DEBROMINATION OF HIGH IMPACT POLYSTYRENE CONTAINING DECABROMODIPHENYL ETHANE

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Abstract

The debromination of high-impact polystyrene (HIPS), containing decabromodiphenyl ethane (DDE), was carried out in NaOH/ethylene glycol (EG) solution, using a ball mill. The results were compared with those obtained by the reaction in a flask. The degree of debromination increased with increasing reaction temperature and was about 98% at 190 °C after 24 hours. The maximum degree of the debromination was reached at 0.5 M NaOH. While the degree of debromination in a flask was 43%, it was found that the ball mill was more effective for the debromination of HIPS/DDE. The debromination in a flask followed an apparent first-order reaction and the debromination rate decreased during the reaction. It is considered that the debromination progressed in a first step at the surface of the HIPS/DDE sample and after that the debromination progressed inside the samples. When a ball mill was used, the debromination process followed the modified shrinking-core model. The debromination rate was constant during the reaction indicating that the reaction always proceeded at the surface of the HIPS/DDE sample due to the grinding by the ball mill.

Keywords: *debromination, brominated flame retardant, high-impact polystyrene, ethylene glycol, shrinking core model*

1. Introduction

In 2000, law for recycling of specified kinds of home appliances took effect in Japan and similarly, the Waste Electrical and Electronic Equipment Directive was enforced in the EU. Since these laws require the recycling of home appliances, recycling of these plastics is needed. However, these plastics contain brominated flame retardants such as tetrabromobisphenol-A and decabromodiphenyl ethane, releasing environmentally harmful brominated compounds during decomposition. Accordingly, debromination is necessary for the recycling of these plastics as a pretreatment.

In this study, the debromination of HIPS containing decabromodiphenyl ethane (DDE) in NaOH/EG solution was proposed., The debromination was studied using a flask or ball mill reactor. We also studied the kinetics of the debromination applying the modified shrinking core model.

2. Materials and methods

2.1. Materials

HIPS containing DDE was used for the debromination experiment. The sample was prepared for research purposes by extrusion using HIPS raw material and DDE.

2.2. Debromination experiments and analytical methods

NaOH/EG solution was prepared by dissolving NaOH in EG. In this study, a flask and a ball mill were used as reactors. In case of using the ball mill, 1 g of HIPS/DDE powder was added to 50 mL of 0 - 1.0 M NaOH/EG solution in a 1 L ball mill reactor (inner diameter 150 mm; width 60 mm) containing 400 Y_2O_3-ZrO_2 balls 5 mm in diameter. The rotation speed of the reactor was 60 rpm at 150 - 190 °C in N_2 atmosphere at a flow rate of 100 mL min^{-1}. The reaction time was 24 hours. In case of using a flask, the procedure was same as for the ball mill. After cooling the reactor with water, the solution was filtered, washed with deionized water and methanol, and dried at reduced pressure.

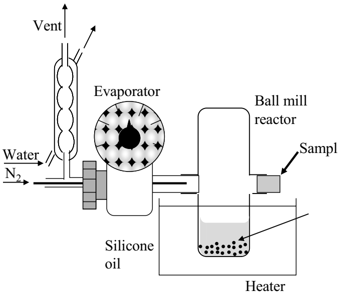

Figure 1. Ball mill reactor

The Br^- level in the filtrate were determined using a Dionex DX-100 ion chromatograph. The degree of debromination was calculated as the amount of Br^- in the filtrate to the total amount of Br.

3. Results and discussion

3.1. Debromination behavior

Fig. 2 shows the debromination as a function of temperature in 0.5 M NaOH/EG solution. The degree of debromination increased with increasing temperature.

When a flask was used, the debromination reached 43%, when a ball mill was used, it exceeded 98% at 190 °C after 24 hours. It was found that the ball mill was more effective for the debromoination than the flask.

