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Alkaline hydrothermal treatment of brominated high-impact polystyrene (HIPS-Br) for bromine and bromine-free plastic recovery

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Abstract

A method to recover both Br and Br-free plastic from brominated flame retardant high impact polystyrene (HIPS-Br) was proposed. HIPS-Br containing 15 % Br was treated in autoclave at 280 °C using water or KOH solution of various amounts and concentrations. Hydrothermal treatment (30 mL water) leads to 90 % debromination of 1 g HIPS-Br but plastic is strongly degraded and could not be recovered. Alkaline hydrothermal treatment (45 mL or 60 mL KOH 1 M) showed similar debromination for up to 12 g HIPS-Br and plastic was recovered as pellets with molecular weight distribution close to initial material. Debromination occurs at melt plastic/KOH solution interface when liquid/vapour equilibrium is attained inside autoclave (280 °C and 7 MPa in our experimental conditions) and depends on the plastic amount/KOH volume ratio. The antimony oxide synergist from HIPS-Br remains in recovered plastic during treatment. A pictorial imagination of proposed debromination process is presented.

Keywords: debromination, alkaline hydrotreatment, HIPS-Br, bromine recovery

1. Introduction

Nowadays increasing plastic consumption leads to accumulation of huge amount of waste that poses serious environmental problems. There are many techniques to convert the plastic waste into valuable materials (Aguado and Serrano, 1999; Tukker, 2002). However special methods for treatment/recovery of plastic waste are needed, as plastic materials become more and more complex.

High impact polystyrene (HIPS) is the main component of waste from electrical and electronic equipment (WEEE) being followed in amount by acrylonitrile-butadiene-styrene (ABS) (Tange, 1999). These polymers are widely found in TV housing, computers and office

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equipment. Brominated flame retardants (Br-FR) such as polybrominated diphenyls, polybrominated diphenyl oxides, tetrabromo bisphenol-A or polybrominated epoxy resins (BSEF Report, 2000) are used in plastic materials to prevent combustion during accidental fires. Antimony oxide is widely used as synergist to enhance the flame-retardant effect (Gächter and Müller, 1990).

The treatment methods for the recycling of plastics and recovery of Br-FR have been the topic of many research interests. Br-FR and antimony trioxide synergist remain in HIPS materials after five consecutive mechanical reprocessing without debromination (Hamm et al., 2001). However they create many problems during treatment/recovery of plastic waste due to formation of corrosive compounds such as hydrobromic acid as well as environmentally harmful polybrominated dibenzofurans which appear during incineration or pyrolysis (Vehlow et al., 2002). Br-FR can also interact with polymer matrix producing Br-organic compounds (Brebü et al., 2004a; Yamazaki et al., 2005).

Various methods were proposed for debromination of plastic materials or their degradation products. Gasification of WEEE at 1200 °C followed by shock cooling of gases was found to suppress emission of brominated dibenzofurans (Yamawaki, 2003). Mechanochemical treatment with inorganic additives especially alkali metal hydroxides was proposed for debromination of organic compounds (Fumiyoshi et al., 2002; Zhang et al., 2002). Polypropylene and polyethylene were used for debromination of brominated polymers (Uddin et al., 2003), brominated phenols or pyrolysis oil from WEEE (Hornung et al., 2003). Catalysts were also used for debromination of pyrolysis oils from brominated polymers (Bhaskar et al., 2004a, 2004b; Brebü et al., 2004b, 2004c). Extraction of bromine (Br) from plastic materials by solvolysis was also proposed but this method involves the use of expensive solvents or extreme conditions such as Na/NH₃ or supercritical CO₂ treatment (Bunte et al., 1996; Mackenzie and Kopinke, 1996; Keizo et al., 2004).

In the present work we report the alkaline hydrothermal treatment (KOH, 280 °C) of HIPS-Br with the aim for simultaneous recovery of Br and Br-free plastic.

2. Experimental

Commercially available HIPS-Br with decabromo diphenyl oxide flame retardant and antimony trioxide synergist – 15 weight percent (%) Br and 4.5 % Sb₂O₃ – and grain size of about 3 mm was thermally treated in autoclave (Taiatsu Glass Industries Co. Ltd., TAS-02; capacity 200 mL) using water or KOH solution of various amounts and concentrations. HIPS-Br

was loaded into the autoclave together with demineralised water or KOH solutions (from 30 to 60 mL). The autoclave was closed, purged with nitrogen gas, and heated to required treatment temperature of 280 °C that was maintained for 1 h. The autogenous pressure (water to steam) inside autoclave was measured; it depended on the initial amount of water or KOH solution. At the end of reaction time the autoclave was cooled to room temperature and the content was collected separately; liquid solution and solid plastic.

