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Solid-state polycondensation of poly(ethylene terephthalate) modified with isophthalic acid: kinetics and simulation

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Abstract

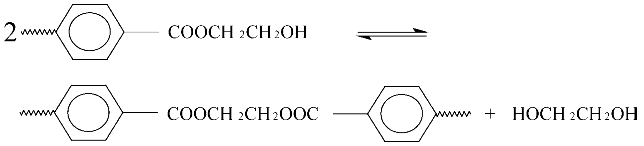
The kinetics for the solid-state polycondensation (SSP) of poly(ethylene terephthalate) modified with isophthalic acid at the protection of nitrogen gas was studied in the paper. A kinetic model controlled by the reversible chemical reactions and the three dimension diffusions of small molecule by-products has been established. The kinetic parameters of the SSP of PET at different temperatures, including the forward rate constants of transesterification reaction (k_1) and esterification reaction (k_2), the diffusion coefficients of EG (D_1) and water (D_2), the concentrations of EG (g_s) and water (w_s) on the surface of PET chips in SSP, and the activation energies of these kinetic parameters were obtained by experiments and solution of the model. Using the model and the kinetic parameters, the SSP of poly(ethylene terephthalate) modified with isophthalic acid can be simulated with good accuracy. In addition, the influences of nitrogen gas flow rate, the chip dimension and the carboxyl end-group concentration of the PET prepolymer on the molecular weight of PET after SSP, and the change of the EG concentration of PET chips with reaction time were also studied by simulation.

Keywords: Solid-state polycondensation; Kinetics; Model

1. Introduction

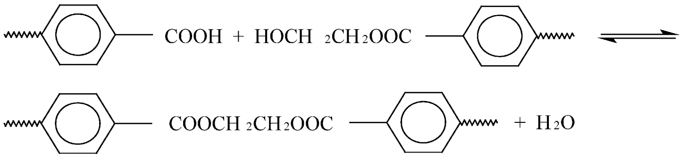
Poly(ethylene terephthalate) (PET) is one of the most important materials for chemical fibers and package materials. Lower molecular weight PET is often used for clothing and decorations; while with higher molecular weight PET finds extensive application in soft drink bottles, industrial filaments, etc. Solid-state polycondensation (SSP) is an efficient way to produce high molecular weight PET. The kinetics for SSP of PET has been studied and various models were adopted [1–9].

In the processing of the SSP of PET, the major chemical reactions that relate to the number-average molecular weight ($\bar{M}_n$) of PET are transesterification reaction (1) between two ester end-groups of two PET molecules and esterification reaction (3) between an ester end-group of one PET molecule and a carboxyl end-group of another PET molecule. The reactions between functional groups, that is, reaction (2) and (4), are used to represent transesterification reaction and esterification reaction, respectively.



(1)

$$2E \underset{k_1/K_1}{\overset{k_1}{\rightleftharpoons}} Z + EG \tag{2}$$



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$$\mathrm{C} + \mathrm{E} \underset{k_2/K_2}{\overset{k_2}{\rightleftharpoons}} \mathrm{Z} + \mathrm{W} \tag{4}$$

Herein E, Z, EG, C and W represent hydroxyl end-groups, diester groups, ethylene glycol, carboxyl end-groups and water, respectively. K_1, k_1 and K_2, k_2 are the equilibrium and forward rate constants of transesterification reaction and esterification reaction.

Other chemical reactions, e.g. decomposition and oxidation can be neglected, as SSP takes place at lower temperature and under the protection of nitrogen gas (N_2). The transesterification reaction between two ester groups of two PET molecules can also be neglected, because it makes no changes in the $\bar{M}_n$ of PET and the amount of by-products.

Because the diffusion speed of small molecule by-products, EG and W, in SSP is very slow, not only the equilibriums of chemical reactions, but also the diffusions of EG and W may also control the reaction rate of SSP.

