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Research Article

Predicting the Swelling Behavior of Acrylic Superabsorbent Polymers Used in Diapers

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Acrylic polymer is a superabsorbent for water and widely used in diapers, in which its swelling behavior can be significantly affected by several factors, i.e., the time, temperature, pH, and salt concentration, and thus the product performance in the applications. In this work, the water absorption behavior of acrylic superabsorbent polymers by each of these individual factors was investigated. The results showed that the water absorbency increases with the pH in the range of 2 to ~7 and decreases when the pH continues to increase. However, it decreases with the increases in NaCl concentration in the solution. Moreover, more water can be absorbed by the acrylic polymers at the higher temperature. Based on a previously developed kinetic swelling model and the information from the above investigations, a semiempirical model for predicting the swelling behavior of superabsorbent polymers (SAPs) under different conditions has been developed. Data showed that the model can predict (with a relative error of <4.5%) the amount of water absorbed by acrylic SAPs under different swelling conditions. The model would be very helpful to the practical application in both product design and its performance evaluation.

1. Introduction

Acrylic superabsorbent polymers (SAPs) are materials with hydrophilic networks that retain huge amounts of water or aqueous solutions, up to 100,000% their own weigh. Fields benefiting from SAPs include health, agriculture, and pharmaceuticals [1, 2]. Modern diapers are typically composed of fluff pulp, acrylic SAP materials, and other materials making up the nonwoven sheets [3, 4]. The function of SAPs mainly keeps moisture and liquids away from the body's skin to maintain it dry and healthy [5, 6]. Because of the variation of urine's salt ions and pH and temperature in the micro environment (between the skin and diaper), it affects the actual water absorption behavior of acrylic SAPs and thus the product's performance in applications [1, 7–9].

Therefore, the comprehensive information of these variables on the swelling behavior of acrylic SAPs would be very helpful to the polymer synthesis/control, product design, and the performance evaluation in the diaper-related applications. No doubt, there is a need to have a model that can accurately predict the swelling behavior of SAP materials.

The mechanism of swelling behavior of hydrophilic polymers in ionic and nonionic networks was initially studied by Flory [10, 11], who found that water absorbency of SAPs was inversely dependent on the ionic strength of the solution being absorbed. Further study showed that the swelling behavior of SAPs is also dependent on the pH of the solution [10, 12]. For example, the swelling capacity for a polyacrylamide–sodium allylsulfonate–sodium acrylate system increased from ~70 to $450 \, \text{g} \cdot \text{g}^{-1}$ when the pH was

increased from 2 to 6; however, it decreased to ~180 g·g⁻¹ as the pH was increased further to 13 [12, 13]. The effect of temperature on the swelling capacity of SAPs is also significant, with higher temperatures generally leading to increased swelling capacity [14].

A number of studies have also reported that the kinetics of the swelling of polymers agree with Fick's equation [15–18]. However, when gel ionization is prominent in the SAPs, a non-Fickian behavior appears [16]. In the common practice, a first-order kinetic equation is used to describe the initial and sometimes also for the middle portion of the swelling process [18]. However, for truly extensive swelling, the discrepancy from the first-order modelling is too large to be ignored [17]. Therefore, a second-order swelling kinetics model has been proposed for the most extensive swelling SAPs [18]. Unfortunately, the effects of the external parameters on the swelling of SAPs were not considered in these kinetic models, which greatly limit their use in comprehensively evaluating performance and in predicting swelling behavior in the many practical applications.

In this work, we present a semiempirical model that can be used to describe the kinetic swelling behavior of acrylic SAPs, in which the pH, temperature, and salinity of external solution are explicitly taken into consideration. The model can be used for optimizing synthesis research, product design, process control, and routine quality evaluation of products.

2. Materials and Methods

2.1. Chemicals and Materials. All chemicals used in the experiment were analytical grade purchased from Sigma-Aldrich, including NaCl (purity > 99.9%), NaOH (purity > 99.8%), and HCl (purity > 36.0%). The SAPs were the type of acrylic polymers purchased from a commercial source. These acrylic polymers are synthesized from homo- or copolymerization reaction with partially neutralized acrylic acid or by grafting acrylic acid onto starch and the chemical main-chain structures of the material can be written as $[CH_2 - CH^{COONa}]_m$ $[CH_2 - CH^{COOH}]_n$. Table 1 lists the detailed information of these acrylic SAPs.

