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# Effect and mechanism of N-alkoxy hindered amine on the flame retardancy, UV aging resistance and thermal degradation of intumescent flame retardant polypropylene

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ABSTRACT

A multifunctional additive N-alkoxy hindered amine (NOR116) possessed free-radical quenching capability was combined with ammonium polyphosphate/pentaerythritol (APP/PER) to flame-retard polypropylene (PP). The effects of NOR116 on the flame retardancy, ultraviolet (UV) aging resistance and thermal degradation of the PP/APP/PER mixture were investigated by limiting oxygen index (LOI), vertical burning test (UL-94), cone calorimetric test (CCT), UV aging test and thermogravimetric analysis (TGA). It was found that NOR116 showed a synergistic effect with APP/PER in flame retardant PP. When the content of APP/PER and NOR116 were 24.5 wt% and 0.5 wt%, respectively, the LOI value of the PP/APP/PER mixture was increased from 31.0% to 35.0% and a UL-94 V-0 rating was achieved. Meanwhile, the UV aging resistance of the PP/APP/PER mixture was improved significantly. The synergistic mechanism between NOR116 and APP/PER was explored and revealed. During the combustion, NOR116 could not only block the radical chain reaction in the gas phase by quenching the active free-radicals, but also promote the formation of the thermostable intumescent char in the condensed phase.



## 1. Introduction

Polypropylene (PP) is widely used in many fields such as electronic equipment, electric wire and cable, automobiles and decorative materials, due to its good processing performance, excellent chemical resistance and low cost [1]. However, the high flammability and poor UV aging resistance severely restricts its further application. Therefore, it is imperative to improve the flame retardancy and the UV aging resistance of PP [2]. In recent years, intumescent flame retardant (IFR) is considered to be one of the most promising halogen-free flame retardants because of its being environmental-friendly, low smoke and anti-dripping [3]. Typically, IFR consists of three components, including an acid source, a charring agent and a blowing agent. The most commonly reported IFR is ammonium polyphosphate/pentaerythritol (APP/PER) [4]. However there are some shortcomings with the APP/PER system, such as poor thermal stability, high loading and relatively low flame retardant efficiency [5]. Besides, the addition of APP/PER would deteriorate the UV aging resistance of PP [6].

To overcome these disadvantages, many meaningful researches have been done, and adding synergists was proved to be an effective way. The most commonly used synergists mainly involve inorganic minerals such as montmorillonite [7], wollastonite [8], halloysite [9], metal oxides [10] and silicone-containing compounds [11], etc. They primarily work by catalyzing the char-forming reactions or enhancing the strength and thermostability of the char layer [12], thus improve the flame retardant efficiency of IFR. Unfortunately, they exerted little effect on the UV aging resistance of the polymer.

N-alkoxy hindered amine light stabilizers (N-alkoxy HALS), such as Chimassorb119, Tinuvin152 and Flamestab NOR116 are the most commonly used light stabilizers for PP [13]. They could slow down the photo-chemically initiated degradation reactions of PP by quenching the alkyl and peroxy radicals [14]. It was reported that N-alkoxy HALS could not only improve the UV aging resistance of polyolefin but also act as a flame retardant in polyolefin [15,16]. Cao and co-workers [6] synthesized an N-alkoxy hindered amine containing silane (Si-NOR) by Tinuvin152 and silane *via* sol–gel reactions, and found that Si-NOR could significantly improve the

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thermal stability and UV aging resistance of the PP/IFR mixture. Nevertheless, it showed little improvement on the flame retardancy of the mixture. Recently, NOR116 is attracted more and more attention due to its good synergistic effect with flame retardants [17]. Kaprinidis et al. [18] combined NOR116 with decabromodiphenyl oxide (DBDPO) to flame-retard PP fiber. The results showed that NOR116 could significantly improve the flame retardancy of DBDPO. However, as far as we known, there were few literature about the study of the synergistic effect between NOR116 and IFR in flame retardant PP.

In this work, NOR116 was employed as a synergist for APP/PER to flame-retard PP. The synergistic effect of NOR116 on the flame retardancy, UV aging resistance and thermal degradation of the intumescent flame retardant PP were investigated by limiting oxygen index (LOI), vertical burning test (UL-94), cone calorimetric test (CCT), UV aging test and thermogravimetry analysis (TGA). The synergistic mechanism between NOR116 and APP/PER was further explored and revealed by Fourier transform infrared spectrometry (FTIR), thermogravimetry-Fourier transform infrared (TG-FTIR), scanning electron microscope-energy dispersive X-ray spectroscopy (SEM-EDX) and laser Raman spectroscopy (LRS).

## 2. Experimental

### 2.1. Materials

N-alkoxy hindered amine (Flamestab NOR116, pale yellow powder, analytical, as shown in Fig. 1) was purchased from Ciba Specialty Chemicals Co., Switzerland. Ammonium polyphosphate (APP, industrial) was produced by Jiangmen Topchem Technology Co., China. Pentaerythritol (PER, analytical) was purchased from Tianjin Kermel Chemical Reagent Co., China. Polypropylene (PP, T30S) was provided by Maoming Petrochemical Co., China. All the materials were used directly without further purification.

