Egypt. J. Chem. **Vol. 64,** No. 10 pp. 5999 - 6005 (2021)

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

Swelling Kinetics Investigation of Polymer Hydrogel Composed of Chitosan-g-(AA-AM)

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Abstract

Swelling is one of the distinct properties and a significant parameter in the characterization of the crosslinked hydrogels. Swelling investigation at different temperatures was conducted for the produced hydrogel of chitosan grafted acrylamide/acrylic acid. Peleg's model is a two parameters model, which can be used to describe the absorption of water or swelling. The data show that the swelling degree increases with temperature until it reaches 60°C, after which it decreases as the temperature rises higher. At RT, 30, 40, 60, and 80 °C, the swelling degree values of 1.4, 1.5,1.4, 2.3 and 0.7 g water/g dry hydrogel were observed after 8 hours. The applied models provided a good agreement with the experimental data with high values of the coefficient of determination (R^2). The observed F values and the standard error indicate the validity of the proposed model to describe the swelling of hydrogel at different temperatures. The swelling rate and swelling degree can be expressed using a 4^{th} degree polynomial. It was concluded that the exponential association equation model represents swelling characteristics better than the others.

Key words: Hydrogel, Swelling, Kinetics, Chitosan, Modeling.

1. Introduction

Biopolymers have received attention due to environmental issues such as reuse and / or minimization of organic waste, and conservation of natural resources [1-3]. Extensive research has been done on biodegradable polymeric materials, mainly because they are, for the vast majority, from renewable sources. Some of them are widely available in nature and can be obtained at a low price. This type of polymer is characterized by properties such as controlled reaction, low toxicity, biocompatibility, biodegradability, and film genic properties [4, 5].

Hydrogels are 3D mesh structures that can absorb large quantities of aqueous fluids in relatively short periods of time without dissolving [6]. Due to their high water absorption and flexible behaviour, hydrogels can be used for biomedical and pharmaceutical applications such as tissue fillings and cartilage regeneration, drug carriers and wound healing and lenses. Smooth adhesives [7, 8]. The development of hydrogels is a rapidly developing field of research and a variety of synthetic and naturally derived materials have been studied and reported in the literature to manufacture hydrogels with well-defined structure and well-controlled properties [9, 10].

As one of the most important polysaccharides, chitosan (CS) has generated a great deal of interest for its desirable properties and wide-ranging applications. In the use of CS materials, hydrogel is a major and vital branch. CS has the ability to coordinate with many metal ions through a demineralization mechanism. While most researchers have focused on applications of complexes between CS and metal ions, the complexes can also influence the gelation process and structure of CS hydrogel. In the present work, this effect has been studied with different metal ions, revealing two different types of mechanisms. Strong affinity between CS and metal ions leads to a structural transition from orientation to multiple layers, while weak affinity leads to a composite gel with inorganic molecules in situ. The study gave a better understanding of the generation mechanism and whether it provided strategies for modifying hydrogel morphology, which benefited from the design of new CS-based materials with a

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Receive Date: 01 August 2021, Revise Date: 31 August 2021, Accept Date: 07 September 2021
DOI: 10.21608/EJCHEM.2021.88530.4260

hierarchical structure and facilitated the use of polysaccharides resources [11,12].

Food industries, nutrition, agriculture, aquaculture, pharmacy, medicine and biomedicine, dentistry, ophthalmology, aesthetics, hygiene, personal care, bio-imaging and veterinary medicine, textile and fibre industries, papermaking, chemistry, catalysis, chromatography, beverage industry, photography, wastewater treatment, sludge treatment. The original characteristics of chitosan are improved by grafting pure chitosan. Chitosan-embedded copolymers are extremely useful and are utilised in a variety of applications [16].

Special attention is paid to the relationships between the formation conditions of hydrogels and their properties such as swelling behavior, elastic modulus, and spatial inhomogeneity [17]. Evaluation of parameters related to swelling motility is important for hydrogel characterization during swelling [18]. The values of the kinetic parameters of the swelling are directly affected by the different chitosan and crossover concentrations [19].

The swelling behavior (swelling or de-swelling) of hydrogels (gels) and polymers can be described using many different models. Understanding these models and the situations in which they may be applied is important regarding the use of these materials in sensors that use material swelling to detect some analyses [20,21].

