

# THERMAL AND FLAMMABILITY ANALYSES OF POLY(HYDROXYAMIDE) (PHA) AND ITS DERIVATIVES

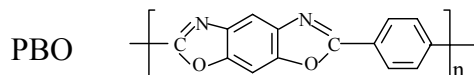
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## INTRODUCTION

Fire is a potential hazard for human life. With the increased use of light-weight high-performance polymeric materials in some advanced applications such as high-rise buildings, submarines, ships and aircraft cabins, their flammability has become a major concern.<sup>1</sup> In order to improve the fire safety, it is important to develop some new inherently fire-resistant polymers that have high thermal stability, resistance to the spread of flame, and low burning rate under high heat flux.<sup>2</sup> Polybenzoxazole (PBO) is one of these polymers with highly stable, aromatic and heterocyclic rings.<sup>3-4</sup>



The PBO polymers have many good properties such as high thermal stability, good chemical resistance, high modulus and strength. However, the high cost of the finished polymers and specialized fabrication techniques greatly limit their applications. Researchers at the University of Massachusetts, Amherst<sup>5-7</sup> found that the precursor polymers---poly(hydroxyamide) (PHA) and its derivatives---have very good solubility in aprotic solvents. Thus, these PHAs can be easily processed as films, composites, and fibers. When cyclized, they will absorb heat and liberate water or some other small molecules such as phosphorus, fluorine or bromine compounds depending on their structures. At the same time they are converted to high-temperature heterocyclic PBO polymers with outstanding flame resistance. These soluble aromatic PHAs with extremely low flammability are potential candidates as solvent-processable polymers for many high-performance applications.

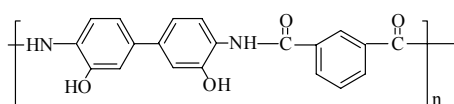
In this paper, three microscale experimental techniques---pyrolysis-combustion flow calorimetry (PCFC), thermogravimetric analysis (TGA) and pyrolysis GC/MS---have been combined to fully characterize the thermal decomposition and flammability of a series of polybenzoxazole (PBO)-precursor polymers, poly(hydroxyamide) (PHA) and its bromine, fluorine, phosphate, or methoxy derivatives.

## EXPERIMENTAL

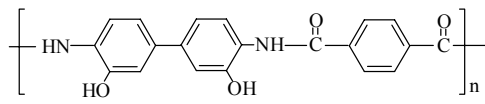
### Materials:

The chemical structures of PHA and its derivatives studied (Scheme a~d) are given below.<sup>8</sup> All the samples were supplied by Dr. Kantor's group at the University of Massachusetts at Amherst.

(a) PHA

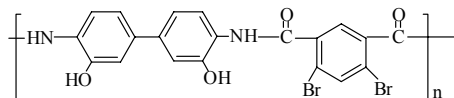


iso--PHA-1 (-OH)

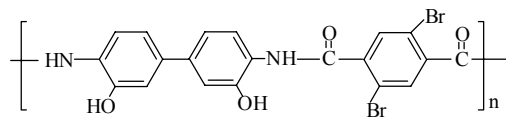


para--PHA-2 (-OH)

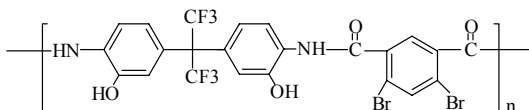
(b) Halogenated PHAs



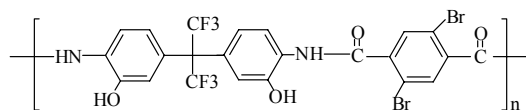
PHA-3 (m-Br)



PHA-4 (p-Br)

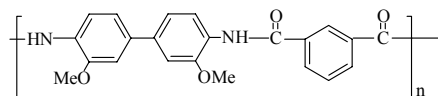


PHA-5 (-CF<sub>3</sub>, m-Br)

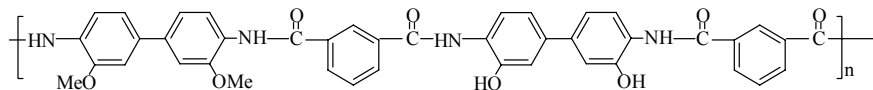


PHA-6 (-CF<sub>3</sub>, p-Br)