The pH of each individual solution was adjusted with a NaOH (pH = 13.0) or HCl (pH = 2.0) solution. The concentration of salt (from 0 to 2.0%) in the saline solution was obtained by dissolving appropriate amounts of NaCl in deionized water. The temperature (25~80°C) of the solution was controlled in a water bath.

2.2. Swelling Measurement. The swelling capacity of SAP was measured by a conventional "tea bag" method, using acrylic/polyester gauze bags with fine meshes [1, 19]. The SAP sample was placed inside a bag which was then dipped into a test solution for a specified time. Then, the excess solution was removed from the bag by suspending the bag in air until no additional liquid dripped off. The swelling capacity of the SAP (W_t, g·g⁻¹) was calculated from

$$W_t = \frac{W_{s,t} - W_0 - W_p}{W_p}, \tag{1}$$

TABLE 1: The information of acrylic SAPs.

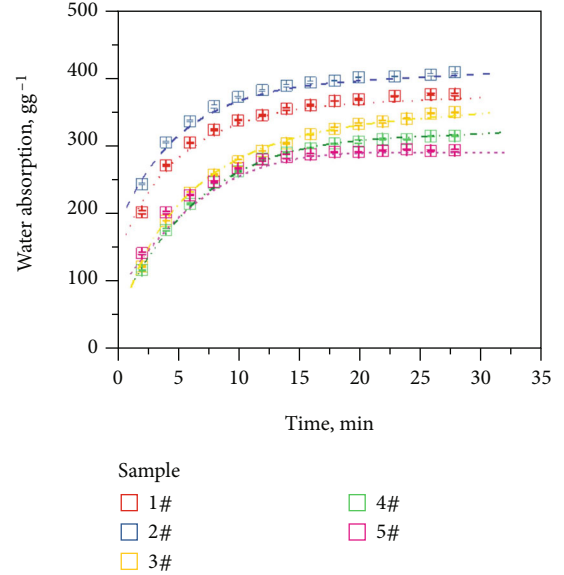| Sample ID	Residual acrylic acid (mg/kg)	pH	Particle size (μm)	Density (g/cm^3)
1	521	6.55	150~250	0.65
2	436	6.28	150~180	0.72
3	50	7.01	106~150	0.58
4	216	6.85	106~120	0.75
5	362	7.69	106~120	0.87

FIGURE 1: Time-dependent profile of acrylic SAP's swelling.

where $W_{s,t}$ is the mass of the tea bag (g) with a sample having swelled for time t, W_0 is the mass of the blank tea bag (g), and W_p is the mass of the SAP sample (g).

3. Results

3.1. Kinetic Swelling Behavior of Acrylic SAPs. In previous studies, three models have been developed to describe the kinetics of swelling of acrylic SAPs; i.e., a second-order equation [16, 18–20], a power function of Fickian diffusion and Case II transport [16, 21, 22], and a Voigt-based viscoelastic model [23]. They are expressed as

$$\frac{t}{W_t} = A + Bt, \tag{2}$$

or

$$W_t = \frac{t}{A + Bt}, \tag{3}$$

$$\frac{W_t}{W_\infty} = kt^n, \tag{4}$$

$$W_t = W_\infty\left(1 - e^{-t/r}\right), \tag{5}$$

Table 2: Results of the model fitting.