Chen et al. [1] and Chang et al. [2] analyzed their data from the SSP of PA6, PA6-10 and PET using a kinetic model where only the influence of the diffusions of small molecules on the reaction rate of SSP was considered. Schaaf et al. [3] made a kinetic model where only the influence of chemical reactions on the rate was considered. And Ravindranath et al. [6] developed a comprehensive model where the influences of both the diffusion of EG and the transesterification reaction were considered. However, the model of Ravindranath et al. is not very complete, as the influences of esterification reaction and the diffusion of by-product water were neglected. After that, Tang et al. [8] set up a more complete model by incorporating the influences of the diffusion of water and esterification reaction into their model, and they studied the SSP of PET at 225 °C using their one dimension (1D) model. In the present work, Tang's model was extended to three dimension (3D) and a complete set of data on the SSP of PET modified with isophthalic acid (IPA) at various temperatures was provided and analyzed using the 3D model, which is instructive to the research, design and control of the SSP of PET.

2. Experimental section

2.1. Materials and sample preparation

Prepolymer of SSP, that is, crystalline PET chips modified with IPA (the molar ratio of terephthalate to IPA is 98.8:1.2), were supplied by Yizheng Chemical Fiber Co., Ltd. The PET chips were $2.7\times2.1\times2.9\ \mathrm{mm}^3$. The intrinsic viscosity ([η]), the packing density and the porosity of PET chips were 0.617 dl/g, 0.803 g/cm^3 and 0.425 cm^3/cm^3, respectively. Before SSP, samples were dried in N_2 flow at 140 °C for 4 h.

The SSP was conducted in a fixed bed reactor. A tube reactor 1 cm in diameter was inserted in a cylinder aluminum heater 20 cm in diameter and 25 cm high. N_2 was preheated by flowing through a labyrinth in the aluminum heater before reaching the tube reactor. Each time about 5 g PET chips were used, and after SSP, all chips were smashed for further measurements.

2.2. Measurements

The [η] of PET chips before and after SSP were measured with an Ubbelohde viscometer using the mixture of 1,1,2,2-tetrachloroethane and phenol (2/3, w/w) as solvent at 25 °C. The concentration of the solutions was 5 mg/ml. Then the $\bar{M}_n$ of PET chips was calculated as follows:

$$[\eta] = 2.52\times10^{-4}\bar{M}_n^{0.08} \tag{5}$$

The concentration of carboxyl end-group was measured by titration. 2 g samples were dissolved in 50 ml of the mixture of chloroform and phenol (2/3, v/v). The titration standard solution was potassium hydroxide solution in alcohol with a concentration of 0.05 mol/l.

3. Fundamentals

In SSP, chain extension of PET is conventionally accomplished by two reversible reactions (2) and (4). It is supposed that the diffusions of EG and water follow Fick diffusion law and SSP is an isothermal process with no change in volume.

An unsteady state diffusion process coupled with the concentration change in PET end-groups can be described by Eqs. (6)–(15):

$$\frac{\partial g}{\partial t} = D_1\left(\frac{\partial^2 g}{\partial x^2} + \frac{\lambda}{x}\frac{\partial g}{\partial x}\right) + R_1 \tag{6}$$

$$\frac{\partial e}{\partial t} = -2R_1 - R_2 \tag{7}$$

$$\frac{\partial w}{\partial t} = D_2\left(\frac{\partial^2 w}{\partial x^2} + \frac{\lambda}{x}\frac{\partial w}{\partial x}\right) + R_2 \tag{8}$$

$$\frac{\partial c}{\partial t} = -R_2 \tag{9}$$

$$z = z_0 + \frac{(e_0 + c_0) - (e + c)}{2} = 1 - \frac{e + c}{2} \tag{10}$$

$$R_1 = k_1\left(e^2 - \frac{4gz}{K_1}\right) \tag{11}$$

$$R_2 = k_2\left(ec - \frac{2wz}{K_2}\right) \tag{12}$$

The relevant boundary conditions are as follows:

$$e = e_0,\ c = c_0,\ g = g_0,\ w = w_0,\ z = z_0,\quad t = 0,\quad 0 \le x \le x_0 \tag{13}$$

$$g = g_s,\ w = w_s,\quad t > 0,\quad x = x_0 \tag{14}$$

$$\frac{\partial g}{\partial x} = 0,\ \frac{\partial w}{\partial x} = 0,\quad t > 0,\quad x = 0 \tag{15}$$

Here e, c, z, g, and w are the concentrations of E, C, Z, EG and W, respectively. R_1 and R_2 are the reaction rates of transesterification reaction and esterification reaction. D_1, D_2 are the diffusivity of EG and water. g_s and w_s are the concentrations of EG and water at the surface of PET chips. x is the distance apart from the center of the chips. λ relates to the shape of sample. When the sample is thin section, cylinder or spheroid, λ is 0, 1, or 2 and the corresponding model is 1D, 2D or 3D, respectively. The shape of the PET chips used in the present work is similar to a cube, which is similar to spheroid 1.58 mm in radius in the specific outside area; therefore, a spheroid model ($\lambda = 2$) is adopted. Thus a 3D model is established.

