Study on Blooming of Tetrabromobisphenol A Bis(2,3-dibromopropyl ether) in Blends with Polypropylene

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ABSTRACT: Blends of polypropylene/tetrabromobisphenol A bis(2,3-dibromopropyl ether) (PP/TBAB) were prepared by twin-screw extruder, and then were molded into PP/TBAB plaques. Blooming of TBAB on the surface of PP/TBAB plaques were studied through heat aging test and theoretical calculation. The heat aging test at 70°C for 45 days was performed. Mass of the blooming TBAB on the surface of the plaque was measured every day in the period. Based on Fick's second law of diffusion, a mathematical method was developed to achieve concentration profile of TBAB dependent on time in the PP/TBAB plaques. Diffusion coefficients of TBAB were calculated by using the set concentration equation of TBAB with the experimental data. It was obtained that the diffusion coefficient of TBAB in PP/18 wt % TBAB is larger than that in PP/45 wt % TBAB. For the sample of PP/18 wt % TBAB, diffusion of TBAB reached an equilibrium after the heat aging for 40 days at 70°C. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 20–24, 2006

Key words: flame retardant; polypropylene; tetrabromobisphenol A bis(2,3-dibromopropyl ether); blooming; diffusion coefficient

INTRODUCTION

The flammability of polypropylene (PP) governs the need to introduce the flame retardants into its composition. The investigations showed that flame retardance requirements for many polymer materials can be achieved with only a few percent of tetrabromobisphenol A bis(2,3-dibromopropyl ether) (TBAB) combined with Sb_2O_3. Moreover, the physical properties of the polymer materials with TBAB added do not reduce when compared with those of the polymer matrix.[1,2]

TBAB is usually used in flame-retarded PP materials.[3] However, blooming of the TBAB on the surface of PP/TBAB products is serious. Blooming of TBAB not only changes the appearance of its final product, but also reduces the flame resistant properties of the polymer materials. If TBAB blooms from flame-retarded polymer materials, the required relative thermal index (RTI) rating cannot be reached.[4] Therefore, studies on searching for a method to reduce the blooming rate of TBAB are very important for applications of PP/TBAB.

In the early years, there are some inventions to reduce blooming of TBAB by incorporating the bloom inhibiting composition into the PP/TBAB.[5–7] Researchers were interested in effect factors of crystalline form of TBAB on the blooming.[8] Despite the previous works, a detailed blooming process of TBAB has not been described yet. Some detailed mathematical models were built to study antioxidant loss from polymer films and pipes.[9,10] In this work, such a mathematical method was developed to obtain diffusion coefficient and concentration distribution of TBAB in the blends of PP/TBAB.

EXPERIMENTAL

Sample preparation

Polypropylene [PP, melting flow rate (MFR) = 3.5 g/10 min] was supplied by the Yanshan Petrochemical Co. TBAB was supplied by the Jiangsu Huading Refining Chemical Industry Co.

Two blends of PP/TBAB, 18 wt % and 45 wt % TBAB, respectively, were prepared through a SLF-35 type twin-screw extruder (screw diameter 0 = 35 mm; length to diameter, L/D = 36). The temperature profile over the screw ranged from 150 to 180°C. The PP/TBAB string delivered off the extruder die was rapidly cooled in water and then pelletized. The PP/TBAB pellets were dried overnight to remove surface moisture. Finally, it was molded into plaques of 70 × 70 × 1 mm^3 by CWI-16 injection molding machine.

Accelerating heat aging test

The two kinds of PP/TBAB plaques were simultaneously aged in an oven at 70°C for 45 days. Every day

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TABLE I
The Loss Concentration of TBAB from the Surface of PP/TBAB Plaque at 70°C

