Research Article

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Experimental study on the dissolution of supercritical CO₂ in PS under different agitators

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Abstract: In the continuous molding of microporous plastics, the polymer/CO₂ homogeneous body needs to be formed in a very short time, which affects the subsequent bubble nucleation, bubble pore distribution, and growth, and is the key to the molding. It is known that the formation time of homogeneous body is shortened during the continuous molding of microporous plastics because of the agitator's effect. However, different agitators have different effects on the dissolution rate. So, it is necessary to study not only the dissolution of gas in polymer melt under static condition but also the dissolution under the action of the agitator. In this article, the solubility and dissolution rate of supercritical CO₂ in polymer melt PS at different temperatures and pressures were experimentally investigated under conical and screw agitators, and the numerical solution was also carried out.

Keywords: CO₂, polymer, solubility, dissolution rate, agitator

1 Introduction

Microporous plastics have many superior comprehensive properties, such as lightweight, high impact strength, good toughness, low conductivity, sound, and heat insulation effect (1–4). There are many methods for forming

microporous plastics, among which the supersaturated gas method has the most potential for industrial application (5,6). The method utilized the fact that the solubility of gas in polymer melt is dependent on pressure and temperature. First, at high pressure, the gas dissolves in the polymer melt to form a homogenous body, then by heating or depressurizing method to reduce the solubility of a gas-forming super saturation state, phase separation, to form a large number of tiny nucleate within the polymer. Then, to further control, the bubble hole growth and microporous plastics are obtained after shaping.

The molding method of microporous plastics has two methods: intermittent extrusion and continuous extrusion. Intermittent extruding takes a long time for CO₂ to permeate into the polymer and reach saturation, the process is intermittent, and so the prospect of industrial application is limited (7). Continuous extruding forming means that the polymer is transported and melted by the extruder, and supercritical CO₂ is dissolved into the polymer melt through the injection port on the machine barrel in the homogenization stage. CO₂ rapidly dissolves under the action of the agitator in the machine barrel, forming polymer/CO₂ homogeneous body. Then rapid decompression results in nucleation and growth of bubbles in homogeneous bodies, and the size of the bubble hole is determined by cooling control. Finally, microporous plastic products are obtained. The continuous extruding forming is the current direction of industrial application (8–11).

In the continuous molding of microporous plastics, the polymer/CO₂ homogeneous body needs to be formed in a very short time, which affects the subsequent bubble nucleation, bubble pore distribution, and growth, and is the key to the molding (12–15). Two important problems should be solved in this process. First, the dissolved mass of supercritical CO₂ in polymer melt should be reasonably determined based on the accurate calculation. Second, whether the polymer melt can dissolve as much supercritical CO₂ as possible within the process time depends on the dissolution rate. The increase of the dissolution rate depends on the reasonable formulation of process parameters and the reasonable design of the agitator (16,17).

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Conversely, it is known that the formation time of the homogeneous body is decreased during the continuous molding of microporous plastics because of the agitator's effect. However, different agitators have different effects on the dissolution rate.

The diffusion coefficient and the solubility of supercritical CO₂ in polymer melts were studied on the basis of adsorption diffusion (18–20). But based on the aforementioned understanding, we think that it is necessary to study not only the dissolution of gas in polymer melt under static condition but also the dissolution under the action of the agitator. In addition, the numerical calculation model of dissolution mass and velocity can also be used in other fields such as interpolymer resins (21). In this article, under different agitators, the dissolution of supercritical CO₂ in polymer melt PS was studied experimentally, and the numerical solution was also carried out.

2 The experimental device

In this study, we used a set of constant temperature and pressure experimental equipment. As shown in Figure 2, the main body of the experimental device is a cylindrical reaction cell with high temperature and high pressure. The inner diameter is 12 cm, and the agitator can be replaced according to the experimental needs. Since constant temperature and constant pressure can be maintained during the experimental process, the number of CO₂ molecules adsorbed on the gas–liquid interface remains constant, and the mass of CO₂ dissolved in the polymer melt can be accurately measured by the volume change of the gas in the gas storage cell. Among them, the system pressure is kept constant by pressurizing and stabilizing devices, and the temperature is kept at the specified temperature by oil bath heating. The details of the experimental device and experimental steps were described in our previously published article (22). In this article, we use two different agitators, as shown in Figure 3. The cone angle is 3° of the conical agitator, and the design imitates the principle of the cone-plate rheometer, that is, the cone-top angle is very small (generally less than 3°). In the process of the experiment, the shear rate of the polymer melt remains constant, and CO₂ molecules were adsorbed at the gas–liquid interface during the experimental process, so the dissolution process under the cone agitator was adsorption–diffusion. The screw agitator is to imitate the screw extrusion of the actual processing.