### 2.2. Preparation of flame retardant PP

PP, APP, PER and NOR116 were dried in a vacuum oven at 100 °C for 6 h before use. APP and PER were uniformly mixed with a mass ratio of 2:1. Then PP, APP/PER and NOR116 were melt-mixed on a two-roll mill (XK-160, Changzhou Shuangfeng Machinery Factory, China) at 170 °C for 15 min. The prepared mixtures were molded under compression (15 MPa) at 180 °C for 6 min and cooled to room temperature naturally to obtain flame retardant PP sheets with standard size for further testing.

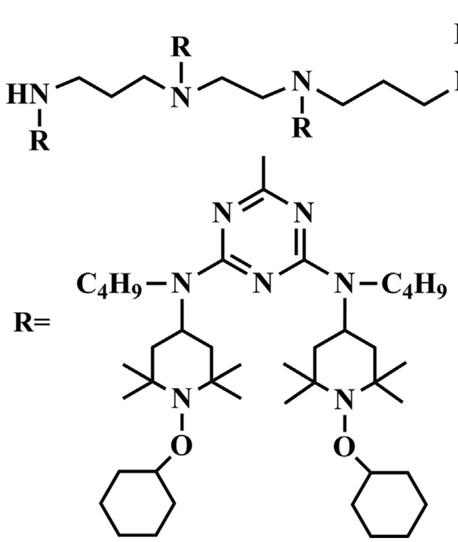


**Fig. 1.** Chemical structure of Flamestab NOR116.

### 2.3. Characterization

#### 2.3.1. Flame retardancy tests

The limiting oxygen index (LOI) test was carried out on an oxygen index meter (HC-2, Jiangning Analysis Instrument Co., China) according to ASTM D 2863-2008. The dimensions of the specimens were 80 mm × 10 mm × 4 mm.

The vertical burning (UL-94) test was conducted on a vertical burn instrument (CFZ-3, Jiangning Analysis Instrument Co., China) according to the UL-94 vertical test standard (ASTM 3801-2010). The dimensions of the specimens were 127 mm × 12.7 mm × 3.2 mm.

The cone calorimetric test (CCT) was carried out by using a cone calorimeter (Fire Testing Technology Co., UK) according to ISO5660. Each specimen, with the dimensions of 100 mm × 100 mm × 4 mm, was wrapped in aluminium foil and exposed horizontally to an external heat flux of 35 kW/m$^2$.

#### 2.3.2. Ultraviolet (UV) aging test

The UV aging test was carried out on a UV accelerated aging box (GT-QUV/SPRAY, Gotech Testing Machines Co., China). The wavelength and the power of the UV lamp in the box were 334 nm and 0.83 W/m$^2$, respectively. And the temperature in the box was kept at 50 °C. The samples were taken out from the box and tested the yellow index (YI) and the mechanical properties for every 5 days.

#### 2.3.3. Thermogravimetric analysis (TGA)

The TGA was carried out on a thermogravimeter (TG209, Netzsch Instruments Co., Germany) from 30 °C to 700 °C at a heating rate of 5, 10, 20 and 40 °C/min under a nitrogen flow of 40 mL/min. All samples were measured in an alumina crucible with a weight of about 10 mg.

#### 2.3.4. Fourier transform infrared spectrometry (FTIR)

The sample was mixed with KBr powder, and then pressed into a tablet. The FTIR spectra were recorded by using a Tensor 27 Spectrometer (Bruker Optics Inc., Germany) by averaging 16 scans at a resolution of 4 cm$^{-1}$. The measurement was carried out in the optical range of 4000–400 cm$^{-1}$.

#### 2.3.5. Thermogravimetry-Fourier transform infrared spectrometry (TG-FTIR)

The TG-FTIR instrument consists of a thermogravimeter (TG209, Netzsch Instruments Co., Germany), a Fourier transform infrared spectrometer (Tensor 27, Bruker Optics Inc., Germany), and a

**Table 1**
Effects of NOR116 content on the LOI value and UL-94 rating of PP and flame retardant PP.

| Samples | Composition ( wt% ) | | | LOI (%) | UL-94 rating |
|---|---|---|---|---|---|
| | PP | IFR | NOR116 | | |
| PP | 100.0 | 0 | 0 | 18.0 | NR |
| PP/NOR116 | 99.5 | 0 | 0.5 | 19.0 | NR |
| PP/IFR | 75.0 | 25.0 | 0 | 31.0 | V-1 |
| PP/IFR/NOR116-1 | 75.0 | 24.9 | 0.1 | 32.5 | V-0 |
| PP/IFR/NOR116-2 | 75.0 | 24.7 | 0.3 | 34.5 | V-0 |
| PP/IFR/NOR116-3 | 75.0 | 24.5 | 0.5 | 35.0 | V-0 |
| PP/IFR/NOR116-4 | 75.0 | 24.0 | 1.0 | 34.0 | V-2 |
| PP/IFR/NOR116-5 | 75.0 | 23.5 | 1.5 | 33.0 | V-2 |

Note: IFR was composed of APP and PER, and the mass ratio of APP to PER was 2: 1.