



# Improved thermal stability of polyethylene with rare earth trifluoromethanesulfonate

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## ABSTRACT

The thermal degradation of polyethylene (PE) is a free radical chain reaction, in other words, free radicals are the primary cause of combustion and degradation. Discovering proper compounds with radical trapping ability is critical for developing flame retardant PE composites. Herein, we introduced rare earth trifluoromethanesulfonate (RE(OTf)<sub>3</sub>), with radical trapping ability, into PE. The effects of ytterbium (Yb(OTf)<sub>3</sub>) and lanthanum (La(OTf)<sub>3</sub>) on the thermal stability and flammability properties of polyethylene (PE) were investigated systematically. Electron spin resonance (ESR) spectroscopy proved the free radical-trapping ability of La(OTf)<sub>3</sub> and Yb(OTf)<sub>3</sub>. The results of thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) showed that Yb(OTf)<sub>3</sub> could improve the thermal stability of PE more significantly compared with La(OTf)<sub>3</sub>. The flame retardancy of PE/intumescent flame retardant (IFR) composite was improved when 0.4 wt% IFR was substituted by RE(OTf)<sub>3</sub>. It changed the PE/IFR26 from UL-94 non-rated to V-0. Vertical flame test, limited oxygen index (LOI) and microscale combustion calorimeter (MCC) indicated that the effect of Yb(OTf)<sub>3</sub> on the flame retardancy of PE was better than La(OTf)<sub>3</sub>. The improvement on the thermal stability and flame retardancy of PE is due to the combined action of anion and cation of RE(OTf)<sub>3</sub>. However, the different effects are attributed to the different reactivity of rare earth elements.

## 1. Introduction

Rare earth compounds have positive effects on the thermal stability and flame retardancy of polymers due to their catalytic properties and distinctive morphologies. On the one hand, Rare earth compounds, especially phosphates and oxides, can promote formation of a homogeneous and compact char layer, which provide a better barrier for the release of heat, smoke and volatile gas, and is also less susceptible to cracking [1–8]. Feng et al. [5] reported that a suitable amount of rare earth oxide played an excellent synergistic effect with IFR on the flame retardancy, thermal degradation at high temperature, smoke suppression, and formation of compact char structures in the PP/IFR composites. On the other hand, some kinds of rare earth compounds, such as rare earth phenylphosphonate, present the synergistic flame retardancy with traditional flame retardants [9–16]. Because of the lamellar structure of rare earth phenylphosphonate with outstanding barrier effect, the effective improvement was induced on the thermal behaviors and flame retardancy of PET/GF composites [9,10]. Although some rare earth compounds have been used to reduce the fire hazards of polymeric materials so far, little work focused on how to utilize the radical

trapping ability of rare earth compounds for reducing the flammability of polymer. In this work, rare earth compounds, ytterbium trifluoromethanesulfonate (Yb(OTf)<sub>3</sub>) and lanthanum trifluoromethanesulfonate (La(OTf)<sub>3</sub>), were introduced into PE. Yb has transformable valence, while La with empty 4f shell only has a fixed valence. Both of them were combined with IFRs to investigate the difference of their influences on the flame retardancy of PE/IFR system. The mechanism of how rare earth trifluoromethanesulfonate (RE(OTf)<sub>3</sub>) affects the thermal stability and flame retardancy of PE will be determined.

## 2. Experimental

### 2.1. Preparation of PE filled with RE(OTf)<sub>3</sub>

PE filled with RE(OTf)<sub>3</sub> [La(OTf)<sub>3</sub> or Yb(OTf)<sub>3</sub>] was melt compounded using a ThermoHaake Minilab II (Minilab II, Germany) at 180 °C for 10 min at a rotor speed of 100 rpm. The formulation is 5 g for one processing cycle. PE containing 0, 0.1, 0.2, 0.5, 1, 2 and 5 wt% of RE(OTf)<sub>3</sub> were designated as PE, PE/RE0.1, PE/RE0.2, PE/RE0.5, PE/RE1,