The experimental materials are as follows: CO₂ (>99.5% purity) was supplied from Guohui Gas Co. Ltd. (Nanchang, China). Polystyrene (PS, >99.7% purity, $T_g = 381.4$ K, $M_n = 105$) was obtained by Taihua polystyrene Co. Ltd (Ningbo, China). All chemicals were used as received, and the characteristics were given by the supplier.

3 Dissolution experiment under conical agitator

3.1 Solution of solubility (C_g^*) and diffusion coefficient (D)

The conical agitator provides shear motion to the polymer melt. Because PS melt only moves in a circle during the experiment, and the dissolution process still conforms to the adsorption–diffusion process, the solubility (C_g^*) and diffusion coefficient (D) can be solved by Fick's second law. By using our experimental apparatus and conical agitator, the solubility and diffusion coefficient of supercritical CO₂ in polystyrene melt at different temperatures and pressures were obtained. The results are presented in Table 1, and the detailed solving process and the solubility and diffusion coefficient under the static condition can be referred to our previously published literature (22). It is presented in Table 1 that the solubility decreases with the temperature, while the diffusion coefficient increase and both solubility and diffusion coefficient increase with the increasing pressure. At the same pressure and temperature, the solubility under the static condition and conical agitator is similar, while the diffusion coefficient under the conical agitator is much larger than that under the static condition. This is because the agitator not only makes the irregular polymer chains orderly but also reduces the distance that CO₂ molecules dissolve between the polymer chains. That ultimately reduces the time required to reach equilibrium. So, the solubility would not change with the agitator, just the dissolution progress will be shortened, and the main factors affecting solubility are still pressure and temperature.

3.2 Solution of dissolution rate

During the experiment, since the temperature and pressure are constant, we believe that the concentration of CO₂ at the gas–liquid interface is constant. At time t , the

Figure 1: Dissolution rate curves at different temperatures and pressures under conical agitator and the time of the inflection point of the dissolution rate.

reduced mass of gas in the gas storage cell is equal to the mass of CO₂ dissolved in the PS melt. So, the dissolution rate of CO₂ can be obtained by Fick's first law:

$$\frac{dm(t)}{dt} = -DA \left(\frac{\partial C_g}{\partial z} \right)_{z=0}, \quad (1)$$

where $dm(t)/dt$ is the dissolution rate, D is the diffusion coefficient (m²/s), A is the cross-sectional area of the diffusion cell, and $\left(\frac{\partial C_g}{\partial z} \right)_{z=0}$ is the dissolution rate at the gas-liquid interface. Finally, Eq. 2 is obtained by integrating both sides of Eq. 1 with respect to time t from 0 to:

$$m(t) = \int_{t=0}^t \frac{dm(t)}{dt} dt = \int_{t=0}^t -DA \left(\frac{\partial C_g}{\partial z} \right)_{z=0} dt. \quad (2)$$

By solving Fick's second law with the boundary conditions, the concentration function (C_g) was obtained by the Laplace transform method as follows (23):

Figure 2: Diagram of the diffusion cell.