The aim of this research was to prepare grafted chitosan hydrogel with (acrylamide-acrylic acid), and then study its swelling kinetics after investigation of a suitable mathematical model which may be used to describe it.

2. Materials and Methods

2.1 Materials

Chitosan (Ch) purity more than 90% with medium molecular weight (Sigma Aldrich, Germany). Acrylamide (Am) with molecular weight 71.08 (Qualikems Co., India), acrylic acid (AA) with molecular weight 72.06 g/gmol (Research Lab), Potassium persulfate (KPS) (Merck, Germany) was used as a chemical initiator, Methylene bis-acrylamide (MBA) (Fluka, Germany) was used as a crosslinking agent. tetramethyl ethylenediamine (TMEDA) were supplied by Merck (Schuchardt, analytical grade). sodium hydroxide pellets (Laboratory chemicals, Modern Lab., Egypt). Acetic acid, acetone and ethanol (ADWIC, El Nasr Pharmaceutical Chemicals Co.), All experiments were performed using distilled water (DW).

2.2 Methodology

2.2.1 *Crystallization of Acrylamide*

Crystallization was applied for purifying acrylamide monomer from organic impurities in which acrylamide was dissolved in excess amount of cold acetone then, the solution was cooled to 10^{o}C till crystals were obtained followed by filtration using a vacuum pump and the acrylamide crystals were stored over anhydrous calcium chloride in a desiccator.

2.2.2 *Chitosan solution preparation*

1 gm of chitosan was dissolved in 70 ml acidified DW (pH 3.8) and stirred for five hours at room temperature then, stored for 24 hours, before use, to ensure complete solubility of chitosan.

2.2.3 *Synthesis of acrylamide- acrylic acid grafted chitosan Hydrogel*

Synthesis of acrylamide- acrylic acid grafted chitosan. 2 g of Am monomer and 2 g AA, 210 ml chitosan solution, 0.2 g of MBA was added. 0.6 APS was added from and 2 mL TMEDA was added. The prepared solution was poured into a three necked round flask containing 5 gm chitosan solutions and held for the gelling process for 60 minutes at 60 ^{o}C under nitrogen medium.

2.2.4 Post treatment

The grafted hydrogels were adjusted to pH 8 using 1 N NaOH then, a solution of 70% ethanol was added and stirred for 15 minutes to remove the formed homo-polymers. Finally, the product was filtered, washed twice with fresh ethanol and dried at 70°C till constant weight was achieved**.**

2.2.5 Measurement of temperature effect on swelling degree

Swelling is one of the important parameters in the characterization of the crosslinked hydrogels. Swelling tests at the temperatures of 25, 40, 60 and 80 °C were conducted using the hydrogel of chitosan grafted acrylamide (Am)/ acrylic acid (AA). One gram of hydrogels on the dry basis was weighed and put inside the beaker with the 100 mL distilled water inside for swelling. Temperatures were controlled using water bath and heater with temperature controller unit. After taking the surface moisture using a strainer at predetermined time intervals, the weights of the hydrogels were weighted. The swelling kinetics were then studied depending on the weights.

2.3 Characterization

The prepared hydrogel has been characterized using Fourier Transform Infrared

Spectroscopy (FTIR) FT/IR-6100 type A Jasco Japan TGS detector with the absorbance technique ranging from 400 to 4000 cm-1 with scanning speed of 2mm/sec.

2.4 Model Equations

2.4.1 Swelling Behavior of the Produced Hydrogel

The dry hydrogel was soaked in distilled water (DW) for periods up to 8 hours at different temperature. The swelling behaviour can be described using the amount of water absorbed during swelling of water by hydrogels.

a. Swelling Degree:

The equations used to build the swelling model are presented below. The swelling degree can be calculated in (gwater/gdry hydrogel) using the following equation [22,23].

$$S = \frac{w_s - w_d}{w_d} \quad (1)$$

Where, w_s and w_d are the weights of the swollen and dry samples, respectively.

b. Swelling Rate:

The swelling rate defined as the change of the hydrogel swelling degree as a function of time can be calculated using the following Equation (2) [23].

