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Removal of brominated flame-retardants from High-Impact Polystyrene by Extraction in an Alkaline Organic Medium

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ABSTRACT

The treatment of brominated flame-retardant containing plastics is one of the big issues in waste plastics management. In this investigation, we examined the possibility of removing decabromodibenzyl (DDB) from the polymer matrix of high-impact polystyrene (HIPS) in an alkaline ethylene glycol (EG) solution. This procedure was already successfully used for the dehydrochlorination of polyvinylchloride, making use of the high boiling point of EG (196 °C). A debromination yield of about 42% was reached at 190 °C after 24 h. However, debromination reaction was significantly accelerated by ball-milling leading to an almost complete debromination. The reaction was diffusion controlled with an activation energy of about 205 kJ mol^{-1}.

1. INTRODUCTION

The treatment of brominated flame-retardant containing plastics is one of the big issues in waste plastics management. The use of decabromo diphenylether (DPE) is already restricted in many parts of the world. In many cases, it has been replaced by decabromo dibenzyl (DDB). It is well known that during the thermal treatment of DPE polybrominated dibenzofurans (PBDFs) are released. However, polybrominated phenanthrenes, which share similar structural features as PBDFs, are formed from DDB at temperatures of more than 320 °C (Grause 2011), and therefore, this temperature range should be avoided.

With our experience in the dehydrochlorination of poly(vinyl chloride) (PVC) (Yoshioka 2008), the debromination of flame retarded polymers seems to be applicable even if major differences are present. The dehydrochlorination of PVC occurred by a common nucleophilic elimination and substitution mechanism initiated by sodium hydroxide dissolved in ethylene glycol (EG) at temperatures between 150 and 190 °C.

Chlorine was substituted by hydroxyl-groups to some extent. However, the elimination was dominant. The efficiency was strongly improved by applying a ball-mill (Kameda 2008). In contrast to PVC, DDB is an aromatic halogen compound on which nucleophilic substitution cannot be applied. Furthermore, as a small molecule, it might be accessible by extraction (Schlummer 2006). In this work, the removal of DDB in an alkaline EG solution was investigated.

2. EXPERIMENTAL

The high-impact polystyrene (HIPS) sample was prepared for research purposes and contained 13 wt% of DDB (Grause 2011). The 3 mm pellets were grinded to a size below 250 µm.

Experiments were carried out in EG with NaOH in different concentrations. Two different reactor types were used: a stirred three-neck flask and a ball mill. The flame retardant removal was carried out at temperatures between 150 and 190 °C. Details of the experimental procedure can be found in Yoshioka et al. (2008) and Kameda et al. (2008).

The progress of the debromination was determined by the bromine concentration in the EG solution. The quantification was carried out using a Dionex DX100 ion chromatograph and an IonPac AG16/AS16 column set (Dionex).

Thermogravimetric analysis of the residual polymer was carried out using a Seiko TG/TDA6200 at a heating rate of 5 K min^{-1} between 50 and 700 °C.

3. Results and Discussion

The merit of this process is that it can be performed at atmospheric pressure due to the high boiling point of EG (196 °C). The HIPS is insoluble in the solvent and can be recovered after treatment. DDB is also insoluble in EG, thus, making it unlikely to observe undegraded DDB in the solvent.

As expected, the debromination ratio increased with the temperature, reaching at 190 °C 42% after 24 h in the stirred flask (Fig. 1a). At the lowest temperature, the reaction rate was still slow, making it unnecessary to proceed at lower temperatures. The initiation of the debromination was characterized by a temperature dependent lag time. This lag time took about 18 h at 150 °C, so that the reaction just started at the end of the experimental time of 24 h. At a temperature of 190 °C, the lag time was reduced to less than 1 h, allowing the reaction to proceed rapidly for the next 2 h. After that, the reaction rate decreased and the reaction proceeded slowly without being finished at the end of the experimental time.

The reaction in the stirred flask was barely concentration dependent (Fig. 1b). An NaOH concentration of 0.1 mol l^{-1} was already sufficient to ensure a high reaction rate. Further increase of the NaOH concentration caused only a slight rise of the debromination ratio. No significant differences were observed between 0.25 and 2 mol l^{-1}. It can be assumed that the reaction was not under chemical control and rather diffusion or processes at the phase boundary were the velocity determining steps. In the absence of NaOH, debromination was not observed, indicating that NaOH was essential for the debromination.