Table 1: The solubility and diffusion coefficient under static condition and conical agitator (2 r/s)

<i>P</i> (MPa)	<i>T</i> (K)	Static condition		Conical agitator (2 r/s)	
		Solubility (g-CO ₂ /g-PS)	Diffusion coefficient (10 ⁻⁸ × m ² /s)	Solubility (g-CO ₂ /g-PS)	Diffusion coefficient (10 ⁻⁸ × m ² /s)
7.5	443	0.0265	5.985	0.0267	9.715
	453	0.0242	6.025	0.0245	10.312
	463	0.0224	7.136	0.0226	11.023
8.5	443	0.0295	7.258	0.0297	11.475
	453	0.0269	8.165	0.0266	12.326
	463	0.0252	9.227	0.0257	13.458
9.5	443	0.0332	9.316	0.0331	13.426
	453	0.0295	10.221	0.0294	14.663
	463	0.0283	10.986	0.0282	15.317

$$C_g(z, t) = C_g^* \left[1 - \frac{4}{\pi} \sum_{n=1}^{\infty} \frac{1}{2n-1} \times \exp\left(-\frac{D(2n-1)^2\pi^2 t}{4H^2}\right) \sin \frac{(2n-1)z\pi}{2H} \right], \quad (3)$$

where H represents the height of the polymer melt. In our experiments, the height of our polymer melt is 1 cm, and by substituting Eq. 3 into Eq. 2, we can get Eq. 4:

$$m(t) = \frac{8AC_g^*H}{\pi^2} \left[1 - \exp\left(-\frac{D\pi^2 t}{4H^2}\right) \right]. \quad (4)$$

Finally, we get the expression of the dissolution rate function $v_c(t)$ under conical agitator as follows:

$$v_c(t) = \frac{dm(t)}{dt} = \frac{2AC_g^*D}{H} \exp\left(-\frac{D\pi^2 t}{4H^2}\right). \quad (5)$$

By using the solubility (C_g^*) and diffusion coefficient (D) obtained in Table 1, we can obtain the numerical solution of the dissolution rate at different temperatures and pressures under the conical agitator (Figure 1).

As shown in Figure 1, at the beginning of dissolution, the dissolution rate is faster due to the lower concentration

of CO₂ in the polymer. As the concentration of CO₂ increases, the dissolution rate drops rapidly, and after a specific time point, the dissolution rate becomes very slow with little change. In this article, we call the specific time point as the inflection point of the dissolution rate. As shown in Figure 1, at the inflection point of the dissolution rate, the bending degree of the dissolution rate curve is the largest. Therefore, we can take the time corresponding to the maximum curvature value of the dissolution rate curve as the inflection point of the dissolution rate. The curvature value (K) can be obtained by the radius of curvature formula, as shown in Eq. 6:

$$K = \frac{|y''|}{(1 + (y')^2)^{\frac{3}{2}}}. \quad (6)$$

Eq. 5 is substituted into Eq. 6, and then we take the derivative of both sides of Eq. 6 with respect to time t and set $K' = 0$, and finally Eq. 7 is obtained:

$$\left(\exp\left(\frac{D\pi^2 t}{2H^2}\right) \right)^2 - \left(\frac{AC_g^*D^2\pi^2}{2H^3} \right)^2 \left(\exp\left(\frac{D\pi^2 t}{2H^2}\right) \right) - 2 \left(\frac{AC_g^*D^2\pi^2}{2H^3} \right)^4 = 0. \quad (7)$$

Figure 3: Dissolving process under interface flipping.

By solving Eq. 7, we can obtain the numerical solution of the time t corresponding to the inflection point of the dissolution rate, as shown in Eq. 8:

$$t = \frac{\ln 2 + 2 \ln \left(\frac{AC_g^* D^2 \pi^2}{2H^3} \right)}{D\pi^2/2H^2}. \quad (8)$$

From Eq. 8, the time t corresponding to the inflection point of the dissolution rate at different temperatures and pressures is obtained and marked in Figure 1. Obviously, with the increase of the temperature or pressure, the time of the inflection point of the dissolution rate is constantly brought forward.

