



# Thermal degradation of polystyrene composites. Part II. The effect of nanoclay



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## ABSTRACT

In this work, thermal degradation behavior polystyrene/organoclay nanocomposites containing tri-bromophenol end-capped brominated epoxy oligomer, (BE) with or without  $\text{Sb}_2\text{O}_3$  were investigated systematically via direct pyrolysis mass spectrometry. Incorporation of organically modified montmorillonite into polystyrene, (PS) matrix not only increased thermal stability but also the probability of radical recombination, disproportionation and carbonization reactions causing increase in the char yield. Exfoliation of organoclay in BE phase of PS-BE matrix affected the extent of radical coupling and disproportionation reactions between the thermal degradation products of PS and organic modifier. In addition, the evolution of BE based products was hindered partly and the attacks of HBr to epoxy units generating  $\text{H}_2\text{O}$  became more efficient. During the pyrolysis of polystyrene/organoclay nanocomposite involving both BE and  $\text{Sb}_2\text{O}_3$ , the relative yields diagnostic products of both oxybromides and bromides of antimony were increased significantly in the temperature region where PS decomposition took place which in turn increased the efficiency of radical scavenging and reduced peak heat release rate while increasing limiting oxygen index.

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## 1. Introduction

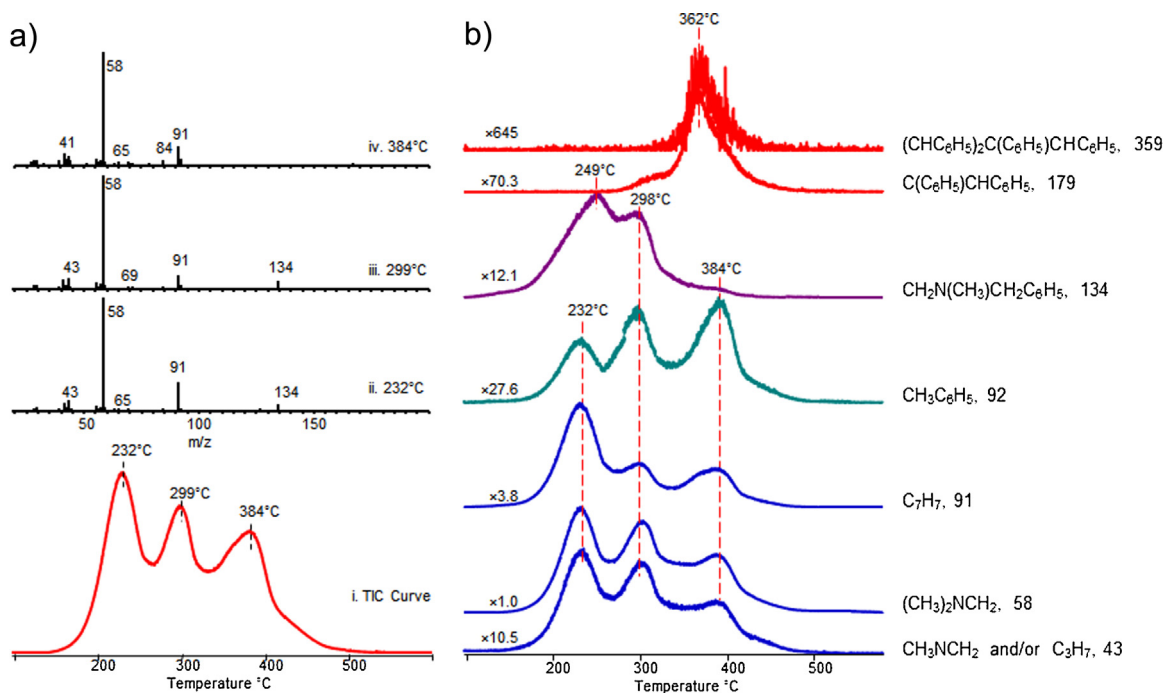
The improvement of thermal stability and flammability performance of widely used thermoplastics is a major concern both in industries and in an academic world. As a consequence, modification of polystyrene, PS, being one of the most commercialized thermoplastic, by addition of flame retardants is crucial. It has been shown that the nanoparticles, brominated flame retardants and  $\text{Sb}_2\text{O}_3$  can be used as flame retardant additives or fillers for polystyrenes [1–24]. The addition of small percentage of nanoparticles with conventional flame retardants seemed to improve the flame-retardant performance. Actually, nanoclay addition not only affects flame characteristics but also thermal behavior. It has been found that the degradation mechanism of PS changes from a chain scission process for the polymer to a complex two-step nucleation-driven reaction upon incorporation of nanoclays and the clay platelets within the composite could act as nucleation centers for the decomposition [2]. Bourbigot et al. determined that by incorpo-

ration of clay into polystyrene matrix, inter-chain reactions became significant [6]. In addition, increase in extent of radical recombination reactions, hydrogen abstraction reactions, and formations of head-to-head compounds and conjugated double bonds were detected [6]. The role of the surface properties and shape of clay type on the morphology, thermal, and thermo-mechanical properties of the polystyrene (PS)/clay nanocomposites prepared via free-radical emulsion polymerization have been evaluated and it has been determined that the composites prepared with montmorillonite clay exhibited greater thermal stability and higher storage moduli than those prepared using attapulgite clay [10].

