Fundamental Modeling and Experimental Investigation of Polymer Washing Process

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Abstract: After polymerization reaction, impurities such as adduct, solvent and catalyst are trapped inside the polymers. These impurities should be removed by a polymer washing process to improve the purity of the polymer products. Also, the optimization of the polymer washing process is essential to reduce the energy, resources and processing time. This work provides a theoretical basis for optimization of polymer washing process by proposing a fundamental model and experimental investigation method of the process. The model describes the impurity distribution inside the polymers, mole balance of impurities inside and outside of the polymers, and impurity diffusion rate at polymer surface. The experimental investigation with SPAEK (sulfonated poly(aryl ether ketone)) samples reports the impurity diffusion coefficient at polymer surface of the performed experiments. The computed $D$(the impurity diffusion coefficient at the polymer surface) shows different values with time as a lumped parameter, including the unmodelled effects for impurity diffusion. However, these values show the same trajectory with the introduction of a dimensionless number $Co$ for each operation. This means unmodelled impurity diffusion factors included in $D$ are only affected by $Co$. Finally, we validate the prediction performance of the model by comparing the predicted pH changes of validation experiment with the experimental data.

Keywords: Polymer washing process, Moving boundary of diffusion, Pseudo steady state, Sulfonated poly aryl ether ketone

1. INTRODUCTION

A polymerization is a chemical reaction in which molecules combine to form a larger polymer. On the completion of the polymerization, the formed polymer is solidified. In this process, a small amount of impurities, which may include adduct, solvent and catalyst components, are still trapped inside the polymers. Since these impurities have a significant influence on microstructural characteristic of polymer products, they should be removed by a washing process [1,2]. When a polymer washing process is operated at a large scale without any optimization, waste of energy, resources, and processing time will be considerable. Thus a detail theoretical model is essential to optimize such a process. Moreover, such a complex dynamics involving mass transfer in the polymer particulate is difficult to model using an empirical model structure fitted to operational data. However, theoretical research for the polymer washing process has not been reported yet to the best of the authors' knowledge. This work proposes a fundamental model and experimental investigations of a polymer washing process, which can be readily used for optimization of the process.

In polymer washing process, solidified polymers are washed with deionized water in batch several times. Prior to the washing process, impurities are assumed to be uniformly distributed inside the polymers. When washing begins, the impurities inside the polymers are dissolved in water and diffuse toward outside with the concentration gradient. As the washing process proceeds, the impurity concentration inside the polymer decreases and that of the outside increases. When impurity concentrations of the polymer inside and outside reach the equilibrium, the impurity concentrations stop changing. These processes are repeated until the pH of washing water reaching near 7.

This work introduces the concept of moving boundary of diffusion inside the polymers where impurities begin to diffuse toward outside to describe the impurity diffusion inside the polymers [3,4]. In addition, pseudo steady state approximation and Fick's law are employed to describe the impurity distribution inside the polymer and impurity diffusion rate at polymer surface, respectively. In experimental investigation, we perform the operation of polymer washing process with SPAEK sample, and estimate the diffusion coefficient of impurity at polymer surface using the experimental data. A dimensionless number $Co$, the ratio of impurity concentration outside the polymer to initial
impurity concentration inside the polymer, is introduced to model temporal change of the diffusion coefficient regardless of the initial concentration of the impurity inside the polymer. Finally, we validate the pH prediction performance of the model by comparing the simulation results with the experimental data. The simulation results are in agreement with the experimental results, and the proposed model and experimental investigation are expected to be useful for optimization of the polymer washing process.

2. MODELING OF POLYMER WASHING PROCESS

A conceptual model of polymer washing process is constructed as follows. The impurity concentration distributions inside the polymers are assumed to be uniform as the initial impurity concentration prior to washing, then the concentration distribution changes with impurity diffusion toward outside due to the concentration gradient as the washing progress. Finally the concentration distribution stops changing at the equilibrium state. After washing, the used water is removed from the batch and a new batch of polymer washing process starts with fresh water.

