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SWELLING KINETICS OF ENERGY EFFICIENTLY SYNTHESIZED HYDROGELS INTENDED FOR HYGIENE PRODUCTS

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ABSTRACT

Environmental threats such as pollution, climate change, depletion of fossil fuels reserves has imposed an urgent need to take action in looking for sustainable solutions. One of the items of environmental protection is energy saving, which is especially important in manufacturing of widespread use materials such as acrylate superabsorbents. The global market for superabsorbents is growing and entails their simple, ecological, cost-effective manufacturing. Energy-efficient production provides reduction of time, production costs and CO_2 emissions and increases product competitiveness in the market. Increasing energy efficiency in the production of acrylate hydrogels can be achieved using the microwave instead of conventional heating, which significantly simplifies the whole procedure, reduces the synthesis duration a few dozen times, resulting in high yield and specific hydrogel morphology that enables fast swelling response. Results of swelling measurements in phosphate buffer (pH 7.4) have shown that swelling ratio increases with increasing in acrylic acid amount in hydrogel composition. Swelling of hydrogels at pH 7.4 and 37 ºC follows the second-order kinetics. Swelling ratio-time dependence was estimated using the regression analysis as a fast and simple method based on the assumption of the equation for a given empirical dependence.

Keywords: microwave synthesis, acrylate hydrogels, regression analysis.

INTRODUCTION

Superabsorbents are hydrogels with great ability to absorb and retain water solution (up to several hundred times their own weight). They are composed of ionic monomers and possess a low crosslinking density, therefore have larger water uptake capacity in comparison with conventional hydrogels (Yu, Liu, Kong, Zhang, & Liu, 2011). Acrylate superabsorbents are widely used in different fields such as agriculture, packaging and auto industry, but the most important is their application in hygiene products. Due to the flexible design and biocompatibility, market demands for these materials are high and it is expected to reach a value of 8.851 million dollars by 2022 on the global level (Erceg, Teofilović, Vukić, & Ristić, 2021). In accordance with the results of market analysis, there is a need for response to increasing demands, in terms of reduction of production costs and price of final products. One of possible ways is using microwaves in synthesis of acrylate superabsorbents instead of conventional heating in aqueous solution. Conventional synthesis requires time and energy, resulting in swollen hydrogel as a final product. Synthesis in microwave field reduces synthesis time (up to 20 times), resulting in high yield of xerogel, which consequently reduces energy and time needed for drying of hydrogel. Regression analysis based on assumption of swelling ratio-time dependence equation has been proved as a fast and simple method for analyzing swelling kinetics (Erceg, Dapčević-Hadnađev, Hadnađev, & Ristić, 2020).

The aim of this work is synthesis of superabsorbent hydrogels with different acrylic acid/acrylamide ratio and investigation of their swelling kinetics using regression analysis.

EXPERIMENTAL PART

Materials

Acrylic acid (AA), acrylamide (Aam), crosslinker *N,N'*-Methylenebisacrylamide (MBAM) and accelerator *N,N,N',N'*-Tetramethylethylenediamine (TEMED) were supplied from Sigma Aldrich (Co., St. St. Louis, MO USA). Iniiator ammonium persulfate (APS) and phosphate buffer solution (pH 7.4) were purchased from Alfapanon, Serbia.

METHODS

Preparation of hydrogel

Hydrogels based on acrylic acid and acrylamide were synthesized via free-radical polymerization in a microwave oven at 2.45 GHz by one-step procedure. Hydrogels were prepared in two initial molar ratios of monomers AA and Aam: 45/55 (0.011/0.014 mol) and 65/35 (0.016/0.088 mol) using a 1mol% of crosslinkig agent MBAM, 3 ml of APS aquose solution and 2 ml of TEMED aquose solution (4.1 g/mol). After homogenization and dissolution of reaction components in minimum amount of water (5 ml), a glass vessels with reaction mixture were put in a microwave oven. After two minutes of simultaneous polymerization and crosslinking followed by water evaporation, the xerogels with cellular structure were obtained (Figure 1) (Erceg et al., 2020; Erceg et al., 2020).

Figure 1. Xerogel obtained in microwave field.

Analysing of swelling behavior

Swelling properties of obtained hydrogels were investigated at physiological pH 7.4 and temperatre of 37 °C, considering its possible application in hygiene products. Swelling ratio (*S*) of hydrogels was determined using the following Equation 1:

$$S = \frac{W_t - W_0}{W_0} \cdot 100\% \qquad (1)$$

Where W_0 is initial weight of dry hydrogel (xerogel), W_t is weight of swollen hydrogel in certain time intervals (30, 60, 120, 240, 360, 720, 1440 min).

Swelling kinetics

Regression analysis was used to determine the swelling ratio-time empirical dependence, applying the principle of assuming the equation for a given empirical dependence. The parameters in the proposed model describing the kinetics of swelling were calculated using the following Equations 2 and 3:

$$b_1 = \frac{n \cdot \sum_i^n x_i \cdot y - (\sum_i^n x_i)(\sum_i^n y_i)}{n \cdot \sum_i^n x_i^2 - (\sum_i^n x_i)^2} \qquad (2)$$

$$b_0 = \frac{1}{n}(\sum_i^n y_i - b_1 \cdot \sum_i^n x) \qquad (3)$$

RESULTS AND DISCUSSION

Swelling analysis

Results of swelling ratio measurements are presented in Figure 2. Swelling ratio at pH 7.4 increases with increasing in AA amount in hydrogel composition, because, at that pH value carboxylic groups in AA units are in ionizated form and in such form contribute to swelling capacity of hydrogels.

