Studies on thermal degradation of acrylonitrile–butadiene–styrene copolymer (ABS-Br) containing brominated flame retardant

Thallada Bhaskar a, Kazuya Murai a, Toshiki Matsui b, Mihai Adrian Brebu c, Md. Azhar Uddin d, Akinori Muto a, Yusaku Sakata a,*, Katsuhide Murata e

a Department of Applied Chemistry, Faculty of Engineering, Okayama University, 3-1-1 Tsushima Naka, 700-8530 Okayama, Japan
b Toda Kogyo Co., Ltd., Hiroshima 739-0652, Japan
c ’P. Poni’ Institute of Macromolecular Chemistry, 41A Gr. Ghica Voda Alley, Ro 6600 Iasi, Romania
d Process Safety and Environment Protection Group, School of Engineering, The University of Newcastle, Callaghan, NSW 2308, Australia
e K. Murata Research Inc., Ichihara 290-0006, Japan

Received 25 June 2002; received in revised form 7 October 2002; accepted 12 November 2002

Abstract

The thermal degradation of acrylonitrile-butadiene-styrene copolymer (ABS-Br; 10 g) containing brominated flame retardant (Br: 9.59 wt.%) was carried out at 450 °C using a semi batch operation using two different temperature programs. The heating rate was found to affect the quality of the degradation oil and yield of products (liquid, gas and residue). Data on the effect of the temperature program on the accumulation of liquid products was presented. It was found that the majority of the bromine was concentrated in the carbon residue and while majority of the nitrogen accumulates in the liquid products irrespective of degradation mode. The use of a one step constant heating rate process (I) produced a higher liquid yield (39%), than a two step process (29%). Differences were also noted in the Br and N contained in the liquids produced by the two processes.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: ABS-Br; Thermal degradation; Flame retardant
1. Introduction

The recovery of resources from waste plastics is becoming a very important issue from the viewpoint of the environmental and energy considerations. The amount of waste plastic is increasing worldwide. The world’s limited reserve of coal, crude oil and natural gas, places a great pressure on mankind to preserve its existing non-renewable materials. The degradation of waste plastics into fuel represents a sustainable way for the recovery of the organic content of the polymeric waste and also preserves valuable petroleum resources in addition to protecting the environment [1]. Municipal waste plastic is a mixture of polymers, which contains about 3–5 wt.% acrylonitrile–butadiene–styrene copolymer (ABS) [2]. The pyrolysis of ABS yields valuable substituted aromatics such as toluene, ethylbenzene, styrene, isopropylbenzene, and α-methyl styrene in sufficient quantities to make the process attractive to obtain hydrocarbons or fuel [1]. However, the Waste from Electrical and Electronic Equipment (WEEE) contains plastics such as high impact polystyrene (HIPS) and ABS with flame retardant. More than half of the computer housings analyzed was made of HIPS with the next biggest fraction being ABS [3]. Recently, Kaminsky has reported on the pathways in plastic recycling and the current status of plastics recycling as a source of raw materials [4]. There is an abundance of literature on the recovery of fuels and chemicals through catalytic pyrolysis of plastic waste [5–11]. Chemical recycling of plastics into useful organic compounds by oxidative degradation and oxidative chemical recycling of polyethylene has been reported by Sen et al. [12].

Uddin et al., reported the thermal and catalytic degradation of HIPS (HIPS-Br) containing brominated flame retardant mixed with PVC which involved simultaneous dehalogenation to produce a fuel oil [13]. Brebu et al. [14–17] reported the thermal and catalytic degradation of ABS copolymers and the distribution of nitrogen containing compounds in the degradation products. They found that during the degradation of ABS, the N could lead to the formation of ammonia or very toxic hydrogen cyanide in the gas fraction while N-containing compounds accumulate in the oil fraction. It is also well known that N present in coal derived liquids and shale oil can lead to the corrosion of engine parts and the formation of harmful compounds such as HCN or NOx when these oils are used as fuels [18]. Some of these problems could be reduced in the case of synthetic oils obtained from polymer waste if the degradation is conducted under suitable conditions. Information on the thermal and catalytic degradation of bromine containing ABS-Br is not available in the literature.