A concept of moving boundary of diffusion is introduced where the impurity concentration inside the boundary remains as the initial impurity concentration, and the impurities start diffusing at the boundary (see Fig. 1).

2.1 Pseudo steady state approximation of impurity distribution inside the polymer

As the washing process proceeds, the impurities diffuse in radial direction from the diffusion boundary. The radius of diffusion boundary is the same as the polymer radius before washing, and then decreases with the progress of washing. Since most of materials have small molecular diffusion coefficients in water [5], we use pseudo steady state approximation to describe the impurity distribution inside the polymer [6,7].

\[ W_{Mr}4\pi r^2 - W_{Mr}4\pi r^2|_{r+\Delta r} = 0 \]  

(1)

\[ W_{Mr} \] is described by the Fick’s law :

\[ W_{Mr} = -D_p \frac{dC_{Mr}}{dr} \]  

(2)

Table 1. Nomenclature

| Symbol | Description |
|--------|-------------|
| R | Radius of the polymer |
| R_b | Radius of the diffusion boundary |
| W_{Mr} | Radial flux of impurities |
| C_{Mr} | Impurity concentration according to radial distance from the center of polymers |
| C_{MR} | Impurity concentration at polymer surface |
| C_{M0} | Impurity concentration inside the diffusion boundary |
| D_p | Impurity diffusion coefficient inside the polymer |
| D | Impurity diffusion coefficient at polymer surface |
| D_r | Impurity diffusion coefficient at polymer surface in the validation experiment |
| M_{out} | Moles of impurities outside the polymers |
| \phi | Volume ratio of water inside the polymer to polymer |
| m | Mass of polymer pieces in the batch |
| n | Number of polymer pieces in the batch |
| V_{out} | Volume of water outside the polymers |
| V_p | Volume of polymers |
| V_{in} | Volume of water inside the polymers |

Fig. 1. Distribution of the impurity concentration inside the polymer

Boundary conditions are

\[ C_{Mr} = C_{MR} \text{ at } r = R \]  

(3)

\[ C_{Mr} = C_{M0} \text{ at } r = R_b \]  

(4)

Substituting (2) into (1) and integrating with the boundary conditions yields the impurity concentration distribution inside the polymers according to the radial distance from the center of polymer.

\[ C_{Mr} = \left( \frac{C_{M0} - C_{MR}}{MR} \right)^{\frac{1}{3}} + C_{MR} \frac{1}{R_b} - C_{M0} \frac{1}{R} \]  

(5)

2.2 Mole balance of impurities inside and outside of the polymers

A mole balance equation of impurities inside and outside of the polymers is derived to obtain a mathematical relationship between the diffusion boundary radius and the impurity concentration outside the polymers. The amount of impurities outside the polymers is the same as the change in the amount of impurities inside the polymers :

\[ M_{out} = 3\pi R^2 C_{M0} - \int_{0}^{R_b} 4\pi r^2 C_{M0} dr - \int_{R_b}^{R} 4\pi r^2 C_{Mr} dr \]  

(6)

Substituting (5) into (6) and expressing \( M_{out} \) as the product of the water volume and impurity concentration outside the polymers yields:

\[ V_{out} C_{MR} = \frac{2}{3} \pi (C_{M0} - C_{MR})(2R^3 - RR_b^2 - R^2 R_b)\phi \]  

(7)

Rearranging (7) by \( R \) and \( C_{MR_b} \) results in (8) and (9), respectively :

\[ R_b = \frac{R}{2} - \frac{f(C_{MR})}{2} \left( f(C_{MR}) = \sqrt{9R^2 - \frac{6V_{out}}{\pi n\phi R} \left( C_{MR} \frac{1}{C_{M0} - C_{MR}} \right)} \right) \]  