The extent of debromination was expressed as Br recovery (based on Br amount in recovered solution) and as plastic debromination (based on Br amount in treated plastic). The Br content in solution was measured using an ion chromatograph (DIONEX, DX-120 Ion Chromatograph). The Br content in plastic was determined by combusting about 20 mg material in a Pyrex combustion flask, adsorbing gaseous products in 50 mL water containing H₂O₂ (0.3 mL) and analysing the solution by ion chromatography.

3. Results and discussion

During hydrothermal treatment of HIPS-Br with 30 mL H₂O the autogenous pressure inside autoclave was of about 5 MPa. Very good debromination but low plastic recovery was obtained for 1 g HIPS-Br (Figure 1a) that remained as a dark coloured material covered by a black carbon-like residue (Fig. 2b) showing a strong degradation of plastic. Lower debromination and consequently higher plastic recovery (less material leaves plastic) occurred when increasing plastic amount up to 2 g, after which no effect of HIPS-Br amount was evidenced. A drastically decrease of debromination was observed between 1.25 and 1.5 g HIPS-Br, that will be explained the following sections. The recovered plastic was highly porous for 2 g HIPS-Br (Fig. 2c) and a compact, hard, single-piece material (defined as bulk) with some pores close to the surface for 3 g and 4 g HIPS-Br (Fig. 2d); the colour was darker than that of initial HIPS-Br (Fig. 2a).

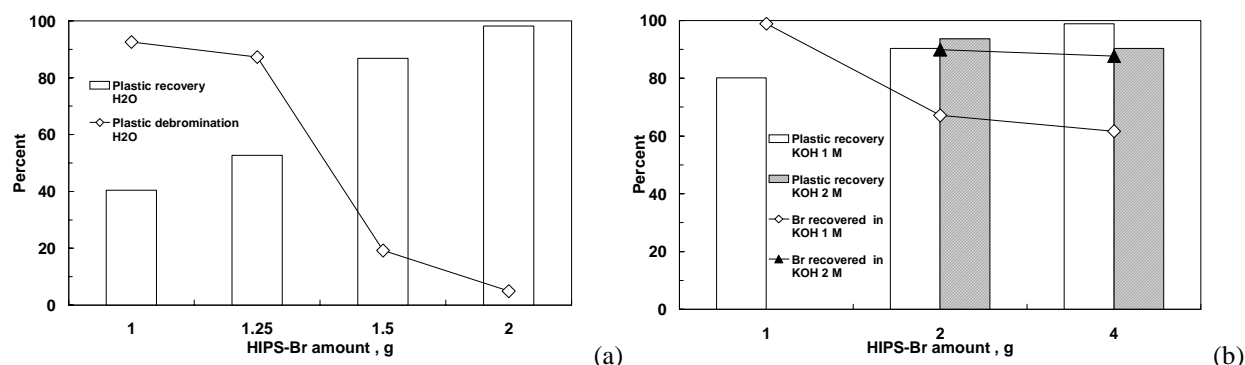


Figure 1. Results of hydrothermal (a) and KOH (b) treatment (30 mL solution) of HIPS-Br at 280 °C (5 MPa)

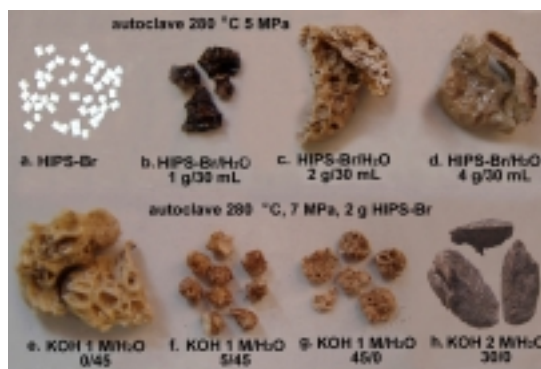


Figure 2. Physical aspect of HIPS-Br before and after hydrothermal and KOH treatment (280°C)

It is known that alkaline hydrolysis of chlorobenzene is a useful method for the synthesis of phenol. High temperature alkaline treatment was also used for conversion of 2-bromophenol (the main thermal degradation product of Br-FR in circuit boards) into useful organic compounds (Uchida et al., 2003). Because hydrothermal debromination of HIPS-Br occurred only for high H₂O/plastic ratio and polymer was degraded, the debromination of HIPS-Br by KOH treatment was tested.