The present investigation reports the results obtained during the thermal degradation of ABS containing brominated flame retardant (ABS-Br).
2. Experimental

2.1. Materials

The commercially available ABS-Br was used in the present investigation. The composite was reported to be with 19–22% acrylonitrile (N: 4.62 wt.%), 37–39% butadiene and 30–32% styrene units. The thermogravimetric analysis (TG) of ABS-Br (about 25 mg) was performed in N₂ (400 ml min⁻¹) at a heating rate of 2 °C min⁻¹ and compared the degradation temperature with ABS (pure—without brominated flame retardant). The grain size of ABS-Br was 3 × 1.5 × 1 mm. The structure of the ABS and brominated flame retardant (Br: 9.59 wt.%) are shown in Fig. 1.

Fig. 1. The structures of ABS and brominated flame retardant compounds, (A) acrylonitrile; (B) butadiene; (C) styrene; (D) brominated flame retardant.
2.2. Degradation procedure

The thermal degradation of ABS-Br was performed in a glass reactor (length: 350 mm; id: 30 mm) under atmospheric pressure using a semi-batch operation. A schematic diagram of the experimental setup is shown in Fig. 2(a) and two temperature programs used for the degradation are shown in Fig. 2(b). A special, transparent glass furnace was used for heating, and the temperature was monitored and controlled using digital temperature controller (CHINO, KP 1000). About 10 g of the ABS-Br polymer was degraded in each experiment. In a typical run, the reactor was purged with nitrogen gas at a flow rate of 50 ml min⁻¹ while the reactor
was heated to 150 °C. Once the temperature of 150 °C was reached, the nitrogen flow was stopped while the temperature programming until the degradation temperature as shown in Fig. 2(b) was obtained. Once the nitrogen was stopped, a teflon bag was connected at the end of the reactor to collect the gaseous products. The temperature of waste plastic bed was taken as the degradation temperature. The condensable gaseous products were collected as liquid products (using cold water condenser) and trapped in a measuring jar (Fig. 2(a)).