By virtue of transformation of variables

$$p = \frac{t}{t_f} \tag{16}$$

$$q = \frac{x}{x_0} \tag{17}$$

Eqs. (6)–(15) are converted to Eqs. (18)–(28) as follows:

$$\frac{\partial g}{\partial p} = \left(\frac{t_f}{x_0^2} D_1\right)\left(\frac{\partial^2 g}{\partial q^2} + \frac{2}{q}\frac{\partial g}{\partial q}\right) + t_f R_1 \tag{18}$$

$$\frac{\partial e}{\partial p} = -2 t_f R_1 - t_f R_2 \tag{19}$$

$$\frac{\partial w}{\partial p} = \left(\frac{t_f}{x_0^2} D_2\right)\left(\frac{\partial^2 w}{\partial q^2} + \frac{2}{q}\frac{\partial w}{\partial q}\right) + t_f R_2 \tag{20}$$

$$\frac{\partial c}{\partial p} = -t_f R_2 \tag{21}$$

$$z = 1 - \frac{e + c}{2} \tag{22}$$

$$e = e_0,\ c = c_0,\ g = g_0,\ w = w_0,\ z = z_0,\quad p = 0,\quad 0 \le q \le 1 \tag{23}$$

$$g = g_s,\ w = w_s,\quad p > 0,\quad q = 1 \tag{24}$$

$$\frac{\partial g}{\partial q} = 0,\ \frac{\partial w}{\partial q} = 0\quad p > 0,\quad q = 0 \tag{25}$$

The average concentrations of the ester end-group ($\bar{e}$) and the carboxyl end-group ($\bar{c}$) in chips are

$$\bar{e} = \frac{3}{x_0^3}\int_0^{x_0} e x^2 \mathrm{d}x \tag{26}$$

and

$$\bar{c} = \frac{3}{x_0^3}\int_0^{x_0} c x^2 \mathrm{d}x \tag{27}$$

The average degree of polymerization can be calculated from $\bar{e}$ and $\bar{c}$ as

$$\bar{P}_n = \frac{2}{\bar{e} + \bar{c}} \tag{28}$$

Eqs. (18)–(28) were solved numerically by combining finite difference method and Runge-Kutta method.

4. Results and discussion

The experimental data are tabulated in Tables 1 and 2.

$$u = \frac{v}{\gamma^{2/3} s} \tag{29}$$

Here v, γ and s denote N_2 flow volume, the porosity of PET chip and the cross-section area of tube reactor, respectively.

4.1. Influence of nitrogen gas flow rate

The influence of N_2 flow rate on the $\bar{M}_n$ of PET for 15 h at different temperatures is shown in Fig. 1. The $\bar{M}_n$ of PET after SSP for 15 h at various temperatures increases with the increase in N_2 flow rate up to a plateau about 15 m/min. Although, Tang et al. [8] used L/min kg PET as the unit for measuring N_2 flow rate, it can be seen that the result of this paper on the influence of N_2 flow rate is the same in quantity as that of Tang et al. after exchanging the unit, which also

Table 1
Influence of N_2 flow rate on the molecular weight of PET at different temperatures after SSP for 15 h

T (°C)	$\bar{M}_n$ ($\times 10^4$ g/mol)					
	N_2 flow rate (m/min)[a]					
	2.25	9.01	13.5	18.0	22.5	27.0
205	2.25	2.32	2.35	2.36	2.37	2.36
215	2.60	2.68	2.70	2.71	2.71	2.72
225	2.92	3.15	3.22	3.25	3.23	3.24

[a] N_2 flow rate (u) is calculated as follows.