Model	Sample ID	$A/k/W_\infty$	$B/n/r$	R^2
Second-order equation	1	0.2816	0.00245	0.9998
	2	0.2127	0.00230	0.9997
	3	0.6877	0.00243	0.9997
	4	0.6429	0.00272	0.9980
	5	0.4131	0.00309	0.9990
Power function	1	0.1301	0.2792	0.8996
	2	0.1817	0.2340	0.9068
	3	0.0354	0.4465	0.9388
	4	0.0119	0.7926	0.9805
	5	0.0861	0.3373	0.8824
Voigt-based viscoelastic model	1	367.3	173.7	0.9683
	2	396.6	145.6	0.9462
	3	343.2	163.9	0.9879
	4	314.2	300.9	0.8924
	5	292.3	212.1	0.9855

where W_t is the mass of absorbed liquid at time t (g/g). W_∞ is the mass of absorbed liquid at equilibrium (i.e., the maximum water-holding capacity, g/g) and t is the swelling time (s); A is a rate parameter expressed in units of the inverse of the initial swelling rate (g·s/g); and B is a rate parameter expressed in unit of the reciprocal of maximum swelling (g/g) [20]. k and n are rate constants of swelling; r is the rate parameter (s) and is the time required to reach 0.63 of the equilibrium (maximum) swelling [23].

Because the synthetic process of acrylic polymers could be different (e.g., neutralization and temperature), there are some differences on the swelling behavior between these SAPs [1]. Figure 1 shows the time-dependent swelling behaviors of five different SAPs conducted at room temperature, in which the initial swelling is very rapid and approaches equilibrium in ~15 min. Table 2 shows that each of the models fits the observations reasonably well with substituting data shown in Figure 1, although the second-order equation model provides the best description ($R^2 > 0.99$) for the swelling of SAPs.

Therefore, we used the second-order equation model as the basis for developing a model that integrates the other variables; i.e., temperature, pH, and salt concentration.

3.2. Effect of pH on the Acrylic SAPs' Swelling. Figure 2 shows the effect of pH on the swelling of acrylic SAPs over time. The absorbency increases with the pH in the range of 2 to ~7 and decreases when the pH continues to increase, at a given swelling time. This phenomenon could be qualitatively explained from the viewpoint of hydration of ion. The number of anion on the chain of the polymer becomes small, which made the electrostatic distraction force and the elastic force weaker. Thus, the network of polymer shrank and the absorbency decreased [13]. The relationship between the water absorbency and pH can be mathematically described by
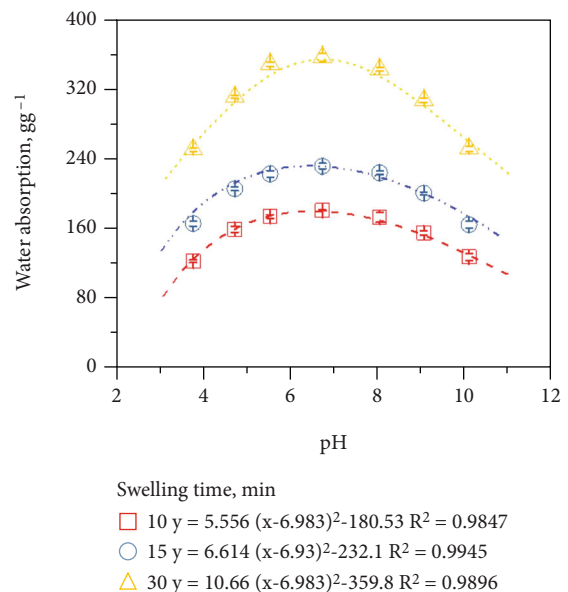

Swelling time, min
☐ 10 $y = 5.556\ (x-6.983)^2 - 180.53$ $R^2 = 0.9847$
○ 15 $y = 6.614\ (x-6.93)^2 - 232.1$ $R^2 = 0.9945$
△ 30 $y = 10.66\ (x-6.983)^2 - 359.8$ $R^2 = 0.9896$

Figure 2: Effect of pH on the acrylic SAPs' swelling (sample 1#).

$$W_t = a_1 - a_2(a_3 - pH)^2, \tag{6}$$

where a_1, a_2, and a_3 are coefficients.