2.3. Analysis procedure

The degradation products and methods of analysis are shown in Fig. 2(c). A quantitative analysis of the liquid products (collected at the end of formation of liquid products) was performed using a gas chromatograph equipped with a Flame Ionization Detector (YANACO G6800) to obtain the quantity of hydrocarbons and carbon number distribution of the liquid products. The temperature program and the column used for the analysis of liquid products are 40 °C (hold 15 min) → 280 °C (rate 5 °C min⁻¹; hold 37 min) and column, 100% methyl silicone (50 m × 0.25 mm × 0.25 μm), respectively. The distribution of bromine and nitrogen organic compounds in the liquid products was analyzed by a gas chromatograph equipped with atomic emission detector (AED; HP G2350A; column, HP-1; cross-linked methyl siloxane; 25 m × 0.32 mm × 0.17 μm). 1-Bromohexane and nitrobenzene were used as internal standards for the quantitative determination of bromine and nitrogen, respectively, in the GC-AED analysis. The liquid products were also analyzed by a gas chromatograph using a mass selective detector (GC-MSD; HP 5973; column, HP-1; cross-linked methyl siloxane; 25 m × 0.32 mm × 0.17 μm; temperature program, 40 °C (hold 10 min) → 300 °C (rate 5 °C min⁻¹) hold for 10 min). The gaseous products collected in a sealed teflon bag were analyzed by a gas chromatograph equipped with a thermal conductivity detector (GC-TCD; YANACO). The weight of the reactor including the mixed plastics was measured before and after the degradation process. The weight differences before and after the degradation was used to calculate the weight of a residue. Only a small amount of liquid products collected on the reactor walls and side arm. The composition of the liquid products using C–NP gram was characterized (C stands for hydrocarbon and NP from normal paraffin) [15,17]. In a similar way, the organic bromine and nitrogen compounds were characterized using Br–NP and N–NP grams (Br stands for bromine, N stands for nitrogen and NP stands for normal paraffin) [15,17]. Ammonia absorbed in a water trap was determined by using an ORION ammonia electrode Model 95-12 using Ionic Strength Adjuster (ISA-5 M NaOH/0.05 M disodium EDTA/10% methanol with a color indicator). Hydrogen cyanide absorbed in the water was determined by means of an ion meter (WTW inoLab pH/Ion Level 2) using a cyanide ion selective electrode (ORION Model 9406 Cyanide Half-Cell and Model90-02 double junction reference electrode). The residue (carbon residue and wax residue) were recovered from reactor and quantitative determination of bromine and nitrogen content in residue was measured using combustion flask and then subjected to ion chromatograph [14–17]. In brief, a small portion (about 10 mg)
of residue sample was combusted with O₂ in a Pyrex flask, containing a pair of electric wires, a Pt sample pan held by the pan-holder, and a Pt filament for firing the sample. The combustion products were absorbed in about 40 ml water containing H₂O₂ and subsequently analyzed by ion chromatograph. The analysis of the nitrogen content in residue was complicated, as the nitrogen species can be converted into various nitrogen oxides, and acids during combustion process. In addition, the nitrogen oxides are not detectable by ion chromatograph. However, the acids content such as HNO₂, and HNO₃ were analyzed and discussed in the following section. The anion chromatograph used in the present study can detect the NO₂⁻ and NO₃⁻ ions. The bromine and nitrogen content in the residue might be the mixture of organic and inorganic compounds.

3. Results and discussion

The results of the thermogravimetric analysis of ABS with and without flame retardant (bromine compound) are presented in Fig. 3. It is clear from Fig. 3 that the presence of brominated flame retardant decreases the onset of degradation (50 °C) from 400 to 350 °C.

The ABS-Br thermal degradation products were classified in three groups: oil, gas, and degradation residue that include the tar remaining at the bottom of the reactor. In addition, the degradation residue was classified into two parts, the carbon residue (the residue at the bottom of the reactor which is black in color) and the wax (the residue in the top portion of the reactor, which is coated on the walls of the Pyrex glass reactor and is a white color). The pictorial representation of the thermal degradation behavior of ABS-Br with temperature is presented in Fig. 4. The thermal degradation of ABS-Br was carried out with special attention being given to

![Fig. 3. Thermogravimetric analysis of ABS and ABS-Br.](image)

The visual changes noted in the reactor and the collection of the liquid product. It can be clearly seen from Fig. 4 that at a temperature of 353 °C, dense white fumes begin to appear. At a temperature of 370 °C, the formation of a light reddish-yellow color appears indicating that the decomposition of the brominated flame retardant has started. As the temperature increases from 370 to 378 °C, dark reddish-yellow colored compounds begin to coat the walls of the glass reactor. At a degradation temperature of 390 °C, pale yellow fumes are noted and the reddish-yellow fumes stop. At 407 °C, the formation of intense dark yellow colored compounds commences while at the same time, the presence of reddish-yellow fumes stops. At the end of the degradation experiment, residues in the reactor are separated into two portions residue (Fig. 4), i.e. a-carbon residue (bottom of reactor—black portion) and a wax residue (top of the reactor—white portion coated on the reactor walls) and analyzed individually for Br and N content.