3.3 Dynamic viscosity under shear conditions

As shown in Figure 2, the cone angle of the conical agitator is 3° and the principle of cone-plate rheometer is adopted. When the angle is less than 4°, the flow of polymer melt between the conical agitator and the bottom of the reactor cell can be regarded as a shear flow. Therefore, the shear rate is approximately constant when its rotational angular velocity is constant. So, the PS melt viscosity can be obtained from the torque of the agitator, and the torque T_e is expressed as follows:

$$T_e = 2\pi \int_0^R \sigma_\theta r^2 dr = \frac{2}{3} \pi R^3 \sigma_\theta, \quad (9)$$

where R is the radius (m) of the agitator, and σ_θ is the shear stress (Pa) and can be expressed as follows:

$$\sigma_\theta = -\eta \gamma_\theta = -\eta \frac{\sin \theta}{r} \left[\frac{\partial}{\partial \theta} \left(\frac{V_\phi}{\sin \theta} \right) \right] \approx \eta \frac{\Omega}{\theta_0}. \quad (10)$$

In Eq. 10, η is the PS melt viscosity, γ_θ is the shear rate (s^{-1}), Ω is the rotation angular velocity (rad/s) of the agitator, and θ_0 is the cone apex angle (°) of the agitator. By combining Eqs. 9 and 10, we can obtain Eq. 11:

$$\eta = \frac{3\theta_0 T_e}{2\pi R^3 \Omega}. \quad (11)$$

The torque T_e of the agitator is obtained mainly by measuring the current with the current detector in the experimental device. The specific calculation formula is as follows:

$$T_e = 9.55 \frac{U \times I}{n}, \quad (12)$$

where U is the working voltage (V), I is the effective current (A), and n is the rotation speed of the agitator (rpm). Finally, the dynamic viscosity of PS at different temperatures, pressures, and rotational speeds is shown in Table 2.

It can be seen from Table 2 that under different temperatures and pressures, the variation trend of dynamic viscosity under shear condition is similar to that of solubility, that is, it decreases with the increase of temperature and increases with the increase of pressure. The difference is that the solubility does not change with the increase of rotational speed, but the dynamic viscosity decreases with the increase of rotational speed.

Table 2: The dynamic viscosity (Pa s) of PS under shear condition

Rotation speed (r/s)	$T = 443 \text{ K}$			$T = 453 \text{ K}$		
	7.5 MPa	8.5 MPa	9.5 MPa	7.5 MPa	8.5 MPa	9.5 MPa
0	55624.71	60240.05	65238.35	22468.47	24332.74	26351.71
1	4074.17	4131.57	4189.51	3446.45	3500.742	3555.03
2	2296.62	2328.09	2359.93	1961.43	1989.51	2017.81
3	1640.45	1662.77	1685.36	1404.47	1424.05	1443.83
4	1291.74	1309.26	1327.01	1107.08	1122.34	1137.77

Rotation speed (r/s)	$T = 463 \text{ K}$		
	7.5 MPa	8.5 MPa	9.5 MPa
0	10428.91	11294.22	12231.33
1	2908.15	2966.58	3024.18
2	1697.87	1725.04	1752.19
3	1224.07	1242.31	1260.61
4	967.71	981.65	995.69

4 Dissolution experiment under screw agitator

4.1 Analysis of dissolving process

In the extrusion processing of foaming materials, to obtain a better homogeneous body in a short time, screw agitators are often used to accelerate the dissolution rate of supercritical CO₂ in polymer melts (24,25). Through the careful analysis of the continuous extrusion process and the mixing action of agitators, we find that under the stirring action of this type of agitator, the gas–liquid interface of the polymer melt will be continuously flipped and buried into the polymer melt, while the new gas–liquid interface will continuously emerge from the polymer melt. We call this phenomenon as interface flipping. Under the effect of interface flip, CO₂ adsorbed on the gas–liquid interface is also flipped and buried into the polymer melt, and at the same time, new interfaces from the polymer melt continually appear at the gas–liquid interface and re-adsorb CO₂ molecules, but the buried CO₂ does not dissolve directly into the polymer melt, still absorbed on the surface of the polymer molecules. As shown in Figure 3a, CO₂ molecules not only adsorbed on the gas–liquid interface but also exist in polymer melts due to the interface flipping. This is equivalent to “increasing” the area of the gas–liquid interface. As shown in Figure 3b, since the volume of the polymer melt remains constant, the diffusion height “decreases,” thus accelerating the dissolution rate and reducing the time to saturation.

4.2 Mathematical model of solubility calculation

Before we go into the mathematical model, we need to make two assumptions:

- (1) The rate of interface flip is dependent only on the structure and stirring speed of the agitator. For a particular agitator, it only depends on the stirring speed. Under the condition of a certain speed, the interface flip rate is constant during the experiments.
- (2) Since the temperature and pressure were constant, the adsorption concentration of CO₂ on the gas–liquid interface remains unchanged during the experiment, which is the saturation concentration C_g^* (26).