Table 2
Molecular weight ($\bar{M}_n$) and concentration of carboxyl end-group (c) of PET after SSP for different times at different temperatures (N_2 flow rate was 13.5 m/min)

T (°C)	$\bar{M}_n$ ($\times 10^4$ g/mol)				c ($\times 10^{-3}$ mol/⌬)			
	0 h	5 h	10 h	15 h	0 h	5 h	10 h	15 h
200	1.69	1.91	2.06	2.25	5.95	5.36	4.74	4.34
205	1.69	1.94	2.20	2.35	5.95	5.01	4.45	4.03
210	1.69	2.06	2.31	2.47	5.95	4.90	4.19	3.69
215	1.69	2.10	2.45	2.70	5.95	4.61	3.94	3.44
220	1.69	2.30	2.63	2.87	5.95	4.40	3.74	3.23

corresponds with the results reported by other investigators. As N_2 flow rate increases, the concentrations of EG and water on the surface of PET chips approach thresholds, accompanied by the appearance of a plateau in the molecular weight of PET.

4.2. Influence of temperature

The influences of temperature on the $\bar{M}_n$ and the concentration of carboxyl end-group (c) of PET after SSP for different times are shown in Figs. 2 and 3, respectively. It can be seen that as the temperature rises, $\bar{M}_n$ increases and c decreases, and the changes in both $\bar{M}_n$ and c become larger at higher temperature. This is understandable that as the temperature rises, the chemical reactions and the diffusions of by-products speed up.

4.3. Solution

The kinetic parameters of SSP of PET cannot be easily obtained, as the distributions of the end-groups and by-products in the PET chips after SSP are not uniform, hence the numerical calculation method is adopted here. As we can see in Eqs. (6)–(15) that the eight parameters, that is, K_1, K_2, k_1, k_2, D_1, D_2, g_s and w_s are required to solve the model. Among which, the equilibrium constants of transesterification reaction and esterification reaction K_1 and K_2 can be estimated from melt polycondensation of PET in higher conversion, their values are 1 and 1.25, respectively, [10,11]. Thus, given parameters k_1, k_2, D_1, D_2, g_s and w_s, the simulated curves of $\bar{M}_n$ and c could be gotten. After comparing the simulated values of $\bar{M}_n$ and c with the experimental ones, the parameters were adjusted and new simulated curves were gotten. Comparing and adjusting the parameters continued until the deviations between the simulated and experimental values of $\bar{M}_n$ and c were small enough. The values of the parameters thus obtained are listed in Table 3.

Using the kinetic model and the parameters listed in Table 3, we can obtain the $\bar{M}_n$ and the c of PET after SSP under different conditions by calculation. The small errors between the experimental and the calculated values of $\bar{M}_n$ and c shown in Table 4 indicate that the accuracies of the model and its solutions, that is, the values of the parameters are quite satisfactory.

4.4. Activation energies

By virtue of the parameter values in Table 3 and Arrhenius equation, we calculated the activation energies of

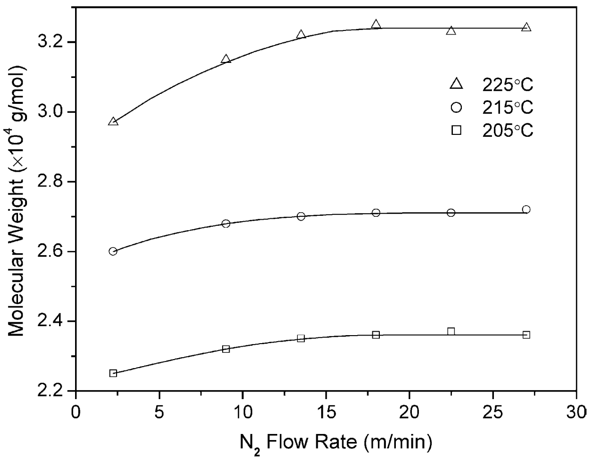

Fig. 1. Influence of N_2 flow rate on the $\bar{M}_n$ of PET after SSP for 15 h at different temperatures.