$$S_R = \frac{S_{t+\Delta t} + S_t}{\Delta t} \quad (2)$$

Where,

S_t: The swelling degree at time t calculated in g water/g dry hydrogel

$S_{t+\Delta t}$: The swelling degree at time t plus Δt calculated in g water/g dry hydrogel

c. Swelling Kinetics:

Peleg's model is a two parameters model, which can be used to describe the absorption of water or swelling. The model can be used to study the welling process between room temperature and 100°C [23,24]. The kinetic of water absorption by hydrogel during welling can be expressed by the following equation (Peleg's model) [23]:

$$S = S_o + \frac{t}{k_1 + k_2 t} \quad (3)$$

Where,

S_0: The swelling degree at time t=0 calculated in g water/g dry hydrogel

$k_1 and\ k_2$ are the reaction rate kinetic constants for the model expressed by Equation (3), in g dry hydrogel. min/g water, and g dry hydrogel/g water.

3. Results and Discussion

3.1 FTIR

The free radical polymerization of AA and AM in the presence of chitosan results in a hydrogel in which chitosan chains become grafted with the copolymer [25]. The FTIR spectra of Ch, Am, AA, (Ch-grafted (AA- co-Am)) are shown in Figure (1).

The IR spectrum of PAA exhibits the characteristic absorption band at 1728 cm^{-1} due to the C=O stretching vibration of the carboxylic groups. The intense band at 1670 cm^{-1} in the spectrum of PAM corresponds to the C = O stretching vibration (Amide I). The main absorption bands of the Ch, Am, AA infrared spectra, appeared also in Ch-grafted (AA- co-Am)) spectra. The bands at 1558 cm^{-1} (asymmetric COO- stretching) and 1406 cm^{-1} (symmetric COO– stretching).

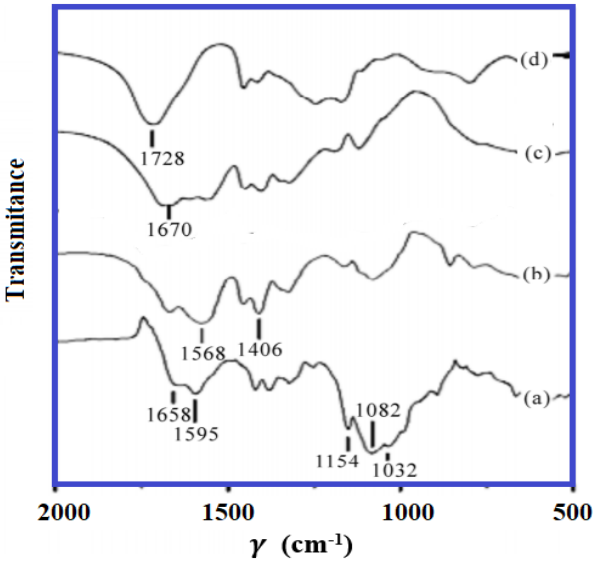

Figure (1) FTIR for (a)Chitosan (b)Ch- g- (Am-co-AA) (c)Am and (d) AA

3.2 Effect of Temperature on Swelling

Figure (2) shows the swelling degree at different temperatures as a function of time. The results indicate that the swelling degree increases with temperature until it reaches 60°C, then the swelling degree is decreased due to further temperature increasing.

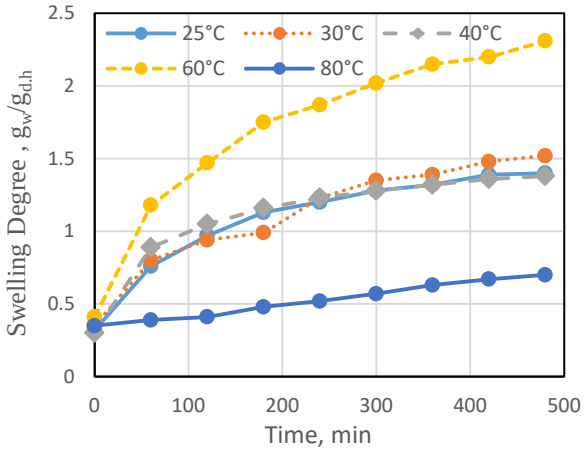

Figure (2) Swelling Degree in Terms of Water Absorbed Per Dry Hydrogel as a Function of Time

The swelling degree gradually increased after soaking the hydrogel in distilled water and the swelling degree kinetic studies of the hydrogels were conducted at the first 8 hours where the hydrogels swelling degree at the three different temperatures are very high as seen from Figure (2).