According to the adsorption theory (27), when the temperature is T and the pressure is P , there are N/N_0 (mol) CO₂ molecules adsorbed on the polymer surface per unit area with a mass of MN/N_0 (g). N is the number of CO₂ molecules adsorbed per unit gas–liquid interface area, N_0 is Avogadro constant, and M is the mass of the CO₂ molecule. Due to the action of the agitator, the gas–liquid interface is always renewed with the rotation of the agitator. For a specific agitator, the renewal speed of the interface is only related to the stirring speed, and the renewal speed is constant at a certain rotational speed. So, we define the area of gas–liquid interface buried per unit time as the interface renewal ratio and represent as I (m²/s).

When the interface is updated at the rate of I , the interface area of I is updated in unit time, that is, the interface with the surface area of I is buried in the polymer melt and the CO₂ molecule with the mass of IMN/N_0 (g) is buried. At the same time, the polymer interface is replaced by the same area.

As the interface flips, the CO₂ buried in polymer melt will not all dissolve, but only part dissolves, and with the increase of the concentration of CO₂ in the polymer melt, the number will decrease. The ratio of the number of newly dissolved carbon dioxide molecules to the number of buried carbon dioxide molecules in the polymer is defined as a function of time t and is called the flip dissolution coefficient $W(t)$. Then, at time t , the dissolved mass of CO₂ is expressed as follows:

$$S(t) = W(t)IMN/N_0 \quad (13)$$

and the amount of CO₂ dissolved in time t is:

$$m(t) = \int_0^t S(t) dt = \frac{M}{N_0} \int_0^t W(t)IN dt, \quad (14)$$

where M represents the mass of the CO₂ molecule ($M = 44$), N_0 is Avogadro constant ($N_0 = 6.02 \times 10^{23}$), $W(t)$ is the flip dissolution coefficient, I is the interface renewal ratio, and N is the number of CO₂ molecules adsorbed per unit gas–liquid interface area.

4.3 Analysis of parameters N , I , and $W(t)$

4.3.1 Parameter N

According to the kinetics of molecular adsorption, if n molecules collide on the unit surface in unit time and the average adsorption time is τ , the number of molecules

per unit surface area (N) can be calculated by the following formula (28):

$$N = n\tau = \frac{N_0 P}{\sqrt{2\pi MRT}} \tau, \quad (15)$$

where P (Pa) and T (K) are pressure and temperature, respectively, and R is constant ($R = 8.31 \text{ J}/(\text{mol K})$). τ is the time that molecule stays on the surface, in the simple case, for CO₂, NH₄, and so on, and the value of τ could be 10^{-7} (s). It can be seen from Eq. 15 that the number of molecules adsorbed on the gas-liquid interface per unit area is only related to pressure and temperature.

4.3.2 Parameter I

Parameter I is the interface renewal ratio and represents the polymer melt interface renewal rate under screw agitator. Parameter I depends on many factors, such as the structure and speed of the agitator, the viscosity of the polymer, and the mechanical properties of the motor. If the influence of polymer viscosity and motor power on interface renewal rate is ignored, $I = f(\text{Stru}, V_r)$, where Stru is the structural parameter of the agitator and V_r is the stirring speed parameter.

For the determined agitator, since its structure has been determined, the interface renewal rate is only a function of stirring speed, so the formula can be simplified as follows:

$$I = Kf(V_r), \quad (16)$$

where K is the stirring constant, determined by the structure of the agitator and can be obtained directly by calculation. It can be seen from the formula that the interface renewal rate is proportional to the stirring constant and the stirring speed. In the given agitator and speed, the interface renewal rate is also constant.

4.3.3 Parameter $W(t)$

Parameter $W(t)$ is the flip dissolution coefficient, representing the ratio of the number of newly dissolved carbon dioxide molecules to the number of buried carbon dioxide molecules in the polymer.