The cumulative volume of liquid products obtained during thermal degradation of ABS-Br using the different temperature programs (Mode I and Mode II) are presented in Fig. 5. The curves of the oil accumulations are specific for each mode in the 0–120 min duration of the experiment. The oil started to accumulate in the graduated cylinder after about 40 min corresponding to a furnace temperature of about 400 °C (T₀ = T₄₀). The slope of the cumulative curve is equivalent to the initial degradation rate [19]. It can be concluded from the Fig. 5 that the increasing temperature from 400 to 450 °C (Mode I) should be continued at a rate of 10 °C min⁻¹ in order to obtain high yield of liquid products (Table 1). The Mode I found to be suitable for getting the maximum liquid products in a considerable time. The materials balance for the ABS-Br thermal degradation products (wt.%) and density
of liquid products are shown in Table 1. Table 1 shows that the Mode I degradation method yields higher liquid products (39%) than the Mode II degradation (29%). The small differences in gas, residue yields and also in density was observed during Mode I and II degradations of ABS-Br. The gaseous products during both modes are found to be same. However, the carbon residue in Mode I is lower than Mode II degradation, which might be converted into liquid products. The wax residue is almost the same in Mode I and II degradations. The density of liquid products produced by Mode I (0.857 g cm\(^{-3}\)) are comparatively higher than those obtained during mode II (0.833 g cm\(^{-3}\)) due to the presence of brominated compounds present in the liquid products produced in Mode I.

The normal paraffin gram (NP-gram) used to characterize the liquid products proposed by Murata et al. [20] has been applied to characterize the liquid products in this study. Fig. 6 shows the carbon number distribution of the liquid hydrocarbon products (C–NP gram) obtained in this study. These values were obtained by plotting the weight percent of hydrocarbon compounds (g (Cn) × 100/g (oil)% from

![Graph of cumulative volume of liquid products obtained during ABS-Br thermal degradation.](image-url)
GC-FID) in the product oil against the carbon number of normal paraffins (equivalent to their boiling points). The notation C–NP gram stands for normal paraffin gram of hydrocarbon. This value represents the volatility distribution of the liquid products. The liquid hydrocarbon products from ABS-Br degradation were distributed in the range of \(n-C_5-n-C_{23}\) with major peaks at \(n-C_6, n-C_9, n-C_{16}\) hydrocarbons etc., and were composed of aromatics. Analogous to a C–NP gram approach, the volatility distribution of bromine compounds in the liquids can be shown by Br–NP gram data (Fig. 7). The volatility distribution of nitrogen compounds is similarly shown in Fig. 8. The Br–NP gram (Fig. 7) was obtained by plotting the quantity of bromine (g (Br) \times 100/g (oil)% from GC-AED) on \(y\)-axis against the carbon number of normal paraffin. Majority of the bromine present in the ABS-Br plastic converted into gaseous HBr, and only a small quantity of bromine observed as brominated hydrocarbons in liquid products. The GC-MS analysis of liquid products shows the presence of aliphatic and aromatic brominated hydrocarbons. Aromatic hydrocarbons containing bromine, nitrogen and oxygen were also found by GC-MS. The brominated compounds found in the liquid products analyzed by GC-MS and are presented in Fig. 7. The nitrogen containing hydrocarbons in the liquid products was shown in Fig. 8, taking quantity of nitrogen (g (N) \times 100/g (oil)% from GC-AED) on \(y\)-axis and carbon number on \(x\)-axis. The various compounds in liquid products were analyzed by GC-MS and they are presented in Figs. 6–8. Figure 8 shows that there are only two major nitrogen-containing compounds such as R–CN (where \(R = C_1–C_3\) etc.) and Ph–R–CN (where \(R = C_1–C_3\) etc.). In addition to a small amount of bromine and nitrogen containing compounds, about 50 wt.% of styrene, toluene, cumene, ethyl benzene was found in liquid products (GC-MS).
In our previous studies, we found that the thermal degradation of ABS by semibatch operation, at temperatures between 400 and 440 °C, gave 50–63 wt.% oil.

Fig. 7. Br–NP gram of liquid products from thermal degradation of ABS-Br at 450 °C.