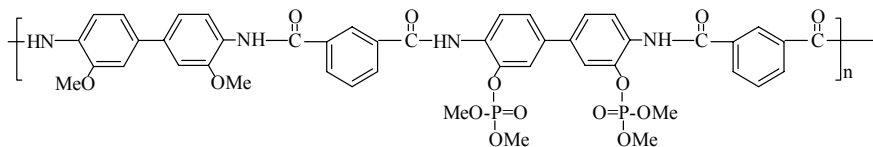
(c) PHAs containing -OMe group



PHA-7 (-OMe)

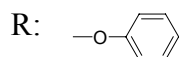
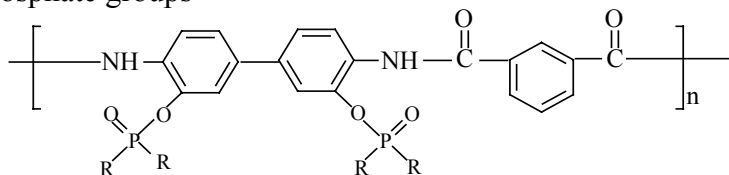


PHA-8 (-OH, -OMe)



PHA-9(-OMe, -PO<sub>2</sub>(OMe)<sub>2</sub>)

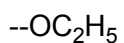
(d) PHAs containing phosphate groups



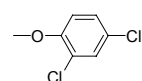
PHA-10



PHA-11



PHA-12



PHA-13



PHA-14

## Characterization:

The thermal decomposition process of all the polymers is examined by TGA under a nitrogen atmosphere. The sample weight is around 10 mg and the heating rate is 10°C/min. The flammability of the polymers is measured by pyrolysis-combustion flow calorimetry (PCFC).<sup>9-11</sup> 1.0±0.1 mg samples are pyrolyzed in a commercial device (Pyroprobe 2000) to 930°C at 4.3°C/s under nitrogen and the volatiles are completely combusted at 900°C. The composition of the volatiles is analyzed by pyrolysis GC/MS. 0.2~0.3mg samples are pyrolyzed under the same conditions used in PCFC measurements. Then the volatiles from pyrolysis are separated by Hewlett Packard 5890 series II gas chromatography and analyzed by Hewlett Packard 5972 series MS spectroscopy.

## RESULTS AND DISCUSSION

### *Thermal decomposition process*

Results of TGA analyses of PHA and its derivatives under N<sub>2</sub> are shown in Figure 1.