3.3. Effect of Salinity on the Acrylic SAPs' Swelling. Figure 3 shows the effect of salinity on the swelling of acrylic SAPs at different swelling times. In short, the liquid absorbency of acrylic SAPs decreases with the increases in NaCl concentration in the solution. It is because the expansion of the acrylic SAP network decreases due to the repulsive counter ion (carboxylate group) on the polymeric chain, in which the osmotic pressure difference between the SAP network
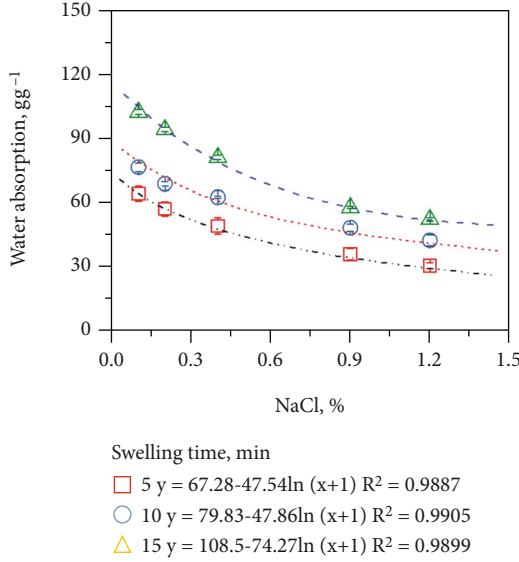
FIGURE 3: Effect of salinity on the acrylic SAPs' swelling (sample 5#).

Swelling time, min
☐ 5 y = 67.28-47.54ln (x+1) R² = 0.9887
○ 10 y = 79.83-47.86ln (x+1) R² = 0.9905
△ 15 y = 108.5-74.27ln (x+1) R² = 0.9899

and the external solution decreases with the increase in the ionic strength of the salt solution [2]. With a linear fitting, the relationship can be well described by

$$W_t = b_1 - b_2 \ln (C + 1), \tag{7}$$

where b_1 and b_2 are coefficients (g·g^{-1}) and C is the concentration of NaCl (wt %) in the solution.

3.4. Effect of Temperature on the Acrylic SAPs' Swelling.

It is well known that the water absorption of acrylic SAPs increases with the temperature increasing, since higher temperature can cause more molecular thermal motion dilating the internal network of SAPs [6]. In Figure 4, it shows the temperature-dependent profiles of acrylic SAPs' water absorption at different swelling times (i.e., 5, 8, 12, and 20 min). It can be seen that more water can be absorbed by the polymers for a solution with the higher temperature.

It can be seen from Figure 4 that the effect of temperature on the swelling of SAPs is well expressed by a linear relationship between the mass absorbed by the SAPs and the reciprocal of the temperature (K^{-1}); i.e.,

$$W_t = c_1 - \frac{c_2}{T}, \tag{8}$$

where c_1 and c_2 are constants.

3.5. Establishment of the Integrated Swelling Model

3.5.1. The Integrated Swelling Model.

Based on the above relationships between the liquid absorption, swelling time, pH, salinity, and temperature, i.e., Equations (3), (6), (7), and (8), a semiempirical model for calculating the swelling
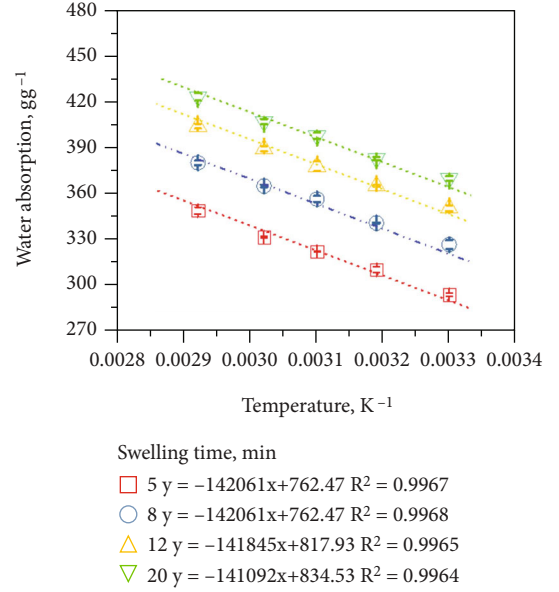

FIGURE 4: Effect of temperature on the acrylic SAPs' swelling (sample 2#).