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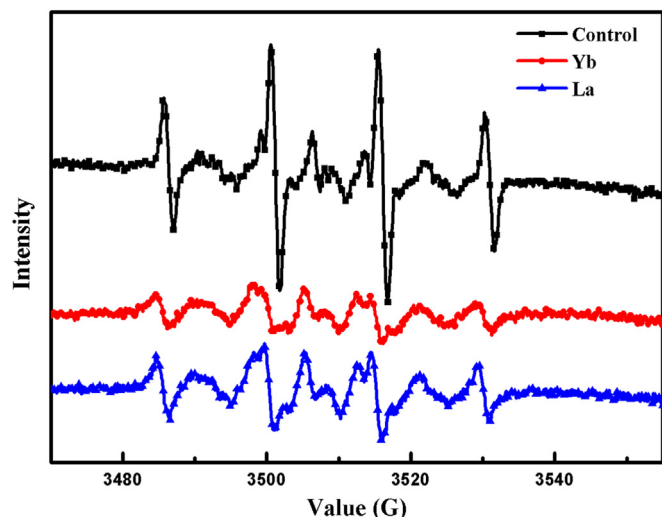


Fig. 1. ESR spectra measuring the generation of hydroxyl radicals by the Fenton reaction in the presence of RE(OTf)<sub>3</sub>.

PE/RE2 and PE/RE5, respectively.

### 2.2. Preparation of flame retardant PE composites

The flame retardant PE composites were melt compounded using a ThermoHaake Rheomixer (Typ557–8310, Germany) at 180 °C for 8 min at a rotor speed of 60 rpm. The formulation is 50 g for one processing cycle. The formulation was designated as PE/IFRx/REy. x represents the weight percent of IFRs which is composed of APP and PER with the weight ratio of 3:1. y represents the weight percent of rare earth trifluoromethanesulfonate. For instance, PE/IFR23.6/Yb0.4 means that the weight ratio of PE: APP: PER: Yb(OTf)<sub>3</sub> is 76:17.7:5.9:0.4.

## 3. Results and discussion

### 3.1. The thermal stability of PE filled with La(OTf)<sub>3</sub>

Fig. 1 presents the generation of hydroxyl radicals (HO·) by the Fenton reaction ( $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO\cdot$ ) in the presence of La(OTf)<sub>3</sub> and Yb(OTf)<sub>3</sub>. The generation of radical species was monitored by ESR spectroscopy with DMPO as trapping agent. The yield of HO· radicals is monitored by measuring the intensity [17]. The number of generated radicals is proportional to the intensity of the ESR signal. The radical scavenging capacity can be determined by measuring and

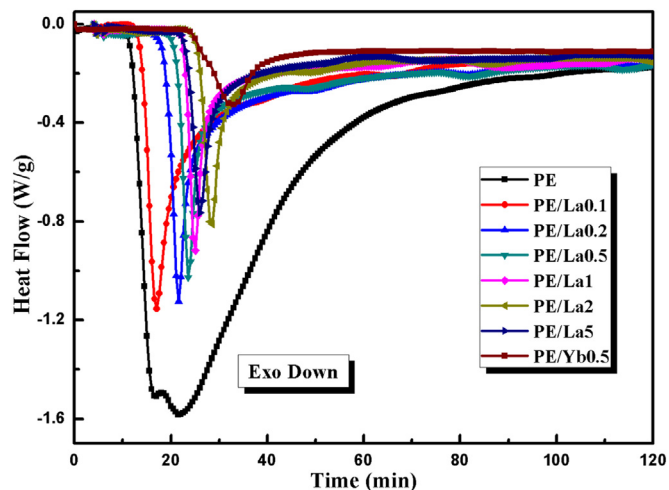


Fig. 3. DSC curves of PE filled with RE(OTf)<sub>3</sub> under 200 °C.

Table 1  
Data obtained from TGA and DSC tests of PE filled with La(OTf)<sub>3</sub>.