Fig. 8. N–NP gram of liquid products from thermal degradation of ABS-Br at 450 °C.
Substituted aromatics represented more than 50 wt.% of the degradation oil produced from ABS. Nitrogen was also present in the oil mainly in the form of aliphatic and aromatic nitriles along with dissolved as HCN. 4-Phenylbutyronitrile was the main N-containing compound (ca. 19 wt.%) obtained in the thermal degradation of ABS [14]. Day and co-workers also reported similar N-containing compounds in the ABS pyrolysis oil obtained by pyrolysis/gas chromatography/mass spectrometry experiments [21].

A complete analysis and distribution of the bromine and nitrogen compounds in the degradation products obtained using both Mode I and II are presented in Tables 2 and 3. It can be clearly seen from Table 2 that the majority of the bromine is present in the wax residue, suggesting that the bromine compounds on degradation end in the wax products. In contrast to the bromine distribution, the majority of nitrogen concentrates in the liquid products. The concentration of nitrogen in the Mode I liquid products are lower than those in the Mode II liquid products. The results of the analysis of the gaseous products trapped in the sealed teflon bag are presented in Fig. 9. The concentration of the lower hydrocarbons such as methane and ethane were higher in Mode I degradation, while butene and butane were higher in Mode II degradation. An analysis for gaseous halogenated hydrocarbons was not performed.

4. Conclusion

The thermal degradation of brominated flame retardant (Br: 9.59 wt.%) containing ABS-Br (10 g) into a fuel oil represents a method for waste plastic treatment with a potential to save valuable petroleum resources. The use of the temperature program (Mode I) room temperature $\rightarrow$ 450 $^\circ$C (heating rate $\beta = 10$ $^\circ$C min$^{-1}$) then isothermally at 450 $^\circ$C was found to be the best for producing maximum yields of the liquid products. However, a range of bromine and nitrogen compounds was found in the liquid products. Studies to remove the bromine and nitrogen products from the ABS-Br degradation liquid products are in progress.

Table 2
The distribution of bromine content in various degradation products during thermal degradation of ABS-Br (10 g) at 450 $^\circ$C using two different temperature programs

<table>
<thead>
<tr>
<th>Temperature program</th>
<th>Yield of degradation products (wt.%)</th>
<th>Bromine content in oil (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Liquid ($L$)  Gas ($G$)$^a$  Residue ($R$)</td>
<td>Carbon  Wax</td>
</tr>
<tr>
<td>Mode I</td>
<td>2.9      n.d.  2.0  78.8</td>
<td>7120</td>
</tr>
<tr>
<td>Mode II</td>
<td>1.8      n.d.  9.0  56.0</td>
<td>6150</td>
</tr>
</tbody>
</table>

$^a$ $G = 100 - (L + R)$. 
The distribution of nitrogen content in various degradation products during thermal degradation of ABS-Br (10 g) at 450 °C using two different temperature programs

<table>
<thead>
<tr>
<th>Temperature program</th>
<th>Yield of degradation products (wt.%)</th>
<th>Nitrogen content in oil (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Liquid (L)</td>
<td>Gas</td>
</tr>
<tr>
<td>Mode I</td>
<td>50.2</td>
<td>0.0</td>
</tr>
<tr>
<td>Mode II</td>
<td>37.7</td>
<td>0.6</td>
</tr>
</tbody>
</table>

* Inorganic gas.

Fig. 9. GC-TCD analysis of gaseous products from thermal degradation of ABS-Br at 450 °C.

Acknowledgements

The authors would like to thank New Energy Development Organization (NEDO), Japan for financial support to carry out this research work under the Chugoku regional consortium project (2000-2003). We are grateful to Dr Emma P. Jakab (Research Laboratory of Materials and Environmental Chemistry, Chemical Research Center, Hungarian Academy of Sciences), Dr K. Nagata and H. Nigo (Industrial Technology Center of Okayama Prefecture), for their valuable discussions.

References


