Polymer Degradation and Stability 112 (2015) 86–93

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

A novel process for the removal of bromine from styrene polymers containing brominated flame retardant

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ARTICLE INFO

Article history:
Received 15 October 2014
Received in revised form
2 December 2014
Accepted 21 December 2014
Available online 27 December 2014

Keywords:
High impact polystyrene
Decabromodiphenylethane
Ball mill
Bromide
High performance liquid chromatography
mass spectrometry

ABSTRACT

High-impact polystyrene (HIPS) is one of the main plastic fractions of waste electric and electronic equipment (WEEE). Although recycling of this material is desirable, the presence of brominated flame retardants requires the removal of bromine prior to further treatment steps in order to avoid deterioration. In this study, a new method was developed for the removal of bromine from the polymer without destroying the polymer matrix. Organic bromine from the flame retardant (decabromodiphenyl ethane) was converted into inorganic bromide using a solution of NaOH in ethylene glycol ($NaOH_{(EG)}$). Using a stirred flask as the reaction vessel, a debromination ratio of 42% was obtained at 190 °C regardless of the NaOH concentration. The same reaction in a ball mill reactor reduced the bromine content in the HIPS to 0.02 wt%. The conversion of organic bromine into inorganic bromide reached 98%. Degradation products from the flame retardant were identified using high performance liquid chromatography coupled with mass spectrometry. In both the flask and ball mill reactor, the reaction was diffusion controlled with an activation energy of about 205 kJ mol^{-1}. The thermal stability of the residual plastic was enhanced during the treatment, which opens up the possibility of reusing waste HIPS by mechanical recycling.

1. Introduction

The production of electric and electronic equipment (EEE) is currently one of the fastest growing areas of the manufacturing industry. Rapidly advancing technology together with increasingly short product life cycles have led to the disposal of huge volumes of relatively new electronic goods. Polymers represent approximately 16 wt% of waste EEE (WEEE) and include approximately 23 different types of engineering polymers, the most important being acrylonitrile-butadiene-styrene copolymer, polypropylene, high-impact polystyrene (HIPS), and other styrenic copolymers [1,2].

The main drawback that obstructs material recovery from WEEE containing plastics is the wide variety of polymers that are being used, which result in elaborate sorting and recycling processes. Another relevant drawback in dealing with the treatment of WEEE is that brominated aromatic compounds are often used as flame retardants. The annual production of brominated flame retardants is around 200,000 tons [3]. Moreover, investigations have shown that these flame retardants find their way back into our lives as contaminants in material recycled plastics [4,5]. Chemical recycling of such plastics is frequently used for the recovery of monomers and fuel and it is likely that extremely toxic brominated dibenzodioxins and dibenzofurans are produced under pyrolytic conditions [6–8]. Hall and Williams [9] found that more than 90% of the bromine remained in the product oil after the pyrolysis of flame-retardant HIPS in a fluidised bed between 450 and 550 °C. Blazsó et al. [10,11] found significant reduction of brominated flame retardants by using zeolites as catalysts during pyrolysis. Bhaskar et al. reported the development of a catalyst/sorbent for the removal of bromine in the pyrolysis of a brominated flame retardant mixed with plastics [12]. However, during this process, it was found that the bromine was still present in liquid, solid, and gaseous products. Li et al. [13] reported the debromination of decabromodiphenyl ether (DBDE) using resin-bound iron nanoparticles and showed that the debromination was stepwise; less brominated congeners were produced with increasing reaction time up to 10 days. All these results show the possibility of reducing the bromine content of the product fractions after thermal

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http://dx.doi.org/10.1016/j.polymdegradstab.2014.12.017
0141-3910/

treatment of waste materials. However, the formation of hazardous materials is not prevented in these methods. Therefore, treatment of waste at the temperature range in which dibenzodioxins and furans are formed should be avoided in order to protect human health and the environment. Peng et al. [14] and Grause et al. [15] reduced the bromine content of product oil from the pyrolysis of HIPS by an initial degradation step around 300 °C, concentrating hazardous brominated products in a separated fraction.

Taurino et al. [16] developed the facile characterisation of polymer fractions from WEEE for mechanical recycling. There has been a plethora of research on the decomposition and recycling of flame-retardant plastics by several processes [17,18]. Extensive investigations on the debromination of different flame retardants using various metallic catalysts have been reported [19–21]. The microwave process involves mixing plastic-containing wastes, which are known to have very high transparency to microwaves, with a highly microwave-absorbent material such as particulate carbon. Bhaskar et al. [22] observed a bromine removal efficiency of about 85 wt% in triethylene glycol at 250 °C with 30 min of microwave irradiation. In the presence of activated carbon as microwave absorber and $CaCO_3$, 95% of bromine was removed from the products of printed circuit board degradation [23]. Chemical recycling of polymers from WEEE using different solvents was carried out for polycarbonate, acryl nitrile-butadiene-styrene copolymer (ABS), and polystyrene (PS) by Achilias et al. [24] The alkaline reforming of brominated flame-retardant plastics in various supercritical fluids resulted in debromination efficiencies of more than 95% [25–27]. Zhang and Zhang [28] extracted tetrabromobisphenol-A (TBBPA) from ABS with methanol and debromitated the flame retardant in the presence of metallic copper. Zhang et al. [29] used CaO for the debromination of TBBPA by means of mechanochemical degradation and found carbon-like residue as a product.