Samples	T <sub>5%</sub> (°C) <sup>a</sup>	T <sub>max</sub> (°C) <sup>b</sup>	OIT (min) <sup>c</sup>	ΔH <sub>d</sub> (J/g) <sup>d</sup>
PE	334	374	11.0	61.0
PE/La0.1	339	390	13.1	28.4
PE/La0.2	345	400	17.1	27.6
PE/La0.5	380	423	19.7	25.5
PE/La1	395	424	22.0	20.2
PE/La2	391	432	24.5	19.2
PE/La5	389	429	22.2	18.3
PE/Yb0.5	407	440	24.3	13.0

<sup>a</sup> T<sub>5%</sub>, the temperature at which 5 wt% mass loss occurs.  
<sup>b</sup> T<sub>max</sub>, the temperature corresponding to the maximum rate of weight loss.  
<sup>c</sup> OIT, the oxidative induction time at which the heat flow is 0.05 W/g.  
<sup>d</sup> ΔH<sub>d</sub>, the heat evolution produced in the process of oxidation.

comparing the decrease of ESR signal intensity. The spectrum gives a characteristic quartet signal of DMPO/ HO· spin adduct with an intensity ratio 1:2:2:1 (Control). The presence of La(OTf)<sub>3</sub> makes the ESR signal intensity of characteristic peak weakened, proving the radical trapping capacity of La(OTf)<sub>3</sub>. But the reduction is much less compared with Yb(OTf)<sub>3</sub> under the same concentration. In other words, the HO· trapping capacity of Yb(OTf)<sub>3</sub> is better than La(OTf)<sub>3</sub>.

The thermogravimetry (TG) and differential thermogravimetry (DTG) curves of PE filled with La(OTf)<sub>3</sub> under air are shown in Fig. 2. Fig. 3 presents the DSC curves of PE filled with La(OTf)<sub>3</sub> under 200 °C,

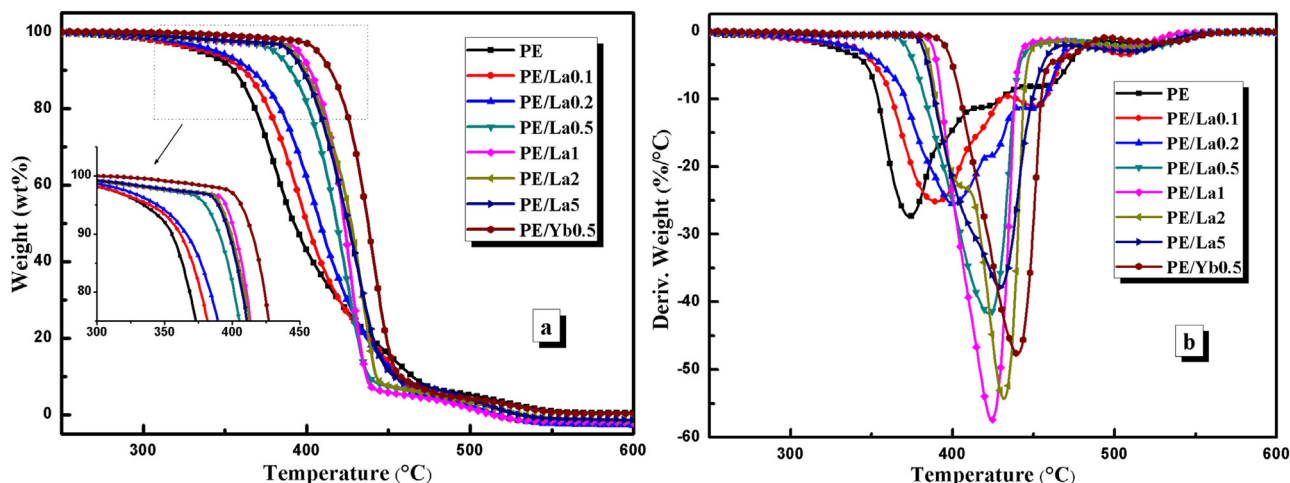


Fig. 2. TG (a) and DTG (b) curves of PE filled with RE(OTf)<sub>3</sub> in air.

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