	C_0 = 18 wt % TBAB			C_0 = 45 wt % TBAB		
t/d	m_0 (g)	W_1 (g)	$C_{Loss} = W_1/m_0$	m_0 (g)	W_2 (g)	$C_{Loss} = W_2/m_0$
1	5.4547	0.0162	0.0030	5.7247	0.0105	0.0018
3	5.4783	0.0306	0.0056	5.7254	0.0240	0.0042
5	5.4536	0.0560	0.0103	5.8604	0.0247	0.0042
7	5.4780	0.0623	0.0114	5.7746	0.0275	0.0048
9	5.4453	0.0792	0.0145	5.8122	0.0544	0.0094
11	5.4449	0.0892	0.0164	5.8097	0.0579	0.0010
13	5.4446	0.0802	0.0147	5.6694	0.0706	0.0125
15	5.3511	0.0878	0.0165	5.7689	0.0716	0.0124
17	5.4738	0.0942	0.0172	5.8430	0.0867	0.0148
18	5.3521	0.0817	0.0153	5.8212	0.0917	0.0158
21	5.4070	0.0873	0.0161	5.8270	0.0859	0.0147
24	5.4244	0.0903	0.0166	5.8228	0.0856	0.0147
26	5.4365	0.0981	0.0180	5.8399	0.1157	0.0198
30	5.3677	0.0950	0.0177	5.7301	0.1190	0.0208
32	5.4224	0.0878	0.0162	5.7614	0.1236	0.0215
33	5.4299	0.1054	0.0194	5.8380	0.1288	0.0221
36	5.4163	0.0857	0.0158	5.7049	0.1277	0.0224
39	5.3716	0.0972	0.0181	5.7614	0.1289	0.0224
42				5.7298	0.1395	0.0243
45				5.6820	0.1343	0.0236

a plaque was taken out from the oven, and then the plaques were placed into desiccator so as to make it cool, until all plaques were taken out. The absorbent cotton impregnated with solvent of dichloromethane was used to wash surface of the plaques. After washing, the plaques were weighed. Amount of the blooming TBAB could be calculated according to the mass loss.[11]

Scanning electron microscopy

The surface and inner morphologies of PP/TBAB samples were investigated on a CSM-950 type SEM operating an acceleration voltage of 20 kV. The samples were prepared by cryogenically fracturing them in liquid nitrogen.

MATHEMATICAL METHOD

It is assumed that blooming of TBAB on the surface of PP/TBAB plaques is in conformity with Fick's second law of diffusion. For one-dimensional diffusion that a concentration gradient exists only along the x-axis, in rectangular coordinates system, diffusion equation can be expressed by the eq. (1).[12,13]

$$\frac{\partial C(x,t)}{\partial t} = D\left(\frac{\partial^2 C(x,t)}{\partial x^2}\right) \tag{1}$$

where C is concentration of TBAB, t is time, T is temperature, and D is diffusion coefficient. Here, it is assumed that D is constant at given temperature.

TBAB in PP/TBAB initially distributed at a uniform concentration C_0, that is,

$$C = C_0,\ t = 0 \tag{2}$$

Considering, now a plaque of thickness $2l$. $x = 0$ is at the center of the plaque. x is from $-l$ to l. If surface TBAB concentration is proportional to the initial concentration, it can be defined as βC_0. Therefore, the boundary conditions may be written as

$$C = \beta C_0,\ x = l \tag{3}$$

$$\frac{\partial C}{\partial x} = 0,\ x = 0 \tag{4}$$

where the parameter β is to correct initial concentration at the surface because there has been blooming before the heat aging. Equation (4) indicates that there is no diffusion across the central plane of the plaque.

On the basis of the boundary conditions, the Laplace transform and the method of residues can be applied to solve the eq. (1).[13] The solution of the eq. (1) is

$$C = (\beta - 1)C_0 - \frac{4(\beta - 1)C_0}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{(2n+1)} \times \exp\{-D(2n+1)^2\pi^2 t/4l^2\}\cos\frac{(2n+1)\pi x}{2l} + C_0 \tag{5}$$

Equation (5) can be changed to

$$\frac{C - C_0}{(\beta - 1)C_0} = 1 - \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{2n+1} \times \exp\{-D(2n+1)^2\pi^2 t/4l^2\}\cos\frac{(2n+1)\pi x}{2l} \quad (6)$$

At time t, the average TBAB concentration C_{Ave} in the plaque is[14]

$$C_{Ave} = \frac{\int_0^l C dx}{l} \quad (7)$$

Thus, the intergral of eq. (5) was substituted into eq. (7) which gives

$$\frac{C_{Ave} - C_0}{(\beta - 1)C_0} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{(-1)^{2n}}{(2n+1)^2} \times \exp\{-D(2n+1)^2\pi^2 t/4l^2\} \quad (8)$$

Further, amount of the bloomed TBAB on the surface C_{Loss}, that is concentration loss of TBAB from the surface of the PP/TBAB plaque, is

$$C_{Loss} = C_0 - C_{Ave} \quad (9)$$

According to the eqs. (8) and (9),

$$\frac{C_{Loss}}{C_0} = (1-\beta)\left[1 - \frac{8}{\pi^2} \times \sum_{n=0}^{\infty}\frac{(-1)^{2n}}{(2n+1)^2}\exp\{-D(2n+1)^2\pi^2 t/4l^2\}\right] \quad (10)$$

The loss concentrations C_{Loss} of TBAB at t were obtained through the heat aging experiments. The diffusion coefficient D and parameter β can be determined from the eq. (10). D and β were calculated by MATLAB language program based on the experimental results.[15,16] At any point from $x = 0$ to $x = l$, the concentration C of TBAB can be calculated according to eq. (5).