Various amounts of HIPS-Br were treated with 30 mL KOH 1M at 280 °C (and 5 MPa). Debromination of 1 g HIPS-Br was similar to hydrothermal treatment but plastic recovery becomes double (Fig. 1b). Plastic recovery increased with HIPS-Br amount to the detriment of debromination, similar to hydrothermal treatment. The recovered plastic for 1g HIPS-Br consisted of small individual particles easy to break by finger (defined as pellets) and covered with a dark powder. It was a grey, porous material for 2 g HIPS-Br, and a bulk, grey at surface and black inside for 4 g HIPS-Br. The recovered solution was foaming and had a dark-reddish colour that was different to colourless solution from hydrothermal treatment. Higher concentration of 2M KOH increased Br recovery to 90 % for both 2 and 4 g HIPS-Br. The recovered plastic looked similar to KOH 1M case but was darker and more compact (Fig. 2h).

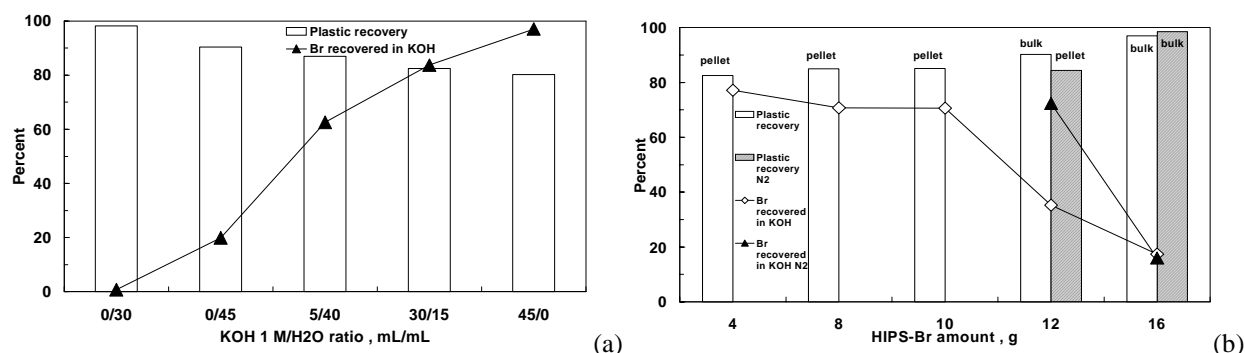


Figure 3. Results of KOH treatment of HIPS-Br at 280 °C and 7 MPa: 2 g HIPS-Br and 45 mL KOH of various concentrations (a); various amounts of HIPS-Br and 60 mL KOH 1M (b)

The effect of KOH concentration was studied by varying KOH 1M/H₂O volume ratio for 2 g HIPS-Br. Simultaneously the total volume of solution was increased to 45 mL that generates a pressure of about 7 MPa. Increasing water amount (hydrothermal treatment) from 30 mL to 45 mL gave better debromination with good plastic recovery (Fig. 3a). The recovered plastic was a grey, porous material in both cases (Fig. 2c and 2e).

When using 45 mL solution of various KOH concentrations the 2 g HIPS-Br was recovered as pellets (Fig. 2f and 2g) slightly darker than initial HIPS-Br. This was different to hydrothermal and 30 mL KOH treatment that gave bulk recovered plastic. 2 g Br-free polystyrene treated with 45 mL KOH 1 M were also recovered as bulk showing that pellets formation is related both to the KOH volume and to the Br in plastic. At high KOH concentration pellets became porous and higher debromination occurs with good plastic recovery (Fig. 3a).