Swelling time, min
☐ 5 y = −142061x+762.47 R² = 0.9967
○ 8 y = −142061x+762.47 R² = 0.9968
△ 12 y = −141845x+817.93 R² = 0.9965
▽ 20 y = −141092x+834.53 R² = 0.9964

TABLE 3: Optimal fitting values of the coefficients in Equation (10).

Coefficient	k_1	k_2	k_3	k_4	k_5	k_6
Value	110	0.218	3.94×10^{-4}	7.94	1.35	0.156
Error*	0.2	3.2×10^{-3}	1.51×10^{-6}	0.06	0.003	3.2×10^{-4}

*The standard deviation is obtained at a 95% confidence level.
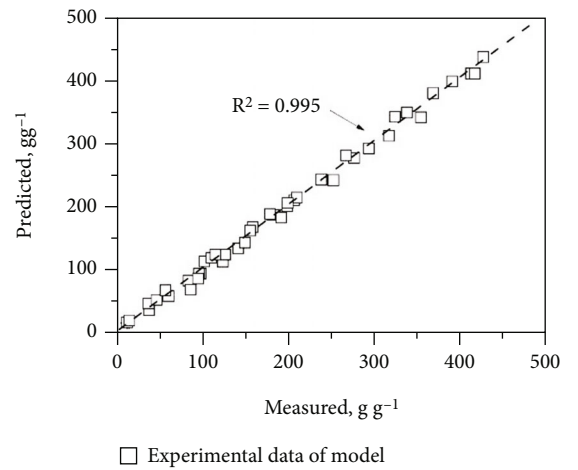

☐ Experimental data of model

FIGURE 5: Prediction model for the swelling of acrylic SAPs.

capacity can be simply written by multiplying the right side of these equations together, i.e.,

$$W_t = \left(\frac{t}{A + Bt}\right) \left[a_1 - a_2(a_3 - pH)^2\right] \left[b_1 - b_2 \ln (C + 1)\right] \left(c_1 - \frac{c_2}{T}\right). \tag{9}$$

TABLE 4: Validation of the model.

| Sample ID	Time (min)	Temp. (°C)	pH	NaCl (%)	Water absorption (g/g) Measured	Predicted	Relative difference (%)
4#	15	25	3.2	0	293	284	3.17
4#	15	25	4.5	0	305	297	2.70
4#	15	25	5.6	0	298	305	-2.30
4#	15	25	7.5	0	325	311	4.51
4#	20	25	8.9	0	318	324	-1.86
4#	15	25	9.2	0	300	309	-2.92
3#	15	25	7.5	0.1	265	271	-2.22
3#	30	25	7.5	0.1	285	297	-4.05
2#	15	25	7.5	0.6	118	113	4.43
2#	10	25	7.5	0.9	37.8	38.3	-1.31
1#	15	25	7.5	0.9	42.3	41.6	1.69
1#	20	25	7.5	0.9	44.6	43.5	2.53
1#	20	25	7.9	0.1	283	284	-0.35
3#	15	30	7.9	0	319	312	2.24
5#	5	40	7.5	0	241	231	4.34
5#	10	40	7.5	0	275	286	-3.85
5#	15	50	7.5	0	305	311	-1.93

(a)