TABLE II
The Calculated Diffusion Coefficient D and Parameter β for Two Kinds of PP/TBAB Blends

Samples (wt %)	β	$D \times 10^7$ (mm^2/s)	Correlation coefficient
18	0.90	5.79	0.9527
45	0.94	1.62	0.9830

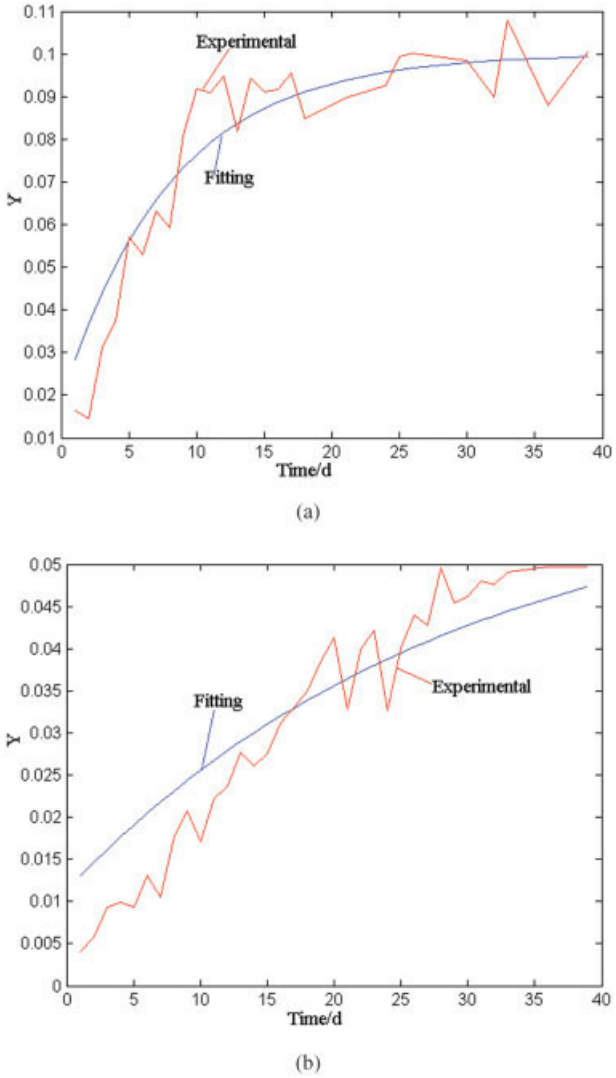


Figure 1 The fitting curve of blooming TBAB concentration PP/TBAB versus time for two kinds of PP/TBAB blends ($Y = C_{Loss}/C_0$). (a) 18 wt % TBAB; (b) 45 wt % TBAB. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

RESULTS AND DISCUSSION

The loss concentrations of TBAB versus time from heat aging tests of the PP/TBAB plaques were calculated every day. The results were listed in Table I every 2 days. m_0 is initial mass of the PP/TBAB samples. W_1 and W_2 are mass of TBAB blooming at C_0 = 18 wt % and C_0 = 45 wt %, respectively.

On the basis of the data in Table I, the diffusion coefficient D and β can be calculated with the eq. (18). The best β and D (Table II) can be obtained by calculating the minimum mean square error of the equation

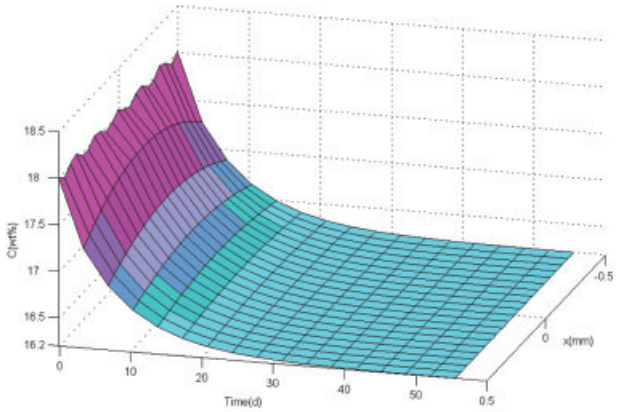


Figure 2 Concentration distribution of TBAB in the plaque of PP/18 wt % TBAB versus the time and the depth x. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

on the basis of the MATLAB program, and the fitting curve can be obtained (Fig. 1).

