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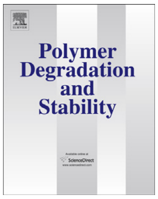

Synergistic effect of hydroquinone bis(di-2-methylphenyl phosphate) and novolac phenol in ABS composites

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ABSTRACT

A new phosphorus-containing flame retardant hydroquinone bis(di-2-methylphenyl phosphate) (HMP) was successfully synthesized and characterized by ^{31}P NMR and Fourier transform infrared spectroscopy (FTIR). The crystallization and melting point was measured by wide angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC) separately. HMP was applied to prepare acrylonitrile-butadiene-styrene (ABS)/HMP/novolac phenol (NP) composites. The limiting oxygen index (LOI) value of ABS/HMP/NP composites increased with a decreasing ratio of HMP to NP, then declined with a further decrease in the ratio. The ABS/HMP/NP-3 had an LOI value of 33.5 and passed the vertical burning tests (UL-94) V–I rating at the ratio of HMP to NP was 2 to 1, when the synergistic effect of HMP and NP in the ABS composites was especially obvious, which were carefully characterized by thermogravimetric analysis (TGA), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS).

1. Introduction

As a commercial material, acrylonitrile–butadiene–styrene copolymer (ABS) is widely used in many applications due to its good mechanical and physical properties such as easy processing, toughness, impact resistance, and excellent appearance [1–4]. However, wider applications of ABS have been restricted due to its poor properties regarding flammability, so fire retardation is important and necessary with this material. The most common flame retardants are halogen-containing compounds [2]. However, the halogen-containing compounds such as hexachlorocyclopentadiene [5], brominated epoxy [6,7], brominated polystyrene [8], etc. cause reduction in tracking index, cause corrosion to the processing equipment and generate corrosive and toxic combustion products with deleterious effects on the environment and human health [9,10]. Flame retardancy for ABS is very difficult, and the shortcomings of halogen-containing flame retardants are serious. Therefore, the development of environmentally friendly and highly efficient flame retardants for ABS has attracted great attention in recent years.

Organic phosphates, as halogen-free flame retardants, are known to be good candidates for replacing the halogen type ones owing to relatively high efficiency and no release of toxic and corrosive gases during combustion [2,11]. Many researchers have made efforts to develop a phosphate-containing flame retardant with both high flame retardancy and thermal stability. Among the various phosphorus-based flame retardants, such as resorcinol bis(diphenyl phosphate) (RDP) [12,13] and bisphenol A bis(diphenyl phosphate) (BDP) [14], have been employed as flame retardants for ABS resins with various novolac phenol resins (NP) and epoxy compounds (EP). However, most organic phosphorus-based flame retardants used for ABS are liquid, which is not convenient during the manufacture of flame-retarded products [2]. Therefore, it has become an important goal to develop a high melting point flame retardant.

In a previous study, a high melting point phosphorus-based flame retardant, hydroquinol bis(diphenyl phosphate) (HDP), was synthesized using hydroquinone, phosphoryl oxychloride and phenol. HDP was able to improve the flame retardant properties of ABS/HDP composites [15]. In this study, a new phosphorus-based flame retardant, HMP, was synthesized using hydroquinone, phosphoryl oxychloride and 2-methylphenol, and incorporated into ABS resin. As is well-known, NP is a very promising material in terms of char source [16,17]; as such, it is the most commonly investigated ABS composite in studies on improving flame retardancy. The main aim was to study the synergistic effect of HMP and NP in ABS/HMP/NP composites. The structure and property of HMP were characterized by ^{31}P NMR and FTIR. The crystallization and

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melting point was measured by WAXD and DSC, the flame retardancy of the ABS composites was evaluated by LOI and UL-94 tests, and the thermal degradation behavior was analyzed by TGA. The microstructure and elemental distribution of the charred crusts were investigated by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS).

2. Experimental

2.1. Materials

Oxalic acid, 2-methylphenol and hydroquinone (AR) were supplied by Chengdu Jinshan Chemical Reagent Co. Ltd. (China). Aluminum chloride ($AlCl_3$) (AR) was supplied by Tianjin Fuchen Chemical Reagent Co. Ltd. (China). Phosphorus oxytrichloride (AR) was supplied by Tianjin Guangfu Fine Chemical Research Institute. Sodium hydroxide (AR) was supplied by Chengdu Kelong Chemical Reagent Co. Ltd. (China). ABS (PA-709) was supplied by Qi Mei industrial Co., Ltd. (China). NP (2123 MA) was supplied by Heng Xin Chemical Reagent Co., Ltd. (China).

