# Effects of OMMT on the aging behaviors of halogen-antimony flame-retarded LGFPA6 composites: Flammability and thermal degradation kinetics

Xiaoling Zuo[b,c,*], Haishuo Song[a], Huiju Shao[a], Minh Hang Au[d], Tao Wei[a], Jianbing Guo[a,**]

[a] National Engineering Research Center for Compounding and Modification of Polymeric Materials, and College of Materials Science and Metallurgy, Guizhou University, Guiyang, China
[b] Institut de Science des Materiaux de Mulhouse IS2 M, UMR CNRS 7361, UHA, Mulhouse, France
[c] Laboratoire de Chimie Organique et Bioorganique, EA4566, UHA, ENSCMu, Mulhouse, France
[d] School of Chemical and Pharmaceutical Sciences, Dublin Institute of Technology, Dublin, Ireland

## ARTICLE INFO

## ABSTRACT

After a long-term thermo-oxidative exposure, compared to the long-glass-fiber reinforced polyamide 6 composite containing halogen-antimony flame retardants (FR/LGFPA6), substitution of a certain content of flame retardants with organo-modified montmorillonite (OMMT) was found to positively affect the FR/LGFPA6 composite in some cases (i.e. flammability and thermal degradation kinetics). The aged OMMT/FR/LGFPA6 composite not only was less flammable but also behaved better in the formation of char residues. All the calculated apparent activation energy obtained by the methods of Friedman, Flynn-Wall-Ozawa and Coats-Redfern in a dynamic measurement showed an obvious increase for the OMMT/FR/LGFPA6 composite after aging, a theoretical evidence for its improved flame retardancy.

## 1. Introduction

Recently, the research focus of modification of composites is mainly about using fillers/reinforcements with nano- to macro-scale to fill polymeric matrix. Herein, glass fibers (GF) and flame retardants (FR) have been extensively introduced into materials to improve their mechanical performance and flame resistance, respectively [1–3]. Regarding the flame retardants, of particular interest are studies investigating the synergistic effects of nanoclays with various FR combinations on polymeric materials [4]. Since clay can improve the mechanical and thermal properties of the neat material with the superiorities associated with low cost, few adding quantity and easily processable with polymers [5].

The degradation of materials is an unavoidable phenomenon in a wide range of environments and service conditions, especially during storage and fabrication, thereby resulting in the deteriorated performance [2,6]. Interestingly, not all the flammability and/or flame retardancy of the flame-retarded materials would yield to aging. For instance, our group found that thermo-oxidative aging to some extent optimized the flame retardancy of LGFPA6 composites containing tris(tribromophenyl) cyanurate and antimony trioxide ($Sb_2O_3$), namely,

becoming less flammable and char residues more rich after aging [2]. Besides, Colonna et al. [7a] reported that aging treatment at 90 °C for 120 h enormously delayed the time to ignition (TTI) of EVA/clay nanocomposite, from $64 \pm 1$ to $110 \pm 20$ s. Lesaffre et al. [7b] researched PLA/ammonium polyphosphate/melamine/clay composites under hydrolysis aging at 50 °C with 75% relative humidity. They found that the peak of heat release rate (pHRR) decreased as a function of aging time, from 111 (unaged) to 55 kW/m² (46 days aging), meanwhile, accompanied by the increased LOI values, from 43 to 48%. Based on these conclusions, we infer that the major factor can be ascribed to the differences in the anti-aging properties of the different fire-retardant formulations. So our interest lies in studying the effects of fire-retarding additives on the aging behaviors of a composite, with special emphasis on the degradation behavior and flammability after a period of aging.

The aim of this work is to study the influences of aging on the flammability and thermal degradation kinetics of LGFPA6 composites containing brominated epoxy resin (BER)-$Sb_2O_3$-organomodified montmorillonite (OMMT) (labeled as OMMT/FR/LGFPA6), compared with those of composites in the absence of OMMT (labeled as FR/LGFPA6). To the best of our knowledge, there is no report about the fire behavior

---

* Corresponding author at: Institut de Science des Materiaux de Mulhouse IS2M, UMR CNRS 7361, UHA, Mulhouse, France.
** Corresponding author.
*E-mail addresses:* shanghai0401@163.com (X. Zuo), guojianbing_1015@126.com (J. Guo).

of a composite formulated with such hybrid flame retardants being exposed to an accelerated aging treatment condition at 160 °C. For one thing, this given temperature is slightly higher than the glass transition temperature ($T_g$) of BER (~135 °C, provided in Supporting Information Fig. 1). For another, as for the research of surface pile up of silicate lamellas upon high temperature, most treatment temperatures were carried out within the range 180–250 °C [8,9]. Few studies employed a lower heat treatment temperature to analyze this phenomenon. Except that Colonna et al. [7a] pointed out no significant change in the lamellas surface distribution of nanocomposites after aging 120 h at 90 °C. Additionally, based on our preceding study, aging at 160 °C could make an appreciable difference in the fire behavior of flame-retarded composites relative to the composites before aging [2]. Thus, 160 °C is chosen as our accelerated aging temperature in this study.

Evaluations of the surface elemental concentration and the change of surface morphology, would be performed by energy dispersive X-ray spectrometer (EDS) and scanning electronic microscopy (SEM). The combustion and flame retardancy would be studied by the following tests, cone calorimeter test (CONE), limiting oxygen index (LOI) and vertical burning test (UL-94). The morphology and structure of OMMT would be monitored by energy dispersive X-ray spectroscopy (XRD). And the thermal degradation kinetics would be investigated by thermogravimetric analysis (TGA).