In Table II, the diffusion coefficient D decreases with the initial concentration of TBAB.[13] Figure 1 shows that the fitting curve has better agreement with the experiment data for the 18 wt % TBAB sample. The blooming rate of TBAB is quick at the beginning. With the time, the blooming rate becomes slow. It seems that TBAB blooming is near to its equilibrium at about 35 days in Figure 1(a) for 18 wt % TBAB. Such a blooming equilibrium has not been reached in 40 days for 45 wt % TBAB as shown in Figure 1(b). The large diffusion coefficient for 18 wt % TBAB plaque perhaps is due to enrichment of diffusion channels in its than for 45 wt % TBAB plaque. In the plaque of 45 wt % TBAB, TBAB molecules may be crowd on diffusion way.

Substituting the diffusion coefficients D and the parameter β into the eq. (5), the concentration profile

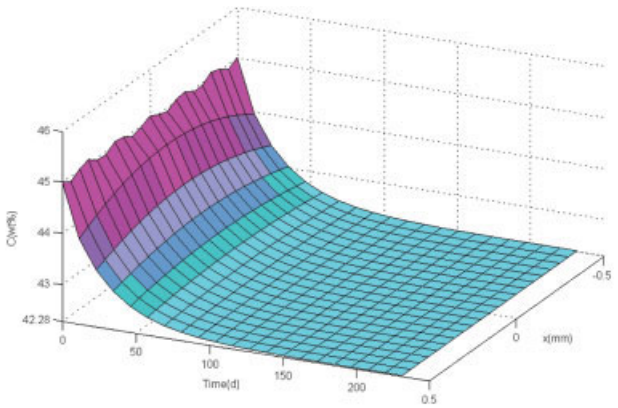
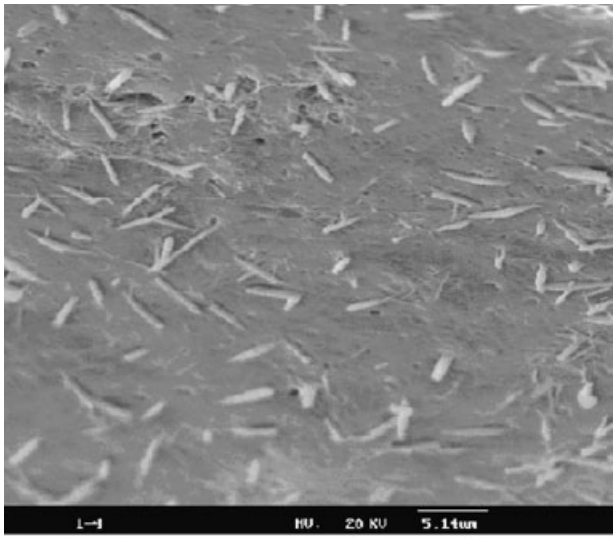
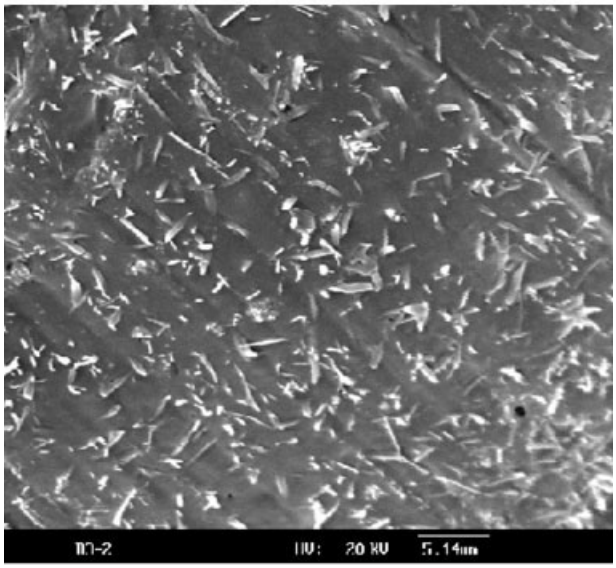


Figure 3 Concentration distribution of TBAB in the plaque of PP/45 wt % TBAB versus the time and the depth x. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



(a)