The flip dissolution coefficient ($W(t)$) is a function of time t , which ranges from 0 to 1. It is related to the temperature, pressure, and molecular properties of the system, such as the structure and the polarity of the molecules, as well as the concentration and distribution of the dissolved solute. At the beginning of dissolution, all the CO₂ buried in the

melt is dissolved into the melt, so $W(t = 0) = 1$. At the end of dissolution, the system reaches dissolution dynamic equilibrium, and the amount of CO₂ dissolved in the polymer is equal to the amount of CO₂ escaping from the polymer, so the dissolution increment is 0 and $W(t \geq t_e) = 0$, and t_e is the dissolution equilibrium time. Obviously, the dissolution coefficient ($W(t)$) decreases with the increase of time and CO₂ concentration in the polymer.

Because the relationship between the flip dissolution coefficient and its influencing factors is very complex, it is often shown as a complex nonlinear relationship, which is generally difficult to be measured directly by the experiment. Similar to the diffusion coefficient, the flip dissolution coefficient can also be obtained through the experimental data fitting or calculation optimization. In practical applications, to reveal a pattern, it is often possible to replace this pattern with some simple relationships.

4.4 Model calculation

In this section, we will verify the aforementioned mathematical model through a calculation example. The inner diameter of the reaction cell is 12 cm, and the CO₂ purity greater than 99.5%. The polymer is polystyrene with a density of 1,050 kg/m³, and the height of the polymer melt in the reaction cell is 3 cm. The experimental temperature and pressure were 453 K and 8.5 MPa, respectively. The dissolution equilibrium time in the experiment is 40 min, that is, $t_e = 40$ min.

First, we need to calculate the interface renewal ratio (I). The interface renewal ratio is related to the structure of the agitator, as shown in Figure 4. For the screw agitator, the interface renewal ratio can be defined as the ratio of the material transfer rate (Q) to the cross-section area (S). Therefore,

$$I = \frac{Q}{S}, \quad Q = UV_f, \quad (17)$$

Figure 4: The structure of the screw agitator.

Table 3: Parameter symbol and description

Symbol	Unit	Explain
M	Constant	The mass of the CO_2 molecule, $M = 44$
R	Constant	$R = 8.31 \text{ J}/(\text{mol K})$
N_0	Constant	Avogadro constant, $N_0 = 6.02 \times 10^{23}$
I	m^2/s	Interface renewal ratio represents the polymer melt interface renewal rate under agitators.
$W(t)$		Flip dissolution coefficient is a function of time t , representing the ratio of the number of newly dissolved carbon dioxide molecules to the number of buried carbon dioxide molecules in the polymer
P	MPa	Pressure
T	K	Temperature
t_e	min	The dissolution equilibrium time, obtained by the experiment
t_c/t_s	min	The time of the inflection point of the dissolution rate under conical/screw agitator

where Q is the material transfer rate, S is the cross-sectional area of the screw agitator, U is the area of the screw groove, and V_f is the feeding speed.

The material transfer rate depends on the geometry of the screw and the friction coefficient between the polymer and the barrel. Without considering the influence of friction coefficient, the relationship among screw groove volume (V), material transfer rate (Q), and screw geometry size can be obtained as follows (29,30):

$$U = \frac{\pi}{4}[D^2 - (D^2 - 2h)^2], \quad V_f = \frac{\pi D V_L \tan \alpha \tan \beta}{\tan \alpha + \tan \beta}, \quad (18)$$

where V_L is the rotating speed of the agitator. So

$$Q = \frac{\pi^2 D h (D - h) V_L \tan \alpha \tan \beta}{\tan \alpha + \tan \beta}. \quad (19)$$

$$I = \frac{Q}{S} = \frac{4\pi h (D - h) V_L \tan \alpha \tan \beta}{D(\tan \alpha + \tan \beta)}. \quad (20)$$

For the screw agitator of our experimental device, forward angle $\alpha = 2\pi/3$, helix angle $\beta = \pi/3$, $D = 80 \text{ mm}$, rotation speed $V_L = 2 \text{ r/s}$, and screw groove depth $h = 3 \text{ mm}$. Finally, the calculated interface renewal ratio $I = 15.45 \text{ ((mm)}^2/\text{s})$.