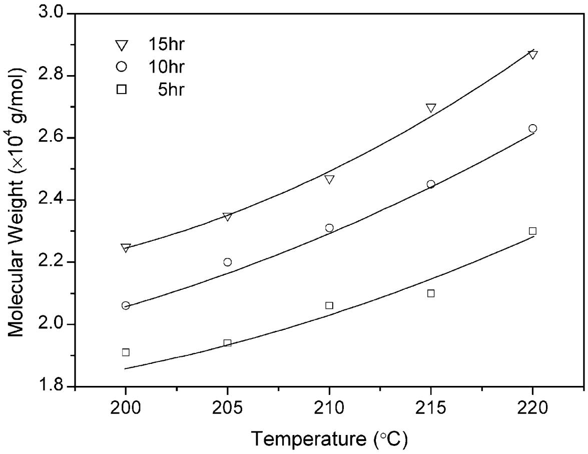

Fig. 2. Influence of temperature on the $\bar{M}_n$ of PET after SSP for different times at N_2 flow rate of 13.5 m/min.

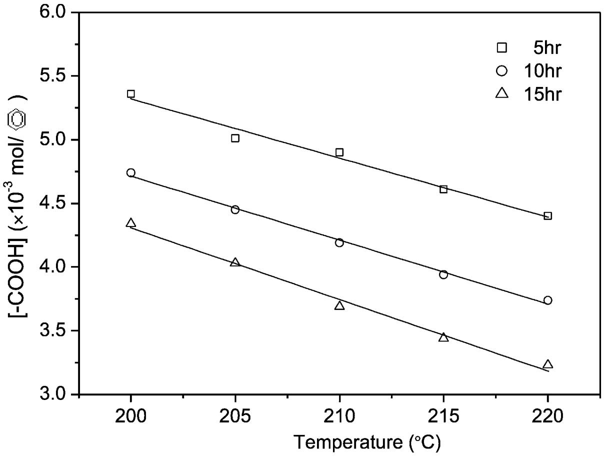

Fig. 3. Influence of temperature on the c of PET after SSP for different times at N_2 flow rate of 13.5 m/min.

esterification reaction, transesterification reaction, and the diffusion of EG and water. The results are shown in Table 5 and the results in literature are also given. Due to the difference between the prepolymer chips adopted, especially the differences in the catalyst species and amount, different values of activation energies of esterification and transesterification reaction were reported (Table 5). However, we can see that all the activation energies of SSP are larger than those deduced from melt polycondensation [12]. PET chips are composed of amorphous phase and crystalline phase dispersed in the amorphous continuous phase. As SSP takes place at a temperature 20–40 °C below the melt point of PET chips, only the end-groups of chains lying in the amorphous phase can move efficiently and thus cause the occurring of the reaction, therefore, the reaction rate of SSP is slower than that of melt polycondensation. Accordingly, the activation energies of SSP are larger. In addition, we can also see in Table 5 that the results obtained by different groups are quite close except for that reported by Ravindranath et al. [6], which is caused by the neglecting of esterification reaction in their model. By comparing the activation energies of chemical reactions with those of the diffusions of small molecules, it can be seen that the former are larger, indicating that the chemical reactions are more sensitive to the reaction temperature than the diffusions of small molecules. This corresponds to the conclusion drawn by Chen et al. [5] and Kang [9] that the chemical reactions control the process of SSP at low temperature, while at high temperature the diffusions of small molecules dominate.

The relation between the temperature and the concentration of EG (g_s) and water (w_s) on the surface of the chips are illustrated in Fig. 4. It can be seen that linear equation can fit the data points of $1/T$ (absolute temperature) vs $\ln(g_s)$ and $\ln(w_s)$ quite well, thus we can also calculate the apparent activation energies of g_s and w_s according to Arrhenius equation. The results are listed in Table 6. It can be seen that the apparent activation energies of g_s and w_s are irrelevant to N_2 flow rate, indicating that the concentration of EG and water on the surface of PET chips is mainly controlled by their absorption to PET molecules.

5. Simulation of SSP

After having the parameter of the kinetic model, we can make simulation calculations on the SSP of PET under different conditions and thus analyze the influences of various parameters on the molecular weight and concentration of carboxyl end-group of PET in SSP.