Thermal degradation of polystyrene and high-impact polystyrene involving brominated flame retardants or their combinations with antimony oxide have also been the subject of several studies [11–19]. Oligomeric brominated flame retardants were preferred because of decreased toxicity, and improved mechanical properties, melt flow characteristics and thermal stability among the conventional non-oligomeric types. The use of  $\text{Sb}_2\text{O}_3$  in combination with halogenated flame retardants was found to increase the release rates of halogens by the generation of antimony halides and oxyhalides during degradation [14–24]. Isitman and coworkers investigated flammability of polystyrene nanocomposites containing brominated epoxy and/or antimony

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**Fig. 1.** (a) The TIC curve and the pyrolysis mass spectra recorded at the peak maxima and (b) the single ion evolution profiles of some selected products generated by pyrolysis of C10A.

oxide using limiting oxygen index, LOI and vertical burning ratings (UL-94) [8]. The enhancement in the fire-retardant effectiveness was associated not only with the gas-phase hot radical entrapment by halogenated flame-retardant system coupled but also with the condensed-phase physical action of nanodispersed organoclay.

Recently, we have studied thermal degradation of PS involving brominated epoxy, BE and/or antimony oxide,  $\text{Sb}_2\text{O}_3$  [24]. The interactions of  $\text{Sb}_2\text{O}_3$  with BE generated antimony bromides and lowered degradation temperatures of all components compared to pure forms and PS/BE. However, the detection of noticeably high char yield indicated the generation of a cross-linked structure as a consequence of reactions between the PS matrix and the additives [24].

In this work, our main purpose is to investigate the thermal degradation behavior of PS/organoclay nanocomposites containing tribromophenol end-capped brominated epoxy oligomers with or without  $\text{Sb}_2\text{O}_3$  systematically via direct pyrolysis mass spectrometry to clarify the processes effective in flame retardancy.

## 2. Experimental

### 2.1. Materials

PS ( $M_w \sim 192,000$  g/mol) was obtained from Aldrich (St. Louis, MO, USA). Montmorillonite nanoclay, Montmorillonite nanoclay modified with dimethylhydrogenated-tallow benzyl quaternary ammonium cation (Cloisite 10A, C10A) was supplied by Southern Clay Products, Gonzales, TX, USA. The brominated flame retardant was a tribromophenol end-capped oligomer, BE, (molecular weight  $15,000$  gmol $^{-1}$ ,  $\sim 53$  wt% Br) obtained from ICL Industrial Products (Beersheba, Israel).  $\text{Sb}_2\text{O}_3$  (99.9%) was an industrial-grade product obtained from a Chinese source.

Materials were prepared via an ultrasound-assisted solution intercalation technique described in detail in a previous work [8]. The samples PS/C10A and PS-BE/C10A and PS-BE- $\text{Sb}_2\text{O}_3$ /C10A, contained 5 wt% C30A. Both of the samples PS-BE/C10A and PS-BE-

$\text{Sb}_2\text{O}_3$ /C10A contained 20 wt% BE, and finally PS-BE- $\text{Sb}_2\text{O}_3$ /C10A contained 3 wt% of  $\text{Sb}_2\text{O}_3$ .

### 2.2. Instrumentation

Direct pyrolysis mass spectrometry, DP-MS, analyses of PS and their composites were done by Waters Micromass Quattro Micro GC Mass Spectrometer coupled to a direct insertion probe. It has a mass range of 10–1500 Da. The temperature was increased to  $50^\circ\text{C}$  at a rate of  $5^\circ\text{C min}^{-1}$ , then was increased to  $650^\circ\text{C}$  at a rate of  $10^\circ\text{C min}^{-1}$  and held at  $650^\circ\text{C}$  for 5 additional minutes during pyrolysis. About 0.010 mg samples were pyrolyzed in quartz sample vials. 70 eV EI mass spectra at a mass scan rate of  $1$  scan  $\text{s}^{-1}$  was recorded during pyrolysis. The pyrolysis mass spectrometry analyses were repeated several times to ensure reproducibility. Every time almost exactly the identical trends were obtained.

## 3. Results and discussion

In order to investigate the effects of organically modified montmorillonite on thermal degradation of PS composites containing tribromophenol end-capped brominated epoxy oligomers BE with or without  $\text{Sb}_2\text{O}_3$ , pyrolysis behaviors of each component and their combinations were also analyzed systematically.

### 3.1. Cloisite 10A, C10A

The total ion current (TIC) curve, the variation of total ion yield as a function of temperature recorded during the pyrolysis of dimethyl, benzyl, hydrogenated tallow, quaternary ammonium modified montmorillonite, C10A, is given in Fig. 1(a) Three overlapping broad peaks are present in the TIC curve with maxima at around 232, 299 and  $384^\circ\text{C}$ . The mass spectra recorded at the peak maxima are almost identical, showing base peak at  $m/z = 58$  Da associated with fragments  $\text{CH}_2\text{N}(\text{CH}_3)_2$  and/or  $\text{CH}_3\text{NHC}_2\text{H}_4$  taking into consideration classical fragmentation patterns for alkyl amines. Moderate peaks at  $m/z = 91$  and  $134$  Da were readily

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