Swelling values of 1.4,1.5,1.4,2.3, and 0.7 g water/g dry hydrogel were observed after 8 hours at RT, 30, 40, 60, and 80 degrees Celsius, respectively. As seen in Figure 2, the degree of hydrogel swelling increased as the temperature increased. At 60 degrees Celsius, swelling is twice as large as it is at room temperature.

This may be explained by the fact that the H-bonds inside the hydrogels were disrupted as the temperature rose, allowing more water to be absorbed. Furthermore, the rise in swelling value with rising temperature up to a specific point for the hydrogel might be due to an increase in thermal mobility of polymer molecules inside the hydrogels.[26]

Figure (3) shows the swelling rate in g water/g dry hydrogel/min. The results shows that the increase of temperature from 25 to 40°C did not show any remarkable effect on the welling rate. By increasing the temperature to 60°C, the welling rate increased significantly. Then, further temperature increases to 80°C, showed a negative effect on the welling rate as observed from Figure (1).

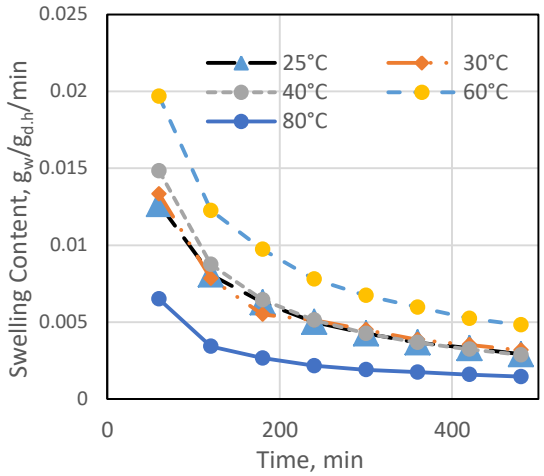

Figure (3) Swelling Rate as a Function of Time

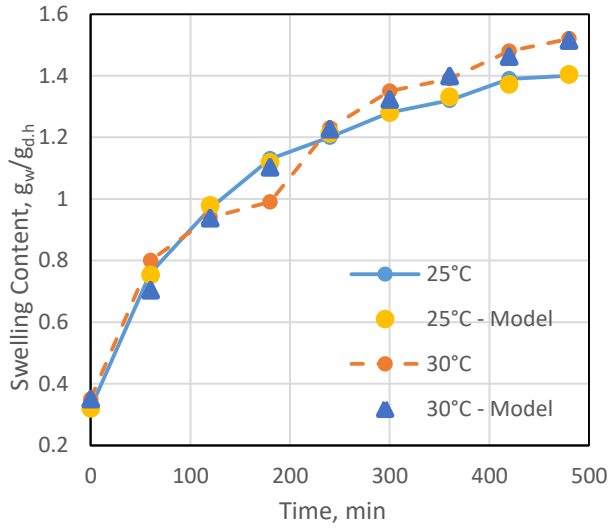

Figure (4) Comparison between model predictions and experimental results at 25 and 30°C

The observed experimental results were used to develop a kinetic model to represent the welling phenomenon using Equations 2-4. Figures (3) and (4) show a comparison between the experimental results and the model predictions. Figures (4) and (5) signifies that the model and the experimental data agree well therefore the developed model can be used to predict the swelling degree at different temperatures as a function of time.

Statistical analysis indicates that the developed model is an excellent presentation of the swelling phenomenon under study. Squared R is 0.99 for all temperatures under study; which exposes a reasonable agreement between the experimental results and model predictions. The observed F values and the standard error indicate the validity of the

proposed model to describe the swelling of hydrogel at different temperatures.