(8)

\[ C_{MR} = \frac{g(R_b)}{3V_{out} + g(R_b)C_{M0}} \]  

\[ g(R_b) = 2\pi n\phi (2R^3 - RR_b^2 - R^2 R_b)C_{M0} \]  

(9)
2.3 Diffusion rate of impurity at polymer surface

Impurity diffusion rate at polymer surface is described as the product of the surface area and the radial impurity flux with the Fick's law. The diffusion rate is the same as the increasing rate of the impurity amount outside the polymers:

$$4\pi n R^2 D \left( \frac{dC_M}{dr} \bigg|_{r=R} \right) = V_out \frac{dC_M}{dt}$$  (10)

Substituting (5) and (8) into (10) yields

$$D = \frac{V_out}{4\pi n R(C_M0 - C_{MR})} \left\{ \frac{3R - f(C_{MR})}{-R + f(C_{MR})} \right\} \frac{dC_{MR}}{dt}$$  (11)

$D$ is the impurity diffusion coefficient at polymer surface, which is a lumped parameter including unmodelled impurity diffusion factors not included in the proposed model such as electrochemical interaction between the impurity components and the polymer [8,9].

3. EXPERIMENTAL INVESTIGATION

We performed polymer washing experiments with SPAEK samples synthesized by condensation reaction and solidified in ethanol. The impurity components are $K_2CO_3$ (potassium carbonate), DMSO (dimethyl sulfoxide), and KF (potassium fluoride). 3g of the polymer samples were washed with 40ml of 50°C deionized water 8 times during 30 minutes for each operation. The experimental condition is described in Table 2. Since most of the impurity components were $K_2CO_3$, we considered the dissociation constant of $K_2CO_3$ as that of impurities.

The pH data of the batch was measured at intervals of 10 seconds. Using the pH data and proposed model, $D$ values for each operation were computed, and a consistent trajectory of $D$ values was obtained with the dimensionless number $Co$.

3.1 Impurity diffusion coefficient at polymer surface

We estimated the relationship between $[OH^-]$ and $C_{MR}$ by a straight line approximation in log scale using the computed impurity concentration and pH data at the equilibrium state for each operation as shown in Fig. 2 and Eq. (12).

$$C_{MR} = 10^{9.41}[OH^-]^{4.03}$$  (12)

$C_{MR}$ values with time for each operation were computed from pH data using (12). Then, $D$ values with time for each operation were computed by substituting the obtained $C_{MR}$ values into (11). Data of the 4-8th operations showing the regular trend are only used in this process. The computed $D$ values for each operation are illustrated in Fig. 3.

Whereas the computed $D$ show quite large changes in time as a lumped parameter, $D$ values for each operation show a similar trend. Thus, we hypothesize this similar trend is related to the ratio of $C_{MR}$ to $C_{M0}$, and introduce the following dimensionless number:

$$Co = \frac{C_{MR}}{C_{M0}}$$  (13)

Describing (11) with $Co$ results in

Table 2. Experimental condition

| Variable | Value | Unit |
|----------|-------|------|
| $R$      | 0.7   | cm   |
| $V_p$    | 7     | ml   |
| $V_{out}$| 40    | ml   |
| $V_{in}$ | 4.2   | ml   |
| $\phi$   | 0.60  |      |
| $n$      | 5     |      |
| $m$      | 3     | g    |
Fig. 4. Impurity diffusion coefficient according to Co for each experiment

\[ D = \frac{V_{\text{out}}}{4\pi n R (1 - Co)} \left( \frac{3R - F(Co)}{R + F(Co)} \right) \frac{dCo}{dt} \]

\[ F(Co) = \sqrt{9R^2 - \frac{6V_{\text{out}}}{\pi n \phi R} \left( \frac{Co}{1 - Co} \right)} \]  

(14)