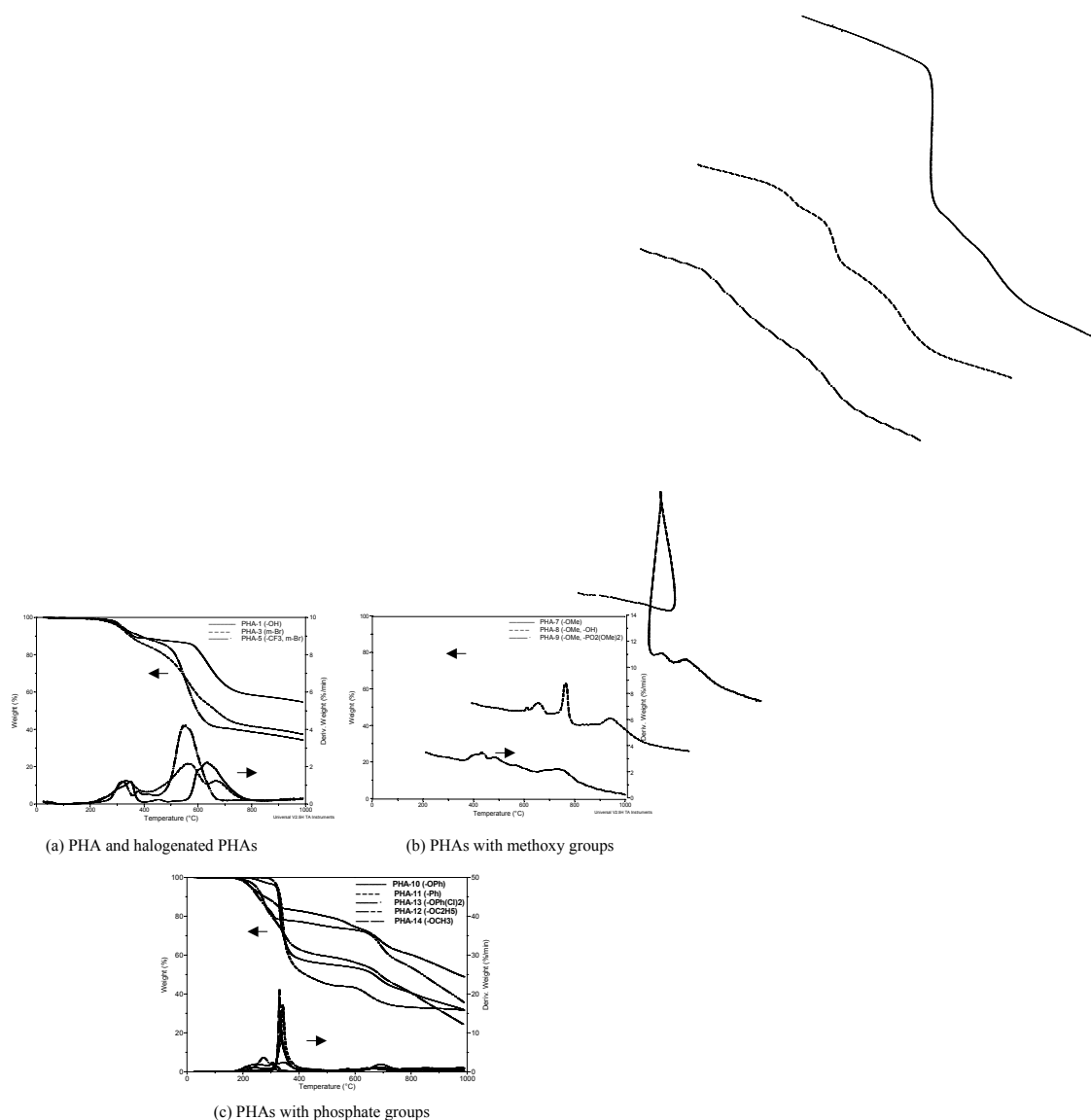


Figure 1 TGA and derivative of TGA (DTG) curves of PHA and its derivatives (in N<sub>2</sub>)

The thermal decomposition process of all the PHAs (except for PHA-8, 9 and some phosphate PHAs) occurs essentially in two major stages. In the case of PHA-1 and 2, the weight loss in the first stage (250~500°C) is about 11%, which agrees very well with the calculated value (11.5%) if we assume that PHA is cyclized into PBO by loss of water. The second stage (580~820°C) is associated with a further 30% weight loss due to the breakage of the polymer main chain. Weight loss then levels off, producing a high char yield of 56%. It is also found that para-substituted PHA-2 is more thermally stable than iso-PHA-1, although they decompose in a similar process.

The introduction of bromine and trifluoromethyl groups (PHA-3 to 6) does not affect the onset decomposition temperature of the first stage (still around 260~290°C), but it does greatly reduce the thermal stability of the second stage (around 500~510°C), which suggests that the halogenated PBOs are less stable than the non-halogenated PBOs.

PHA-7, in which hydroxyl groups are totally replaced by methoxy groups, is quite stable up to about 380°C, but then it has a sharp weight loss in the range of 386~469°C. The main weight loss in the first stage (about 40%) is not only due to the assumed cyclization reaction in which methanol is released, but also to the chemical reactions involving the breakage of the polymer main chain. Therefore, it can be inferred that the thermal decomposition mechanism of this polymer must be quite different from that of PHA-1. PHA-8 with both methoxy and hydroxyl groups shows three stages of decomposition which are almost the overlay of TGAs of PHA-1 and PHA-7.

The thermal decomposition process of PHA-9 ~14 which contain different phosphate groups is much more complicated, but it still can be roughly divided into two stages. At low temperatures (below 500°C), phosphate groups are cleaved from the polymer main chain due to their weak linkages. When increased to high temperatures, the polymer main chain becomes disrupted.

In an inert gas (N<sub>2</sub>), all these PHA polymers can produce high char yield. Char can act as a thermal barrier which can greatly reduce the flammability of polymers.