As shown in the aforementioned analysis, the flip dissolution coefficient ($W(t)$) is a function of time t , and which ranges from 0 to 1. At the beginning of dissolution, $W(t = 0) = 1$, and at the end of dissolution, $W(t \geq t_e) = 0$. Therefore, $W(t)$ can be set as follows:

$$W(t) = -t^2 + Bt + C, \quad (t \geq 0). \quad (21)$$

Substitute the initial conditions: $t = 0$, $W(t) = 1$, and $t = t_e$, $W(t) = 0$, and the following equation is obtained:

$$W(t) = \begin{cases} -t^2 - \frac{1 + (t_e)^2}{t_e} t + 1, & (0 \leq t < t_e) \\ 0, & (t_e \leq t), \end{cases} \quad (22)$$

where t_e is the dissolution equilibrium time. Combined with the aforementioned equations, the dissolution mass function ($m(t)$) under screw agitator is obtained ($T = 453 \text{ K}$, $P = 8.5 \text{ MPa}$) as follows:

$$\begin{aligned} m(t) &= \int_0^t S(t) dt = \frac{IMP10^{-7}}{\sqrt{2\pi MRT}} \int_0^t W(t) dt \\ &= \frac{IMP10^{-7}}{\sqrt{2\pi MRT}} \left(-\frac{t^3}{3} - \frac{1 + (t_e)^2}{2t_e} t^2 + t \right), \quad (23) \\ &\quad (0 \leq t \leq t_e). \end{aligned}$$

The parameters in Eq. 23 are presented in Table 3. The comparison between experimental data and numerical solution under screw agitator is shown in Figure 5.

As with the conical agitator, we can also obtain the expression of the solution rate function ($V_s(t)$) and the time of inflection point of velocity (t_s) for the screw agitator, as shown in Eqs. 24 and 25 and Figure 6.

Figure 5: Comparison between experimental data and numerical solution under screw agitator.

Figure 6: Dissolution velocity curves ($P = 8.5$ MPa, $T = 453$ K) under screw agitator and the time of the inflection point of the dissolution rate.

$$v_s(t) = \frac{dm(t)}{dt} = \frac{IMP10^{-7}}{\sqrt{2\pi MRT}} \left(-t^2 - \frac{1 + (t_e)^2}{t_e} t + 1 \right), \quad (24)$$

$$(0 \leq t < t_e)$$

$$t_s = \frac{(1 + (t_e)^2) \sqrt{2\pi MRT}}{2t_e IMP \times 10^{-7}} \quad (25)$$

As mentioned earlier, the main factors that affect the solubility are temperature and pressure. At the same temperature and pressure, the solubility is similar under different agitators and rotating speeds, but the dissolution rate is different. The aforementioned experiment shows that at the same temperature and pressure, although the mass of polymer melt under screw agitator is three times than that under the cone agitator, the time to reach dissolution equilibrium is basically the same. Obviously, the dissolution rate of carbon dioxide under the screw agitator is much higher than that under the conical agitator, and this is due to the longitudinal mixing effect of screw agitator; the low concentration polymer melt in the lower layer is brought to the high concentration environment in the upper layer, thus maintaining a large concentration difference and accelerating the dissolution of carbon dioxide.

5 Conclusion

Under the conical agitator, the dissolution process is still an adsorption–diffusion process. According to Fick's

second law and graphic method, solubility and diffusion coefficients at different temperatures and pressures can be obtained. The solubility would not change with the agitator, but the dissolution rate is affected. With the increase of temperature and pressure, the time of the inflection point of dissolution velocity will be brought forward continuously.

Under the screw agitator, the accuracy of solubility prediction for interface flipping processes depends largely on the interface renewal ratio (I) and flip dissolution coefficient ($W(t)$). The interface renewal ratio is directly related to the structure of the agitator and the rotation speed. The flip dissolution coefficient reflects the effect of material properties on the dissolution process. In this article, a nonlinear function is taken as an example, and the dissolution law obtained is basically consistent with the experimental process, which theoretically verifies the feasibility of the model. Since the flip solubility coefficient is a complex coefficient of change, which can be improved, the performance of the model will be greatly improved, which is the main direction of future research.

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