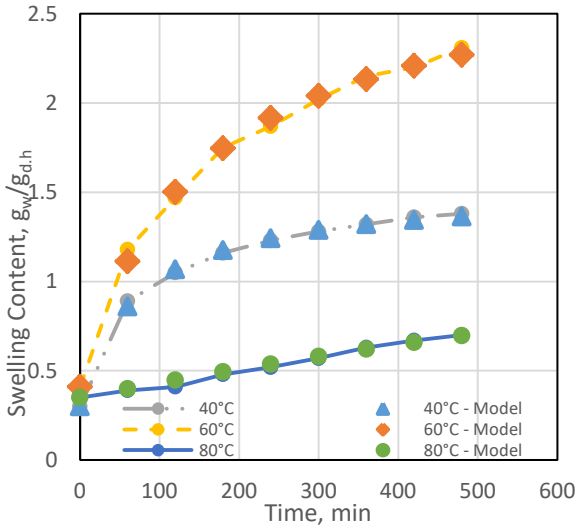

Figure (5) Comparison between model predictions and experimental results at 40, 60, and 80°C

Table (2): The fitted parameters values for Peleg's model as estimated by non-linear regression

Temperature (°C)	k_1	k_2	R^2	Significance F	Standard Error
25	95.2	0.72	0.99	9E4	0.01
30	135.2	0.58	0.99	4E3	0.06
40	58.1	0.82	0.99	4E4	0.02
60	60.5	0.41	0.99	2E4	0.04
80	1170.1	0.43	0.99	1E4	0.02

Significance F: 2.75158

It was hard to fit the estimated reaction rate constants which can be attributed to the fact that the reaction mechanism may change as the reaction temperature changes.

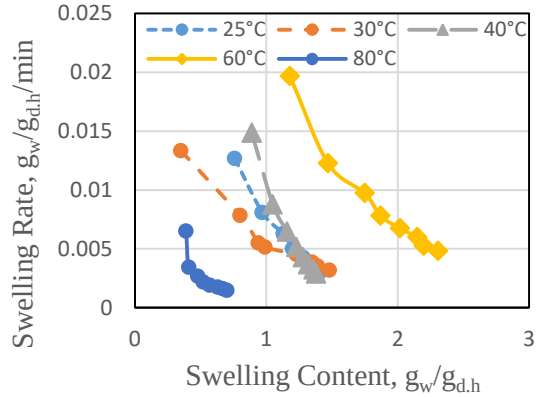

Figure (6): Relation Between the Swelling Rate and The Swelling Degree at Different Temperatures

Figure (6) shows the relation between the welling rate and the swelling degree at different temperatures. The results indicate that the swelling rate is inversely proportional with the swelling degree. The welling rate decreases as the swelling degree increases which can be attributed to the saturation of the hydrogel. The affinity of hydrogel for welling is at maximum when the swelling process started, the affinity for water swelling decreases as the hydrogel getting saturated with more water.

The relationship between the swelling rate and swelling degree can be expressed using logarithmic function for the temperatures 25-60°C. At 80°C, the welling rate and swelling degree are not correlated through logarithmic relationship which can indicate the variation of reaction mechanism at 80°C. The logarithmic relationship used to describe the relation between the swelling rate and the swelling degree is given in Equation (4), the fitted parameters are shown in Table (3).

The swelling rate and swelling degree can be expressed using a 4th degree polynomial.

$$\boldsymbol{Swelling\ Rate = A * \exp(-B * Swelling\ Degree)} \quad (4)$$

Table 3: The parameters for the logarithmic relation between swelling rate and swelling degree

Temperature (°C)	A	B	R^2
25	0.02	1.24	0.99
30	0.07	2.22	0.98
40	0.28	3.28	0.99
60	0.08	1.22	0.99
80	0.02	3.88	0.75

4. Conclusion

The chitosan grafted acrylamide-acrylic acid hydrogel was produced in this work, and the influence of temperature on the hydrogel's swelling kinetics was studied. At RT, 30, 40, 60, and 80 °C, the swelling equilibrium values for the hydrogel were 1.4, 1.5,1.4,2.3, and 0.7 g water/g dry hydrogel, respectively. As a result, by altering the monomer characteristics, a hydrogel may be designed to absorb large amounts of water (variation and amount). The maximal hydrogel swelling was determined to be 60 degrees Celsius in this investigation.

The hydrogel's ability to absorb water improves at that temperature. Hydrogels shrank by absorbing water after being heated to 60 degrees Celsius. The swelling rate and effective diffusivity increase when air temperature rises (swelling content rises as well). Peleg's equation models were used to estimate the water content uptake as a function of swelling time; this model approved well the experimental data.

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