2.2. Synthesis of HMP

HMP was synthesized using the following procedure. Hydroquinone (0.1 mol) and $AlCl_3$ (0.01 mol) were added to freshly distilled phosphorus oxytrichloride (0.4 mol) in a thoroughly dried three-necked flask equipped with a reflux condenser, a nitrogen inlet and an electromagnetic stirrer. The mixture was stirred vigorously and refluxed for 0.5 h. Subsequent distillation of the reaction mixture gave phosphorus oxytrichloride with the protection of nitrogen at 80 °C after 1 h until no HCl gas was emitted. The intermediate product (0.1 mol) and $AlCl_3$ (0.01 mol) were then added to 2-methylphenol (0.48 mol) in a three-necked flask. The reaction flask was then immersed in an oil bath preheated to 120 °C, and the action mixture was refluxed for 2 h with the protection of nitrogen until no HCl gas was emitted, and a transparent liquid was obtained. The liquid was poured into a separatory funnel and washed with an oxalic acid solution and sodium hydroxide solution at 60 °C, three times each. The product was precipitated from the mixture at room temperature, filtered, and dried at 55 °C in a vacuum for 4 h. Finally, HMP was obtained as a light yellow solid.

2.3. Sample preparation

Before melt blending, all the components were dried in a vacuum oven at 80 °C for 2 h. The composites of ABS, with different amounts of HMP and NP, were prepared in a twin-screw extruder at a temperature of about 190 °C, then molded into plates with a thickness of 3 mm. Compression molding was performed under the following conditions: the composites preheated for 5 min at 190 °C, 0.5 MPa, compressed for 10 min at 13 MPa, 190 °C, and then cooled to ambient temperature at a cooling rate of 30 °C/min in the mold at 13 MPa. The blend compositions with their sample codes are listed in Table 1.

2.4. Characterization

2.4.1. FTIR measurements

All the specimens measured by FTIR were prepared by the following steps: powder samples were mixed with KBr powders, and the mixture was pressed into a tablet. Transmission mode was used and the wavenumber range was from 4000 to 500 cm^{-1}. FTIR analysis was conducted using a Nicolet 6700 spectrophotometer (Nicolet, USA).

Table 1
Composition and the flammability properties of ABS/HMP/NP composites.

Sample ID	Components/(wt%)			LOI^1	LOI^2	Δ	UL-94
	ABS	HMP	NP				
ABS/HMP/NP-1	70	30	0	24.9	24.9	0	Failed
ABS/HMP/NP-2	70	25	5	29.7	24.4	5.3	Failed
ABS/HMP/NP-3	70	20	10	33.5	24.0	9.5	V-1
ABS/HMP/NP -4	70	15	15	29.0	23.6	5.4	Failed
ABS/HMP/NP -5	70	10	20	24.1	23.1	1	Failed
ABS/HMP/NP -6	70	5	25	23.1	22.6	0.5	Failed
ABS/HMP/NP-7	70	0	30	22.2	22.2	0	Failed
ABS [15]	100	0	0	20.5			Failed

Note: LOI^1: the actual measured LOI value.
LOI^2: the theoretic LOI value of the sample based on the calculating formula of $W_{th}(A)_{ABS/HMP/NP}$.

$$W_{th}(A)_{ABS/HMP/NP} = \left[x/(x+y)\right] \times W_{exp}(A)_{ABS/HMP} + \left[y/(x+y)\right] \times W_{exp}(A)_{ABS/NP} \quad (A)$$

Where $W_{exp}(A)_{ABS}$: experimental A value of the pure ABS; $W_{exp}(A)_{ABS/HMP}$: experimental A of ABS/HMP when the ratio of ABS to HMP is 7:3; $W_{exp}(A)_{ABS/NP}$: experimental A of ABS/NP when the ratio of ABS to NP is 7:3; x and y are on behalf of the mass of the HMP and NP in the composites, respectively.
Δ: the difference between LOI^1 and LOI^2.

2.4.2. NMR measurements

^{31}P NMR measurement of intermediate was conducted on an Avance II-600 spectrometer (Bruker Biospin, Switzerland) at room temperature using CDCl3 as the solvent.

2.4.3. Wide angle X-ray diffraction

Wide angle X-ray diffraction (WAXD) investigations were carried out with an X'Pert PRO in the reflection mode. Cu Kα radiation was used at 40 kV and 25 mA. Investigations were performed in the range of angles 5–35°, the scan step was 0.026° (in 2θ) with a counting time of 20 s per step.

In order to determine the mass fraction of crystallinity, WAXD curves were deconvoluted into crystalline and amorphous scattering components using the profile fitting program JADE6.5. Each peak was modeled using a Gaussian-Cauchy peak shape. The level of crystallinity was taken as the area ratio of all the crystalline peaks to that of total scattering.

2.4.4. Differential scanning calorimetry

All calorimetric experiments were performed using a Mettler Toledo DSC1 differential scanning calorimeter under a nitrogen atmosphere (50 mL/min). The temperature scale calibration was performed using indium as the standard to ensure the reliability of the data. The samples were heated from 30 °C to 130 °C at a heating rate of 10 °C/min.

2.4.5. Measurement of LOI

The LOI values were measured using an XZT-100A instrument (Kecheng, China). The sample size was 127 × 10.5 × 3.0 mm and a mixed gas of nitrogen and oxygen was used at a flow rate of 14 L/min according to GB/T 2406 (China).

2.4.6. Measurement of UL-94

The UL-94 vertical burning tests were carried out using a CZF-3 instrument (Jiangning Analysis Instrument Company, China). As per the UL-94 test standard, the dimension of specimens in the test was 127 × 12.7 × 3 mm.