5.1. Influence of N_2 flow rate

Fig. 5 shows the change of the $\bar{M}_n$ of PET after SSP with the reaction time at 210 °C and different N_2 flow rate, and curves 1, 2 and 3 show the relations at different concentrations of EG (g_s) and water (w_s) on the surface of PET chips. The situation when both g_s and w_s are equal to 0 denotes the ideal limit that the reaction can reach. Curve 1 gives the ideal values of $\bar{M}_n$ for different times. In fact, since g_s and w_s do not decrease again after N_2 flow rate reaches a certain value, the difference between the real and the ideal value of $\bar{M}_n$ increases with the time continuously.

5.2. Change in the EG concentration of the PET chips

The change in the EG concentration of the PET chips with reaction time in SSP at 210 °C is described in Fig. 6.

Table 3
Rate constants [(mol/◎)$^{-1}$h^{-1}] of transesterification reaction (k_1) and esterification reaction (k_2), diffusion coefficient [cm^2/s] of EG (D_1) and water (D_2), concentration [mol/◎] of EG (g_s) and water (w_s) on the surface of PET chips in SSP

T (°C)	k_1	k_2	D_1 ($\times10^{-6}$)	D_2 ($\times10^{-6}$)	g_s ($\times10^{-5}$)		w_s ($\times10^{-5}$)	
					2.25[a]	13.5[a]	2.25[a]	13.5[a]
200	0.95	2.89	2.60	5.80	3.00	2.63	2.09	1.81
205	1.08	3.30	2.73	5.92	2.88	2.52	2.04	1.76
210	1.49	4.95	2.86	6.09	2.76	2.42	2.00	1.73
215	2.99	7.84	2.99	6.26	2.52	2.21	1.90	1.64
220	3.32	9.49	3.12	6.38	2.40	2.10	1.85	1.60

[a] N_2 flow rate (m/min).

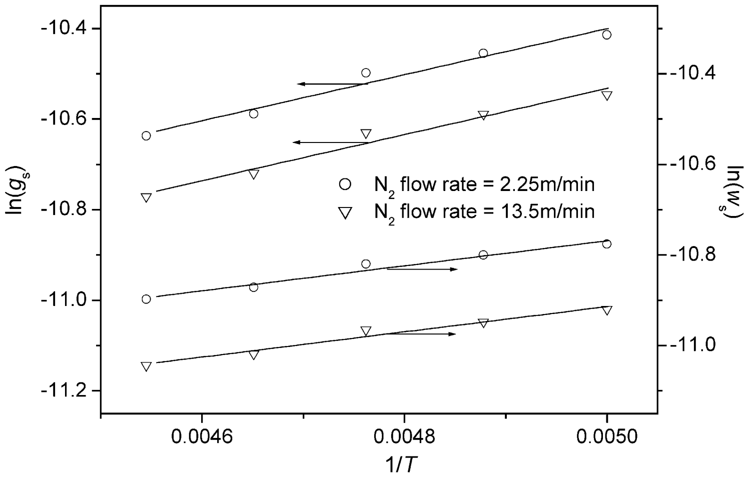

Fig. 4. Relation of $1/T$ vs. $\ln(g_s)$ and $1/T$ vs. $\ln(w_s)$ in SSP.

Table 4

Errors between the experimental and the calculated values of the molecular weight ($\bar{M}_n$) and the concentration of carboxyl end-group (c) of PET after SSP for 15 h at N_2 flow rate of 13.5 m/min

T (°C)	$\bar{M}_n$ ($\times 10^4$g/mol)			c ($\times 10^{-3}$ mol/⌬)		
	Exp.	Calc.	Relative error (%)	Exp.	Calc.	Relative error (%)
200	2.25	2.25	0	4.34	4.32	0.46
205	2.35	2.31	1.72	4.03	4.19	3.89
210	2.47	2.48	0.40	3.69	3.80	2.94
215	2.70	2.65	1.87	3.44	3.46	0.58
220	2.87	2.89	0.69	3.23	3.30	2.14

Table 5

Activation energies (kJ/mol) of chemical reactions and diffusions of small molecules in SSP

	Transesterification reaction	Esterification reaction	Diffusion of EG	Diffusion of water
Our results	135.38	125.24	17.60	9.57
Chen et al. [5]	100.32	79.84	22.57	–
Ravindranath et al. [6]	–	–	130.83	–
Kang [9]	133.76	130.83	16.72	10.03
Yokoyama [12][a]	77.33	73.57	–	–

[a] Deduced from the melt polycondensation.