The effect of KOH volume/HIPS-Br amount ratio was studied by increasing HIPS-Br amount up to 16 g for a constant volume of 60 mL KOH 1M (Fig. 3b). The autogenous pressure remained of 7 MPa, similar to 45 mL case. As the supplementary 15 mL KOH does not contribute to the final pressure of steam it results that a phase equilibrium is achieved inside autoclave at 280 °C and 7 MPa and water co-exists both in vapour and in liquid phase. A good Br recovery of about 70 – 80 % was obtained for up to 10 g HIPS-Br that was recovered as pellets. Higher amounts of 12 g and 16 g HIPS-Br became bulk and debromination strongly decreased.

Two experiments were performed with 12 g and 16 g HIPS-Br, 60 mL KOH 1M and 1 MPa initial pressure of nitrogen inside autoclave. The final pressure remained of 7MPa showing that partial pressure of nitrogen affects the liquid – vapour equilibrium of water by increasing the amount of liquid phase. After experiments with nitrogen the 12 g HIPS-Br became pellets with high Br recovery while the 16 g HIPS-Br remained bulk with very low debromination. Therefore Br removal is strongly related to the amount of liquid phase inside autoclave at reaction conditions, that also affects the physical state (pellets or bulk) of the recovered material, as shown in Fig 2 and presented above.

Based on these experimental results the proposed alkaline hydrothermal debromination process can be depicted as in Figure 4 and discussed below. Low amounts of water are totally vaporised and plastic is in contact with high-pressure steam (Figure 4a). The melting particles stick to each other and became bulk, with low debromination and therefore high plastic recovery, except for very low amounts of plastic that is strongly degraded, with good debromination.

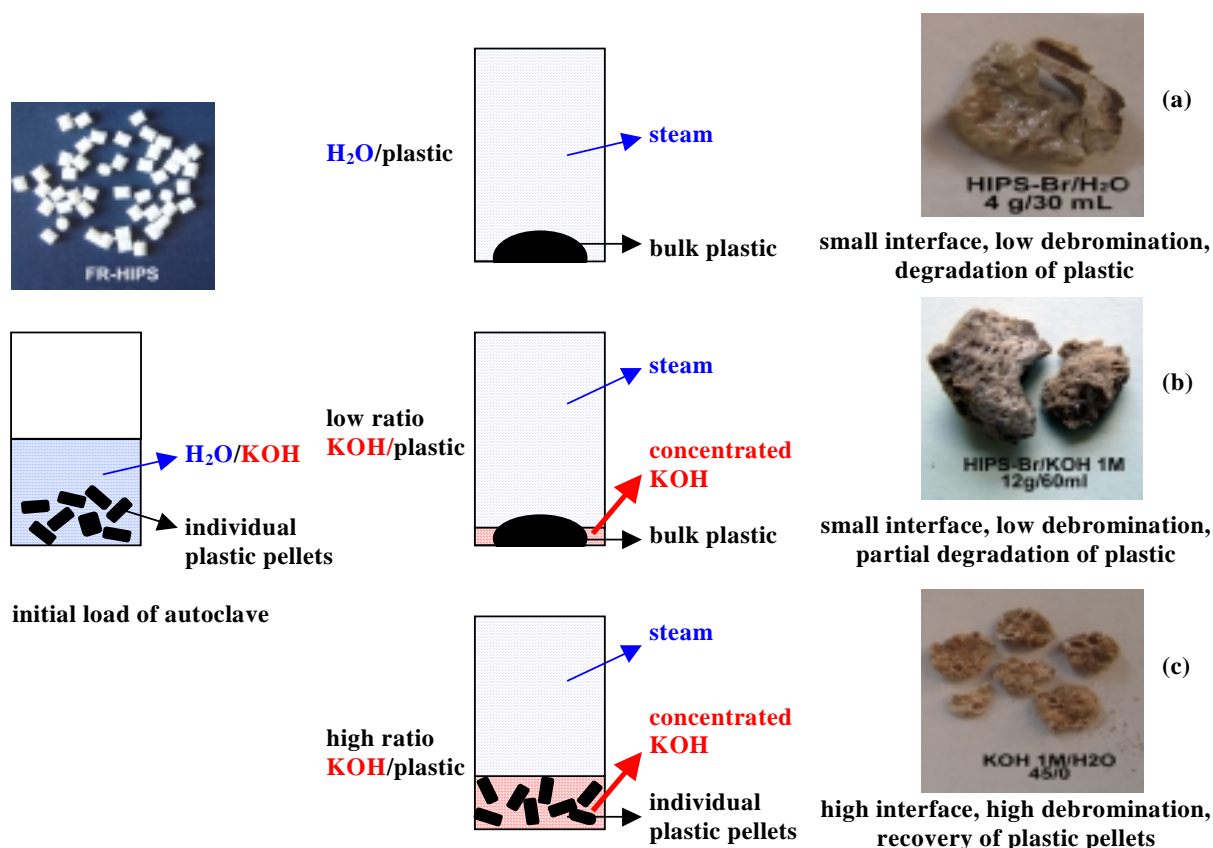


Figure 4. Pictorial imagination of debromination process by hydrothermal and alkaline treatment at 280 °C