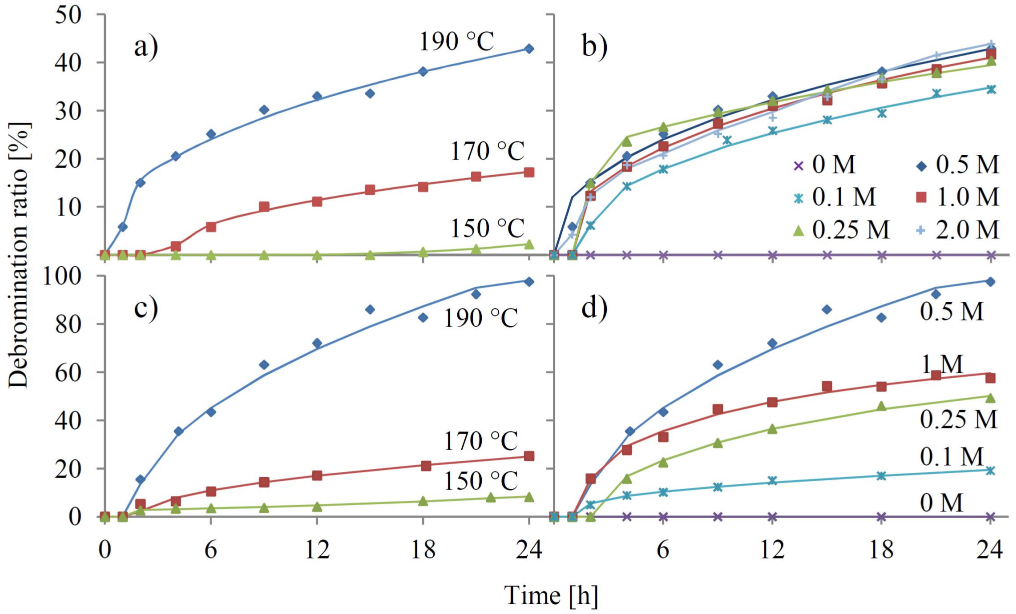

Fig. 1. Debromination of HIPS at a) different temperatures and b) different concentrations in a stirred flask; and at c) different temperatures and d) different concentrations in a ball mill. Temperature dependence was investigated in 0.5 M NaOH solution and concentration dependence at 190 °C.

Using a ball mill treatment for HIPS resulted in a more violent and rapid mass transfer. As a result, debromination was accelerated, leading to an almost complete debromination of the sample after 24 h at 190 °C (Fig. 1c). Debromination at lower temperature was accelerated, as well. Also during ball-milling, as lag time was observed. However, the lag time was about 1 h independent from the temperature.

Compared with the reaction in the stirred flask, a pronounced dependence of the reaction rate from the NaOH concentration was observed. The reaction rate reached its maximum at an NaOH concentration of 0.5 mol l^{-1}. At higher concentrations, the reaction rate decreased. Similar effects were observed for other polymers (Oku 1997, Yoshioka 2008). The fact that the maximum concentration decreases with increasing polarity of the polymer indicates the importance of this property.

Kinetic analysis of both processes lead to the conclusion that in both cases diffusion was the limiting step. The activation energy was independent from the reactor type (stirred flask: 201 kJ mol^{-1}, ball mill: 207 kJ mol $^{-1}$), indicating that the mechanism of the debromination process did not change. In fact, the higher efficiency of the ball mill was caused by the reduction of the pathway of the diffusion. Excessive kneading of the HIPS sample resulted in a frequently renewed surface, opening up areas which had not been accessible to debromination yet.

The residual polymer did not show any sign of degradation. TGA showed that the thermal stability of the HIPS sample was improved compared with the initial flame retarded HIPS sample (Fig. 2). The first DTG maximum was due to the degradation of the flame retardant (Grause 2010) disappeared and the second DTG maximum dedicated to the polymer decomposition became equal for both flame retarded (429 °C) and debrominated HIPS (431 °C).

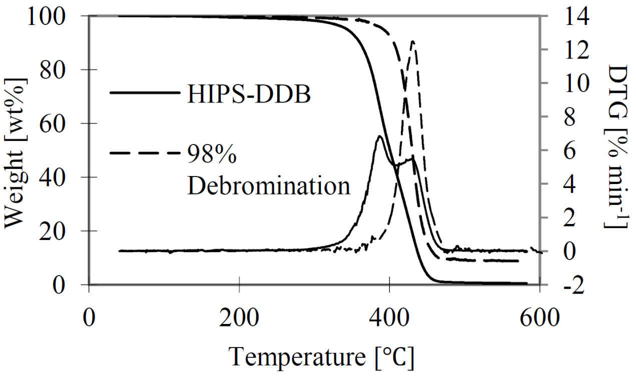

Fig. 2. TGA of flame retarded and debrominated HIPS.

4. Conclusion

Ball milling of HIPS containing brominated flame retardants in an alkaline EG solution was proven to be an appropriate alternative to other possible recycling routes. After the treatment, the residual polymer can be recovered and aimed for mechanical recycling due to its good thermal stability,

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