(b)
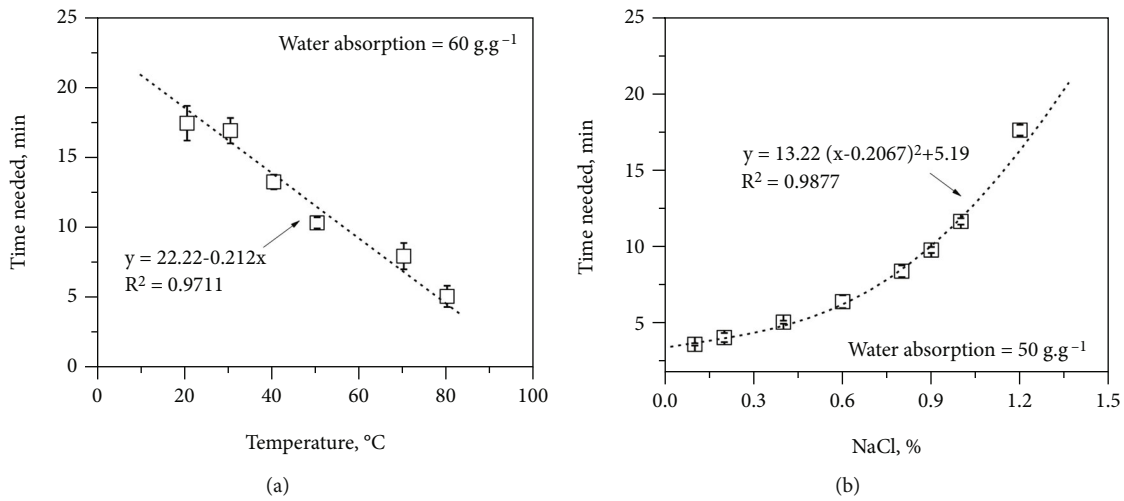
FIGURE 6: Effect of (a) temperature and (b) NaCl on the swelling time needed at the given conditions.

Making a rearrangement, we get

$$W_t = \frac{k_1 t}{1 + k_2 t} \left[1 - k_3 (k_4 - pH)^2\right]\left[1 - k_5 \ln{(C+1)}\right]\left(1 - \frac{k_6}{T}\right),$$

(10)

where the coefficients are $k_1 = a_1 b_1 c_1 / A$, $k_2 = B/A$, $k_3 = a_2/a_1$, $k_4 = a_3$, $k_5 = b_2/b_1$, and $k_6 = c_2/c_1$; k_1 and k_2 are swelling time correlation of coefficients; k_3 and k_4 are pH correlation of coefficients; k_5 is salinity correlation of coefficient; k_6 is temperature correlation of coefficient.

3.5.2. Determination of the Coefficients in the Model. In order to obtain values for the coefficients k_1, k_2, k_3, k_4, k_5, and k_6 in

Equation (10), the experimental data shown in Figures 1–4 were used in a multivariable least-squares fitting. Table 3 shows the values of these coefficients and their errors at the optimal fitting. Figure 5 shows that there is an excellent correlation between the liquid absorption measured and the absorption predicted by the model (Equation (10)) using the values of the coefficients listed in Table 3.

3.5.3. Validation of the Model. To verify the model, a set of experimental data (not included in the above model fitting) was used to calculate the water absorption. Table 4 lists the values from both the experimental measurements and the model calculations. The results show that the values are in good agreement with maximum relative differences (RD)

of less than 4.5%. This indicates that the new model can be used with confidence for predicting the aqueous absorption by SAPs under various conditions.

3.6. Application. The rate of liquid absorption is an important property of SAPs in many applications. For example, faster absorption of disposable diapers reduces the time that the skin is in contact with urine [1, 24]. In general, the time to achieve a given amount of liquid absorption (i.e., swelling time) is used as a measure of performance of SAPs in different application conditions.

Figures 6(a) and 6(b) show the effect of the temperature and NaCl content on the swelling time needed for water absorption of SAPs, i.e., at 60 and 50 g·g^{-1}, respectively. These results show that the swelling time is inversely proportional to the temperature, more than linearly proportional to NaCl content (particularly at concentrations above 0.9%).

4. Conclusions

In this study, we conducted an investigation on the water absorption behavior of acrylic SAPs by the factors that are crucial to the diaper applications, such as pH and salinity. The results showed that the water absorbency increases with the pH in the range of 2 to ~7 and decreases when the pH continues to increase; it decreases with the increases in NaCl concentration in the solution; and more water can be absorbed by the acrylic polymers at the higher temperature. Based on the information and a previously developed kinetic swelling model, a semiempirical model which can accurately predict (RD < 4.5%) the swelling behavior of SAPs under different conditions was developed. Since the model takes into account the swelling time, temperature, NaCl content, and pH of the solutions, it can provide a useful guidance in both product design and the performance check in the diaper-related applications.

Data Availability

All data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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