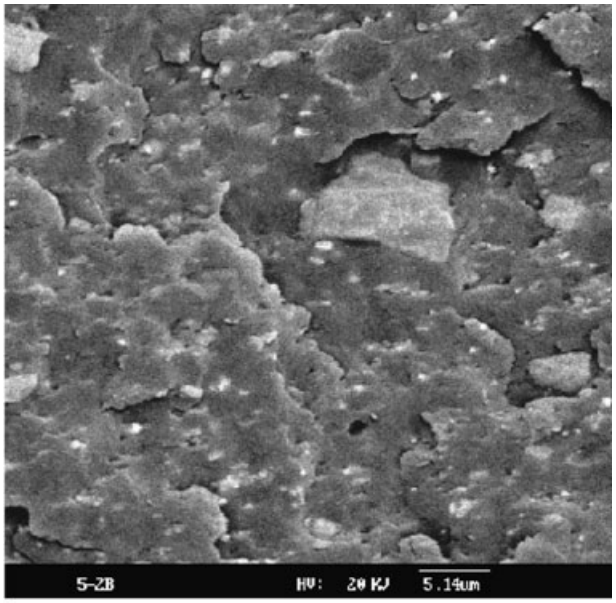


(b)

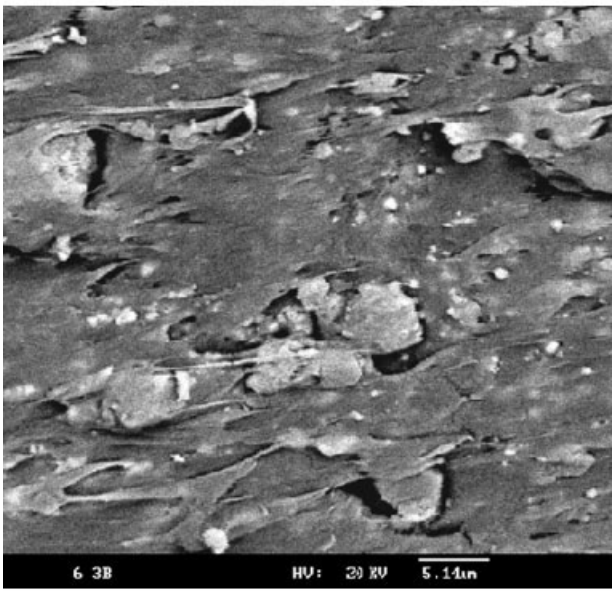
Figure 4 SEM micrographs of the surface of PP/TBAB plaques. (a) 18 wt % TBAB; (b) 45 wt % TBAB.

of TBAB in the plaques can be obtained depending on time and the depth x, and the blooming equilibrium time and equilibrium concentration can be deduced, as shown in Figures 2 and 3.

Figures 2 and 3 show symmetric distributions of TBAB concentration at two sides of the center in a plaque. The highest TBAB concentration is in the center. Figure 2 clearly shows that concentration of TBAB for PP/TBAB 18 wt % becomes constant (16.2 wt %) after about 40 days. Compared with the initial 18 wt % TBAB, the concentration loss of TBAB is 1.8 wt %, which is 10% of all TBAB. In the Figure 3, the concentration of TBAB for PP/TBAB 45 wt % becomes constant (42.3 wt %) after about 120 days. Namely, 2.7 wt



(a)



(b)

Figure 5 SEM micrographs of the inner of PP/TBAB plaques. (a) 18 wt % TBAB; (b) 45 wt % TBAB.

% TBAB, which is 6% of all TBAB, is lost. It is obvious that the blooming equilibrium for the high TBAB concentration is reached later than that for the low TBABs.

In Figure 4, scanning electron micrograph of the surface and inner of PP/TBAB show the blooming TBAB at the surface in the early period of the heat aging test. In Figure 5, the white crystals is TBAB. TBAB particles sizes are larger in the 45 wt % TBAB than in the 18 wt % TBAB (Fig. 1). When TBAB concentration is high, TBAB particles in the PP/TBAB blend are easy to aggregate and form large particles. In this case, the blooming paths can be crowded by the large TBAB particles, which make diffusion of TBAB to the surface become slow.

CONCLUSIONS

Based on the concentration loss of TBAB from the sample surfaces, the model developed here is helpful in describing the blooming of the flame-retardant TBAB in PP. The obtained equations can be used to calculate the diffusion coefficient of TBAB in the blends with PP, and to predict the blooming equilibrium time and concentration. Distribution of TBAB concentration in the samples can be set up with the model. In the blends of 18 wt % TBAB, TBAB has higher diffusion coefficient, and reach diffusion equilibrium earlier than in the blends of 45 wt % TBAB. The reason for this may be that there are richer diffusion paths in the sample of low TBAB concentration than in the sample of high TBAB concentration.

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