## 2. Materials and methods

### 2.1. Materials

The polyamide 6 was a standard viscosity grade product, produced by UBE Co. Ltd, Japan (1013B). The continuous glass fiber rovings (ECT4301H), with a diameter of 17 μm, treated with a silane coupling agent, were obtained from Chongqing Polycomp International Co. Ltd, China. Brominated epoxy resin was supplied by Shenzhen Kemi Chemical Co. Ltd, China (KM-H01, Fig. 1), with a bromine content of 51–53.0% (w/w) and a molecular weight ($M_w$) of 22,000. Antimony trioxide was produced by Huaxing Loudi Antimony Industry Co. Ltd, China. For nanoparticles, organo-modified montmorillonite DK5, modified by bis-(2-hydroxyethyl)methyl tallowalkyl ammonium cations was supplied by Zhejiang Fenghong New Material Co. Ltd, China. All the products were used as received.

### 2.2. Preparation of composites

At first, all products were dried for 24 h at 80 °C in a vacuum oven to remove any moisture before use. The LGFPA6 composites were blended in an intermeshing counter-rotating two-screw extruder (TSE-40A, L/D = 40, D = 40 mm, Coperion Keya Machinery, Co., Ltd. China) in a temperature range of 205–240 °C (maintained 30 wt% glass fiber loading) with a screw speed of 300 r/min and cooled down in an impregnation device. Flame retardant masterbatches were prepared by mixing 40 wt% of PA6 with 50 wt% of BER and 10 wt% of $Sb_2O_3$ using the same two-screw extruder in a range of 205–240 °C with a screw speed of 300 r/min.[2] The OMMT/PA6 masterbatches were obtained by mixing together 70 wt% of PA6 with 30 wt% of OMMT following the same protocol as outlined above [7d]. All continuous extrudates were

then chopped into granules with a length of 12 mm. All granules were dried for 24 h at 80 °C under vacuum before injection molding. FR/LGFPA6 and OMMT/FR/LGFPA6 composites were then injection-molded (Type CJ80M3V, Chende Plastics Machinery Co., Ltd, China) in a range of 225–270 °C into various specimens for testing and characterization (detailed process is shown in Fig. 2). The mass percentage of each component for both composites is listed in Table 1.

Before oven aging, all samples were dried at 80 °C for 24 h under vacuum [2]. Aging of composites was carried out in a circulating air oven (GZX-9240 ME, Boxun, China) at 160 °C for 30 days (the temperature fluctuation range is limited within ± 1 °C). After they were taken out, sealed in a desiccator for 24 h and then subjected to characterizations. The changes of various properties for the aged composites were compared with the unaged composites.

### 2.3. Measurements

The flame retardancy of OMMT/FR/LGFPA6 composite was evaluated by LOI and UL-94 tests. The LOI value was surveyed on a JF-3 oxygen index meter (Jiangning, China) with the dimensions of $80 \times 10 \times 4$ mm$^3$ according to ASTM D2863-2006. The UL-94 test was performed according to ISO 1210: 1996 on a SH5300 instrument (made by HongKong Rehoboth Testing Equipment). The specimens used for this test were of the dimensions of $130 \times 13 \times 3.2$ mm$^3$. The CONE test was carried out by a FTT cone calorimeter (UK device) according to ISO 5660:2002 under a heat flux of 50 kW/m$^2$ at $25 \pm 2$ °C and a relative humidity $50 \pm 5\%$. The specimens used for this test were of the dimensions of $100 \times 100 \times 6$ mm$^3$. The experiment was stopped as soon as the flame was extinguished. Each specimen was wrapped in an aluminium foil and exposed horizontally to the heater with a standard distance of 25 mm. The CONE values were the average of three measurements and the results were considered to be reproducible to ± 10%.

SEM images obtained on KYKY–2800B (KYKY Technology Development, China) were used to investigate the residue chars after LOI tests and the composite surfaces for all samples with an acceleration voltage of 25 KV. All samples were recorded after gold coating surface treating. EDS (INCA 3294, Oxford Instruments, UK) was rapidly performed in SEM, operating at 10 kV and a working distance of 10 mm, for determining the elemental concentration changes in surfaces and char residues of different samples. The samples were surrounded with a conductive silver paint to make contact on the surface and carbon-coated in a rotary evaporator. Each sample was imaged by back-scattered electrons. The composition elements in weight and atom percentages with percent errors were analyzed by an automatic background subtraction and a ZAF correction matrix. The whole micrograph for each sample was analyzed, except for the surface of the aged OMMT/FR/LGFPA6 composite (Fig. 3(d)), where obviously presents some accumulations (under the red circle), so which acted as our selected region for the element measurement.

The thermal degradation kinetics for all composites were studied by a TGA (TA, Q-50 instruments, Co., USA), high purity grade air and nitrogen with 60 ml/min and 40 ml/min flow, respectively, the heating rates were in a range of 10–40 °C/min [2,3e]. The thermal stabilities for the commercially available BER/$Sb_2O_3$ combination and all the com-
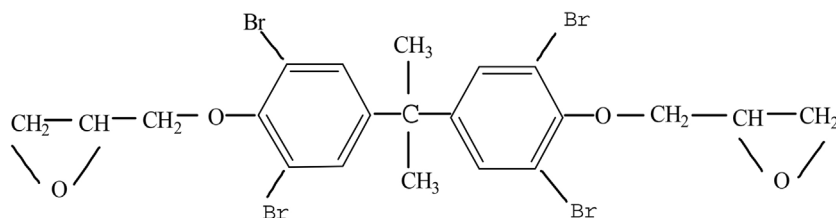


**Fig. 1.** Molecular structure of brominated epoxy resins.