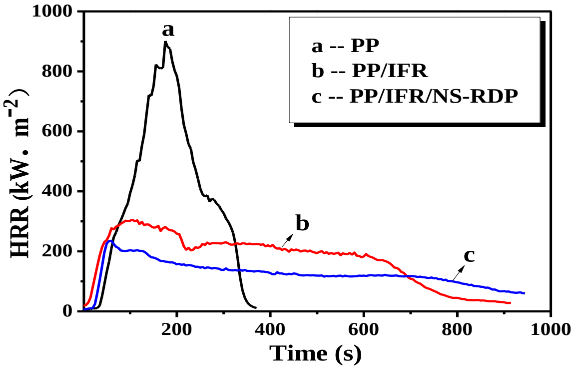

Fig. 3 HRR curves of PP and flame retardant PP

Fig. 3 shows the HRR curves of PP and flame retardant PP. The LOI, UL94 rating and peak heat release rate (pHRR) data are also listed in Tab.1. NS-RDP and IFR had good synergistic effects on flame retardant PP. When the content of NS-RDP was 3.0 wt%, LOI was increased from 28.5% to 32.5%, and the UL-94 rating was improved from V-1 to V-0. Moreover, the pHRR value was decreased from 305.0 kW m^{-2} to 235.3 kW m^{-2}.

Tab. 1 LOI, UL94 rating and pHRR of flame retardant PP

Sample	LOI (%)	UL-94 rating	pHRR (kW m^{-2})
PP	17.0	Failed	900.9
PP/IFR	28.5	V-1	305.0
PP/IFR/NS-RDP	32.5	V-0	235.3

The morphology of the char residue of PP/IFR and PP/IFR/NS-RDP is shown in Fig. 4. The char residue of PP/IFR was loose and the char layer could be peeled off from the substrate easily. The interface between the char layer and PP matrix was white and loose (see Fig. 4a′), indicating that the charring performance of PP/IFR was not unsatisfactory. Contrastively, the char residue of PP/IFR/NS-RDP was compact and the char layer could hardly be peeled off from the substrate. The interface between the char layer and PP matrix was yellow and compact (see Fig. 4a′), implying that NS-RDP could obviously improve the charring performance of PP/IFR. Therefore, PP/IFR/NS-RDP had better flame retardancy than PP/IFR.

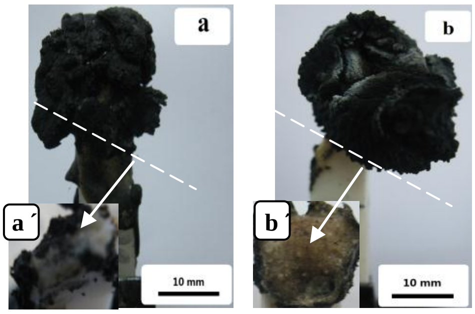

Fig. 4 Char of burned (a)PP/IFR and (b)PP/IFR/NS-RDP after LOI test; (a′)burned PP/IFR peeling the char layer, and (b′)burned PP/IFR/NS-RDP peeling the char layer

Conclusion

Phosphorus-containing nanosponge (NS-RDP) was successfully prepared via absorbing RDP into the nanosponge, and it exhibited a distinct synergistic effect with IFR on flame retardant PP. The LOI, UL-94 and CCT results showed that a small amount (3.0 wt%) of NS-RDP could effectively improve the flame retardancy of PP/IFR, which was attributed to the improvement on forming compact and dense char barrier.

References

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