### *Flammability*

The flammability of all these PHA polymers is measured by the PCFC method developed by Lyon and Walters.<sup>9-11</sup> The heat release rate of the polymers is calculated from the measured oxygen consumption. Heat release capacity, obtained by dividing maximum heat release rate by the sample weight and heating rate, is an important parameter to evaluate the flammability of polymers. Direct integration of the heat release rate versus time gives the total heat of combustion of the fuel gases per unit sample mass. Char yield is determined by weighing the sample before and after test.

Table 1 shows the PCFC results and some TGA results, from which we can see that PHA and most of its derivatives (except for PHA-7, 10 and 11) have relatively low flammability compared with PE, PS, PC, Kevlar and PEEK. It is also found that the flammability of para-type PHAs is the same as that of iso-types. Flammability of PHA-7 is relatively high, but it can be reduced by partially replacing methoxy groups with hydroxyl (PHA-8) or phosphate groups (PHA-9). However, if methoxy or hydroxyl groups are totally substituted by phosphate groups (PHA-10~14), the flammability of polymers is greatly dependent on the types of ester groups incorporated. For example, PHA-10 and 11 have very high flammability due to their fast decomposition rates and release of more flammable compounds such as triphenyl phosphate, benzene and phenol. In addition, from the TGA results, it can be seen that all the PHA polymers with low heat release rates usually have very low mass loss rate.

**Table 1 Flammability of PHA and its derivatives (PCFC and TGA results)**

Polymers	H.R.capacity* (J/g.K)	Total heat* (kJ/g)	T <sub>max</sub> (°C)	Max. mass loss rate (x 10 <sup>3</sup> /s)	Char yield (%)
PHA-7 (-OMe)	130	17	409	1.4	43
PHA-1 (-OH) (iso)	42	10	633	0.4	56
PHA-8 (-OMe, -OH)	33	11	425	0.5	55
PHA-9 (-OMe, PO <sub>2</sub> (OMe) <sub>2</sub> )	18	9	658	0.2	60
PHA-3 (-OH, m-Br)	17	5	563	0.4	39
PHA-5 (-OH, -CF <sub>3</sub> , m-Br)	8.0	3	553	0.7	36
PHA-10 (-OPh)	340	15	327	3.3	36
PHA-11 (-Ph)	210	21	341	2.9	32
PHA-12 (-OC <sub>2</sub> H <sub>5</sub> )	73	9	304	0.4	41
PHA-13 (-OPh(Cl) <sub>2</sub> )	59	8	271	0.6	29
PHA-14 (-OCH <sub>3</sub> )	19	8	319	0.2	52
Polyethylene (PE)	1558	40	471	9.1	0
Polystyrene (PS)	1199	37	417	5.2	0
Polycarbonate (PC)	382	19	514	3.3	17
Kevlar	292	15	576	2.5	32
Poly(ether ether ketone) (PEEK)	163	13	586	2.2	46
Polyimide (PI)	29	9	602	0.5	50