Table 6

Apparent activation energies (kJ/mol) of the concentration of EG and water on the surface of PET chips

N_2 flow rate (m/min)			
2.25		13.5	
Eg_s	Ew_s	Eg_s	Ew_s
−4.23	−2.29	−4.24	−2.31

Because the prepolymer chips come from melt polycondensation, their EG concentration is fairly small. Much EG is produced at the beginning of SSP reaction due to the fairly high concentration of ester end-group in the chips, which can not be fully diffused out of the chips and brought away subsequently by N_2 flow. As a result, the EG concentration of the chips increases at the initial stage of SSP. As the reactions of SSP proceed, $\bar{M}_n$ of PET increases and ester end-group decreases, EG produced by reactions decreases

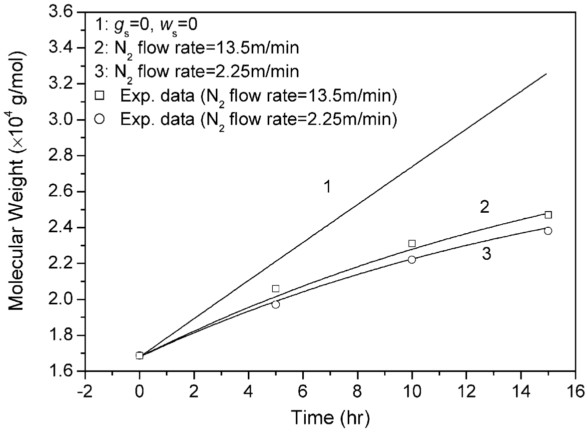

Fig. 5. Change of the $\bar{M}_n$ of PET with the reaction time in SSP at 210 °C and different N_2 flow rate.

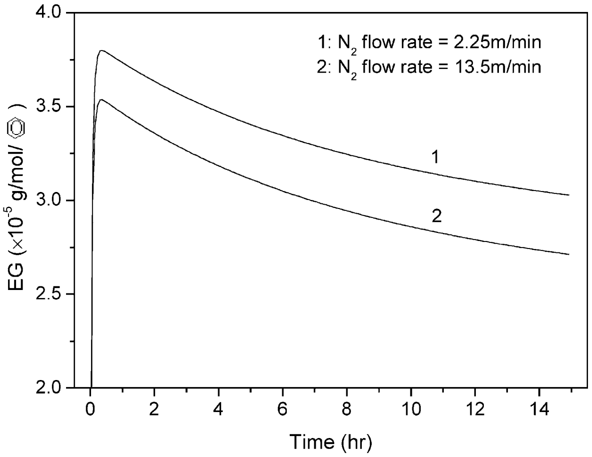

Fig. 6. Change of EG concentration of PET chips with the reaction time in SSP at 210 °C.

accordingly. Meanwhile, the diffusion process continues to work. Therefore, the EG concentration of the chips decreases with the reaction time.

5.3. Influence of the chip dimension

Fig. 7 shows the relation between $\bar{M}_n$ and the reaction time of SSP using PET chips with a radius of 1.58 and 2 mm. It can be seen that the molecular weight of PET is higher when the dimension of PET chips is smaller. The smaller the dimension is, the shorter the diffusion distance of EG and water, the smaller the concentration of EG and water in chips, thus causing an increase in the reaction rate of esterification reaction and transesterification reaction. Consequently, after SSP for the same time, the $\bar{M}_n$ increases, as the dimension decreases.

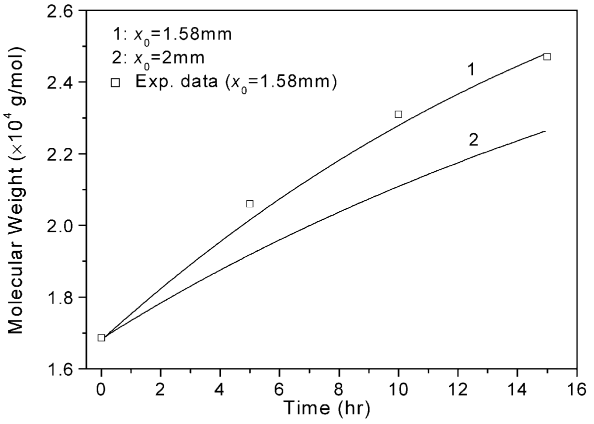

Fig. 7. Influence of the dimension of chips on the SSP of PET at 210 °C and N$_2$ flow rate of 13.5 m/min.