Fig. 4 shows the D values computed from (14). The computed D values according to Co of each operation show almost the same trajectory. This means other impurity diffusion factors included in D are only affected by Co, even if the initial impurity concentrations inside the polymers are different for each operation. We approximated the relationship between D and Co as a straight line in log scale. D is described as

\[ D = 10^{-2.25} Co^{1.67} \]  

(15)

3.2 Simulation for radius of the diffusion boundary and impurity concentration distribution inside the polymers

We derived an ODE for \( R_b \) by substituting (9), (13) and (15) into (14):

\[ \frac{dR_b}{dt} = 10^{-2.25} \frac{4\pi n R b}{V_{\text{out}}(R - R_b)} \left\{ \frac{g(R_b)^{1.67}}{g(R_b)} \right\} \left\{ \frac{3V_{\text{out}} + g(R_b)^{0.67}}{3V_{\text{out}} + g(R_b)^{0.67}} \right\} \]  

(16)

(16) is numerically integrated to simulate \( R_b \) change of the 5th operation. The impurity concentration distributions inside the polymers at 1800 seconds is also simulated using (5) (See Fig. 5).

4. MODEL VALIDATION WITH A DIFFERENT EXPERIMENTAL CONDITION

We performed validation experiments using the same SPAEK sample in a different experimental condition. The experimental condition is described in Table 3. Then, we estimated D of the validation experiment, numerically simulated the pH changes of the validation experiment, and compared the simulation results with the experimental data.

4.1 Estimation of impurity diffusion coefficient at polymer surface

We divide (14) into two parts.

\[ D = \left[ \frac{V_{\text{out}}}{4\pi n R (1 - Co)} \left\{ \frac{3R - F(Co)}{R + F(Co)} \right\} \right] \left[ \frac{dCo}{dt} \right] \]  

(17)
Table 3. Experimental condition in validation experiment

| Variable | Value | Unit |
|----------|-------|------|
| $R$      | 0.75 cm |
| $V_p$    | 7 ml   |
| $V_{in}$ | 50 ml  |
| $V_{in}$ | 4.33 ml |
| $\phi$   | 0.59   |
| $n$      | 4      |
| $m$      | 3 g    |

The experimental conditions are included in part A not in part B. Hence, it is clear that the experimental condition change affect directly part A and indirectly part B. Thus, the influence of the experimental condition change on part B is expected to be negligible compared to that on part A. With this, $D$ values of the validation experiment is estimated by substituting the changed part A value into

$$D_t = 10^{-1.96} Co^{1.67}$$

4.2 Numerical simulation for pH changes and model validation

The pH changes of validation experiment is simulated using (11), (12) and (18). The simulation results are compared with the experimental data to verify the prediction performance of the proposed model and the results of the experimental investigation (see Fig. 6).

There exist some discrepancies between the simulation and experimental results in the 1st operation. This error is caused by the dissociation of small amount of DMSO component in the impurity triggered by the high basicity in the 1st operation due to the high concentration of $K_2CO_3$ [10,11]. The simulation results of 2-8th operations are in agreement with the experimental data. Consequently, the proposed model can be used to predict pH values, thereby the concentration of the impurities, of the general polymer washing process.

5. CONCLUSION

We proposed a fundamental model for the polymer washing process introducing moving boundary of diffusion, pseudo steady state, and Fick’s law. Though the predicted results of the validation experiment are not in agreement with the experimental results of the 1st operations, they agree fairly well in the 2-8th operations. This means the proposed model is suitable for predicting the impurity concentrations in the polymer washing process. We can also see the computed $D$ values show the same trajectory according to the $Co$ in Fig. 4. This means the unmodelled effects for impurity diffusion included in the diffusion coefficient are mainly affected by $Co$ and the introduction of $Co$ is suitable for $D$ investigation.

This work has significance for providing a valid model and experimental investigation methodology for polymer washing processes. Also, important theoretical basis for optimization and automation of polymer washing process such as pH and impurity concentration changes can be predicted. In addition, the model and experimental investigation procedure can be used in various kinds of polymer washing processes.

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