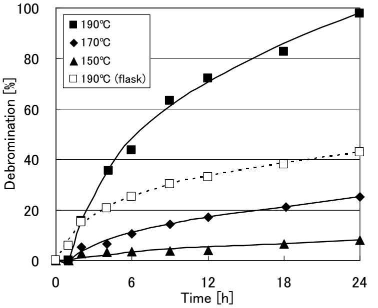

Figure 2. The ball mill assisted debromination as function of temperature in 0.5 M NaOH/EG solution

Fig. 3 shows the debromination as a function of the NaOH concentration at 190 °C. The degree of debromination increased with increasing NaOH concentration and the maximum debromination was reached at 0.5 M NaOH independent from the reactor.

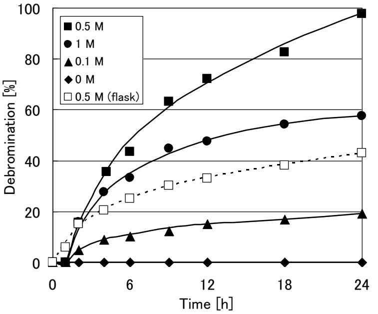

Figure 3. The ball mill assisted debromination as a function of NaOH concentration at 190 °C

3.2. Reaction kinetics

The reaction kinetics were analyzed, using the experimental data shown in Figure 2. When a flask was used, the experimental data shown in Fig. 2 were fitted to Eq. (1).

$$-\ln(1-X) = kt \qquad (1)$$

(X: debromination, k: rate constant, t: time)

In case of using the ball mill, a modified shrinking-core model for debromination was assumed. The reaction rate is proportional to the concentrations of Br in DDE and dissolved OH^- as follows:

$$v = kC_{Br}C_{OH} \qquad (2)$$

(v: debromination rate, C: concentration)

Assuming that the rise in the affected reaction surface area of HIPS/DDE by ball milling is proportional to the increase in the debromination rate, S is proportional to (1 - X)(1 + cX) as follows:

$$v = k_sSC_{OH} = 4\pi r_0^2k_s(1-X)(1+cX)C_{OH} \qquad (3)$$

(k_s: rate constant per unit area, S: surface area, c: proportional constant, r_0: initial radius of the particle)

At last, considering the equations above and the mass balance of the solids, Eq. (4) is obtained.

$$\frac{1}{1+c}\ln\frac{(1+cX)}{(1-X)} = Kt \quad \left(K = \frac{3}{r_0\,\rho}k_sC_A\right) \qquad (4)$$

(r: radius of the particle, ρ: density)

Fig. 4 shows the debromination rate as a function of temperature in 0.5 M NaOH/EG solution. In case of using the flask, the debromination followed an apparent first-order reaction. However, the debromination rate decreased after about 6 h. In opposite, the plot for the ball mill increased linear with the temperature. It can be assumed that when a flask was used, in a first step debromination occurred at the surface of the sample by the contact of DDE with the OH^- in the solution. After the end of the reaction at the surface, OH^- penetrated the particle and reacted with deeper located DDE. As a result, the debromination rate decreased during the reaction. When the ball mill was used, the debromination occurred first at the surface. However, before the reaction at the surface finished, unreacted surface area was created by grinding. Accordingly, the reaction always proceeded at the surface of the sample and the debromination rate was constant during reaction.

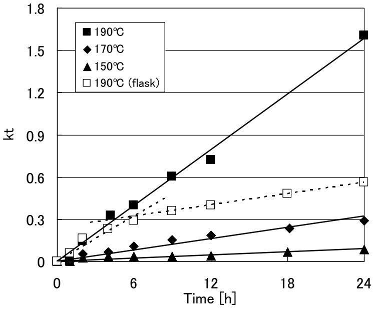

Figure 4. The ball mill assisted debromination rate as a function of temperature in 0.5 M NaOH/EG solution

4. Conclusions

The debromination proceeded most efficiently in 0.5 M NaOH/EG solution at 190 °C. When a flask was used under these conditions, the degree of the debromination was 43%. However when the ball mill was used, the debromination reached 98%. The debromination in a flask followed an apparent first-order reaction and the debromination rate decrease during the reaction indicating that in a first step the debromination occurs at the surface of the sample and aftrer that, the reaction proceeded inside the sample at a lower speed. The debromination by the ball mill was represented by a modified shrinking-core model and proceeded in one stage, indicating that the reaction proceeded always at the surface of the HIPS/DDE sample, since the ball milling provided continuously new surface area.