High volumes of water or KOH solution attain the liquid-vapour equilibrium (around 280 °C and 7 MPa in our experimental conditions) and a liquid phase of water or KOH solution (concentrated by partial evaporation) remains inside autoclave. If the liquid/plastic ratio is low, the plastic is in contact both with liquid and with vapour phase (Figure 4b). Melting particles in contact with steam stick to each other inducing formation of bulk even for the particles inside liquid phase. Low debromination and partial degradation of plastic occurs.

If the liquid/plastic ratio is high, the melted plastic is totally in contact with the liquid phase (Figure 4c). Debromination increases for hydrothermal treatment but plastic in water still stick to become a darkish, single-piece porous material. A reactive plastic/liquid interface appears in presence of KOH before melting of plastic. The reaction between KOH in solution and Br from plastic leads to KBr and phenol derivatives that act as surfactants in solution keeping the particles apart when melting. The plastic/KOH solution interface remains large leading to very good debromination and recovery of material as pellets.

Gel permeation chromatography (GPC) (Fig. 5) shows that the molecular weight of plastic strongly decreased by hydrothermal and KOH 2M (30 mL) treatment that gave about 90 % debromination. For KOH 1M treatment (45 mL) degradation of polymer structure is very low,

for similar debromination. Therefore high amounts of KOH are necessary for both Br and plastic recovery, without significant degradation.

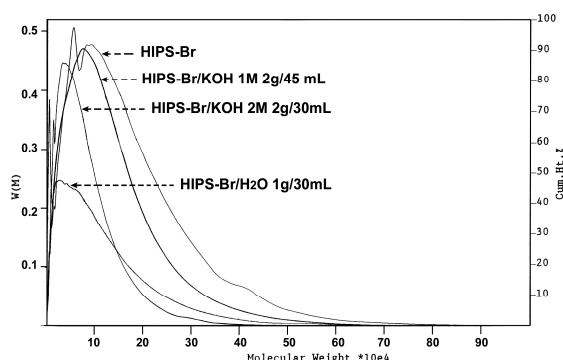


Figure 5. GPC analysis of recovered HIPS-Br after hydrothermal and KOH treatment (280 °C)

The dark-reddish colour solution recovered after KOH treatment was neutralised with HCl. The organic compounds were extracted with ethyl acetate, concentrated by evaporation and analysed by GC-MSD analysis. Phenol and its derivatives (methylphenol, dimethylphenol, tertbutylphenol), benzylalcohol, benzoic acid and its homologues (benzene acetic acid, benzene propanoic acid) and hydroxybenzoic acid were found among organic compounds from neutralised KOH solution. This proves the substitution of aromatic Br in HIPS-Br by the –OH groups in solution under the action of KOH leading to Br-free low-molecular aromatic compounds.

Separate evaporation of the recovered KOH solution gave a powder whose XRD pattern (Rigaku RAD-2R instrument, Cu K α radiation, 40 kV, 200 mA, sampling angle of 0.04 degree) showed the presence of crystalline KBr. Therefore Br from HIPS-Br can be recovered after KOH treatment by crystallisation as KBr and purification from the aqueous solution. XRD analysis of recovered plastic showed that antimony oxide synergist from initial HIPS-Br remains in plastic material after KOH treatment.

4. Conclusion

The alkaline hydrothermal treatment at 280 °C and autogenous pressure of 7 MPa was found to be effective for 80 – 90 % debromination of HIPS-Br. Br can be recovered as KBr from aqueous solution after treatment while plastic can be recovered as individual pellets with similar molecular weight as initial HIPS-Br. KOH treatment does not affect the antimony oxide synergist in HIPS-Br that remains in the recovered plastic. Contrary, debromination using only water occurs only for very low amounts of HIPS-Br but plastic is strongly degraded and cannot be recovered.

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