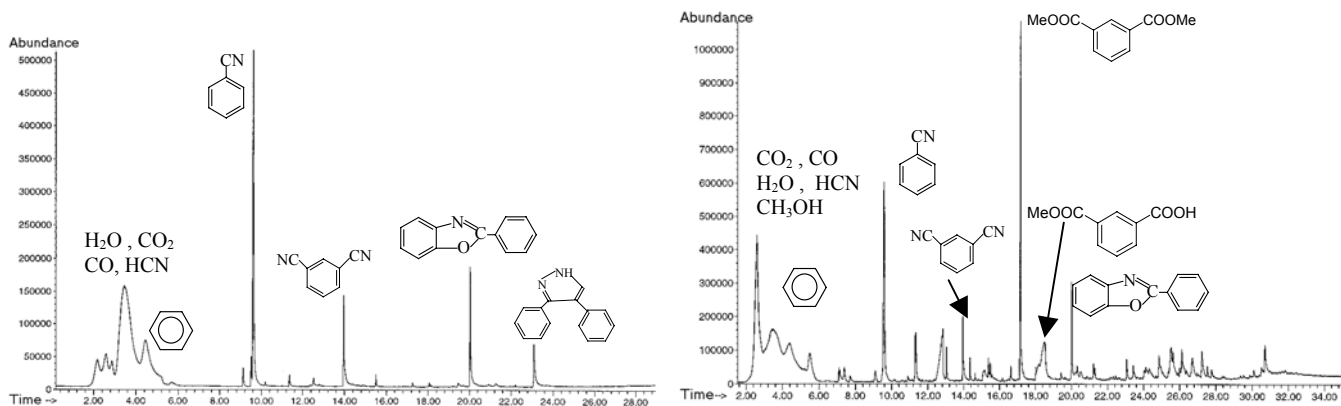
\*: PCFC results

T<sub>max</sub>: the temperature at maximum mass loss rate

Char yield: the amount of residue at 930°C

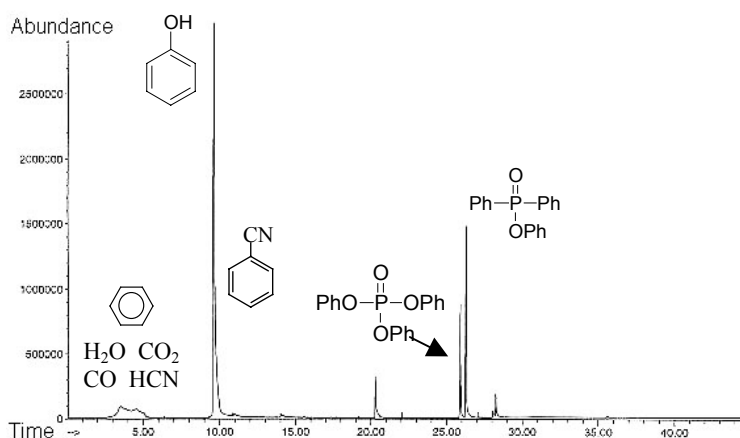
#### *Identification of volatiles by pyrolysis GC/MS*

The thermal decomposition products of all the PHAs are characterized by pyrolysis GC/MS. The total ion current (TIC) pyrograms of PHA-1, 7 and 10 are shown in Figure 2. Generally, the pyrolysis gases from PHAs can be divided into four groups: (1) permanent gases and low-boiling-point products such as CO, CO<sub>2</sub>, H<sub>2</sub>O, CH<sub>3</sub>OH and HCN; (2) aromatic hydrocarbons, aromatic amines, nitriles, benzoxazoles and isocyanates which correspond to partial fragments of the polymer main chain; (3) halogenated compounds and phosphate compounds which are attributed to the cleavage of these substituents from the polymer main chain; and (4) high-boiling-point products formed by isomerization, rearrangement or crosslinking reactions at high temperatures, such as 3,4-diphenyl-1H-pyrazole.



**PHA-1 (-OH)**

**PHA-7 (-OMe)**



**PHA-10 (-OPh)**

**Figure 2** TIC pyrograms (heating to 930°C at 4.3°C/s)

The composition of volatiles at different temperature ranges is also investigated. For PHA-1 to 6, the major volatiles at the first stage are water and a small amount of  $\text{CO}_2$ . However, for PHA-7 to 9 with methoxy groups, the volatiles below 600°C also contain a large amount of 1,3-dimethyl benzoate, which indicates the scission of the polymer backbone at low temperatures. The phosphate PHAs release a large amount of flammable phosphate compounds such as triphenyl phosphate, diphenyl-phosphinic acid phenyl ester, triethyl phosphate and trimethyl phosphate as well as fragments derived from the ester groups such as phenol, benzene, ethanol, 2,4-dichlorophenol and methanol below 500°C, which leads to their high flammability.

Except for phosphate PHAs, about 70 wt% of the volatiles released from the other PHAs are  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{HCN}$ , and around 30 wt % are aromatic compounds.

## CONCLUSIONS

Almost all the PHAs studied, except for PHA-7, 10 and 11, possess very low flammability, especially the ones containing halogen groups. PHA-7 is more thermally stable, but it exhibits higher flammability. Some phosphate PHAs are also very flammable due to the extensive

cleavage of phosphate side groups from the polymer main chain at low temperatures. Generally, the thermal decomposition process of the PHAs can be divided into two stages. In the first stage (below 500°C), small molecules such as water are released to form some structures which contain certain PBO units. In the second stage (above 500°C), the random scission of the polymer backbone occurs. The pyrolysis-GC/MS results suggest that the thermal decomposition of PHA-1, PHA-7 and phosphate PHAs (PHA-10~14) undergoes different mechanisms.

### ACKNOWLEDGEMENTS

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