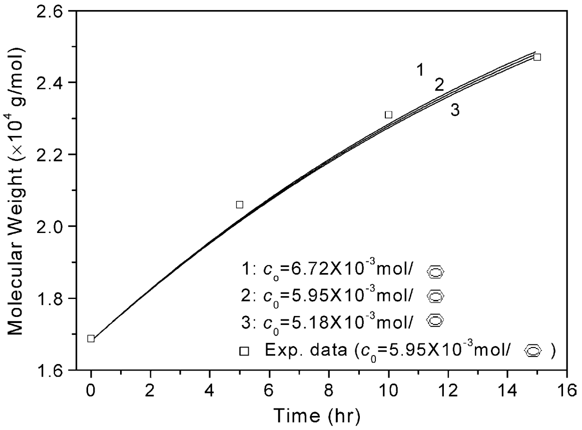

Fig. 8. Change in $\bar{M}_n$ with reaction time in SSP using the PET prepolymer chip with equal $\bar{M}_n$ and different c_0 at 210 °C and N$_2$ flow rate of 13.5 m/min.

5.4. Influence of the carboxyl end-group concentration in the prepolymer chips

The PET prepolymer chip with equal $\bar{M}_n$ and different carboxyl end-group concentration (c) can be obtained by controlling the processing parameters of the melt polycondensation. The changes in $\bar{M}_n$ and c with reaction time using the PET prepolymer chip with equal $\bar{M}_n$ and different initial carboxyl end-group concentration (c_0) are illustrated in Figs. 8 and 9, respectively. The c_0 of the PET prepolymer chip has a little influence on the $\bar{M}_n$ of PET after SSP (Fig. 8). As c_0 increases, the c of PET after SSP also increases; meanwhile, the reaction rate of esterification reaction becomes faster, accompanied with a slightly faster decrease in the c (Fig. 9).

6. Conclusions

A kinetic model co-controlled by the reversible

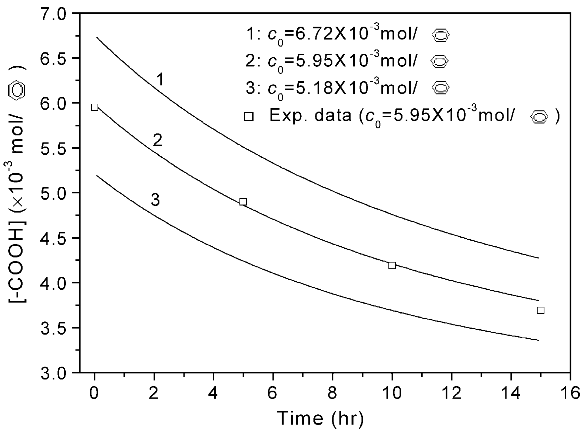

Fig. 9. Change in c with reaction time in SSP using the PET prepolymer chip with equal $\bar{M}_n$ and different c_0 at 210 °C and N$_2$ flow rate of 13.5 m/min.

esterification reaction and transesterification reaction, and the three dimension diffusion of small molecule by-products, for solid state polycondensation (SSP) of spherical PET chips under the protection of nitrogen gas has been established. Using the model, the kinetic parameters for SSP of PET, that is, the forward rate constants of transesterification reaction (k_1) and esterification reaction (k_2), the diffusion coefficients of EG (D_1) and water (D_2), and the concentrations of EG (g_s) and water (w_s) on the surface of PET chips, were determined. The calculated values of the molecular weight of PET ($\bar{M}_n$) and the concentration of carboxyl end-group (c) using the model and the determined parameters are very close to their corresponding experimental ones. Furthermore, the influences of various processing parameters on the SSP of PET were studied by simulation calculation, and the results correspond well with those predicted theoretically.

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