In the present article, we report the first example of efficient removal of a brominated flame retardant from HIPS using NaOH/ethylene glycol solution ($NaOH_{(EG)}$) under mild conditions between 150 and 190 °C in both a stirred flask and a ball mill reactor. Decabromodiphenyl ethane (DBDPE) was chosen as one of the new emerging brominated flame retardants replacing DBDE. EG was selected as the solvent because of its high boiling point of 196 °C, which allows the treatment to be carried out at atmospheric pressure [30]. Moreover, styrenic polymers are virtually insoluble in EG, which allows for easy separation of the polymer from the solvent after the treatment. Therefore, the conditions of the present method reduce operating expenses and energy consumption, while avoiding the formation of hazardous products.

2. Materials and methods

2.1. Materials

The HIPS sample was prepared for research purposes [8]. It consisted of 6 wt% polybutadiene embedded in the polystyrene matrix and 13 wt% DBDPE was added as a flame retardant. The elemental composition is given in Table 1. The HIPS sample was received as pellets with diameters of 3 mm (18 mg). For the experiment, the pellets were ground and sieved to a particle size of less than 250 μm. Methanol, diethyl ether, n-hexane, EG, and NaOH were obtained from Kanto Chemicals.

Table 1
Elemental composition of HIPS.

C	H	Br	Volatiles	Ash
82.29	7.24	10.80	98.1	–

2.2. Stirred flask

A 100-mL three-neck flask equipped with a reflux cooler was heated under a nitrogen flow of 100 mL min^{-1} in a silicone oil bath. Experiments were carried out between 150 and 190 °C with 1 g of the HIPS sample in 50 mL of $NaOH_{(EG)}$ for 24 h at concentrations between 0 and 1 M. The starting point of the reaction was set to the beginning of the heating process. Samples of the solution (0.1 mL) were taken at regular intervals and analysed by ion chromatography for bromide. The residual HIPS was investigated by thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FT-IR).

2.3. Ball mill reactor

Experiments were carried out in a modified rotary evaporator (AS ONE Corporation, NA-1, Osaka, Japan). The distillation flask was replaced with a horizontally oriented cylindrical glass grinding chamber (diameter: 150 mm, width: 60 mm) heated by a silicone oil bath. The chamber was filled with 400 Y_2O_3–ZrO_2 balls, each with a diameter of 5 mm, and rotated with a speed of 60 rpm. It should be noted that the ball milling process caused substantial abrasion of the Y_2O_3–ZrO_2 balls. The ball mill was purged with a constant nitrogen flow of 100 mL min^{-1}. Samples were taken from an opening opposite to the driving shaft of the grinding chamber. The experimental procedure was the same as that for the stirred flask experiments.

2.4. Analytical methods

The liquid samples were filtered and extracted with diethyl ether. The aqueous phase was analysed by ion chromatography for the determination of the bromide content. Organic degradation products of the flame retardant were determined from the organic phase using high-performance liquid chromatography in connection with a mass-selective detector (HPLC-MS).

The residual polymer was washed with methanol and water in order to remove EG and then dried at 40 °C. Soxhlet extraction of the dry polymer was carried out in the presence of n-hexane. The extracted polymer was analysed for the bromine content by X-ray fluorescence analysis (XRF), Fourier transform infrared spectroscopy (FT-IR), and nuclear resonance spectroscopy (NMR). The extract was evaporated at 40 °C for the detection of flame retardant degradation products. However, no residue was found.

A Dionex DX-100 ion chromatograph was used for the determination of the bromide concentration of the ethylene glycol solution. The analysis was carried out using an IonPac AG16/AS16 column set (Dionex). Aqueous NaOH with a concentration of 35 mM was used as the mobile phase.

The debromination ratio was calculated by

$$\text{debromination ratio\%} = \frac{m_{Br^-}}{m_{HIPS-Br}} \times 100\%$$

with m_{Br^-} being the amount of inorganic bromide determined by ion chromatography and $m_{HIPS\text{-}Br}$ being the initial bromine content of the HIPS. This definition implies that organic bromine dissolved in the EG solution is not considered as full-fledged debrominated, even if it is not present in the polymer any more.

The HPLC-MS system (Shimadzu) was equipped with a single quadrupole LCMS-2010 mass spectrometer executed in electron spray ionisation. A CrestPak C18S column was used with 5 mmol L^{-1} aqueous ammonium acetate solution and acetonitrile as mobile phase at 40 °C.