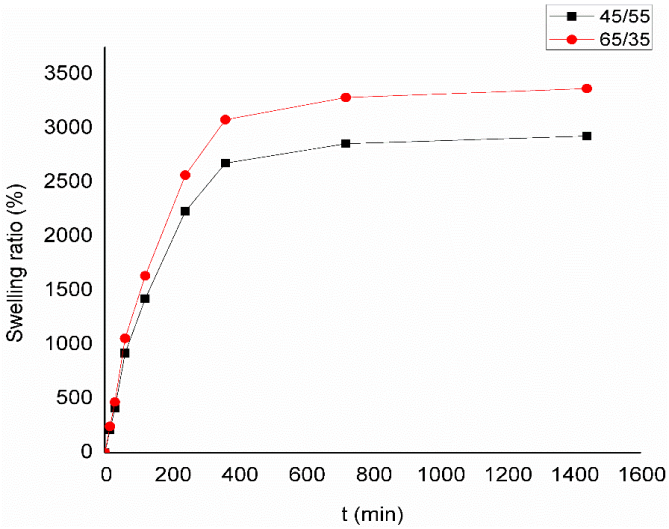

Figure 2. Swelling ratio in function of time for hydrogels 45/55 and 65/35, at pH 7.4 and 37 °C.

By applying of Equations 2 and 3, starting from the mathematical model (Equation 4), the parameters in the empirical model describing the dependence of the swelling ratio on time were obtained. The equation is proposed based on the knowledge of the function of the curves. Linear dependence of the transformed variable *t/S* on time *t* have confirmed that proposed model is approriate for description of swelling ratio-time dependence (Figure 3).

$$S = \frac{t}{b_0 + b_1 \cdot t} \qquad (4)$$

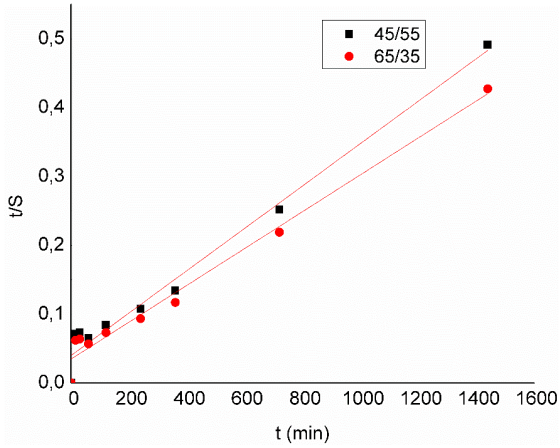

Figure 3. t/S in function of time.

Parameters of Equation 4 for both samples are given in Table 1.

By including the parameters b_0 and b_1 in Equation 4, the predicted values of swelling ratio were obtained. Figure 4 shows the agreement of the experimental data and the values of the swelling ratio calculated by including the parameters b_0 and b_1 in Equation 4, which is satisfactory, considering their close values.

Correlation between integrated form of second-order swelling kinetics (Quintana, Valderruten, & Katime, 1999) equation and parameters b_0 and b_1 are given by Equation 5 and 6:

$$b_0 = \frac{1}{K_2 \cdot S_e^2} \quad (5)$$

$$b_1 = \frac{1}{S_e} \quad (6)$$

Table 1. b_0 and b_1 parameters values for hydrogel samples.

Sample	b_0	b_1
45/55	0.040205	0.000307
65/35	0.034961	0,000268

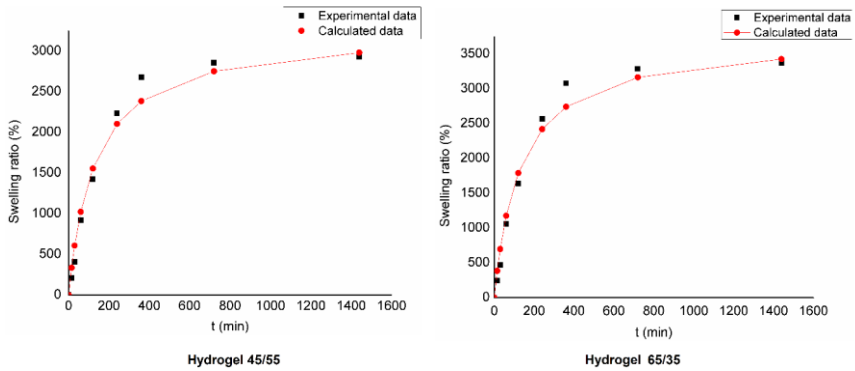

Figure 4. Agreement of experimental and calculated values of swelling ratio for both hydrogel samples at pH 7.4 and temperature 37 °C.

CONCLUSIONS

Acrylic acid/acrylamide hydrogels were obtained via free-radical polymerization in microwave field. Microwave synthesis is economically and energy-efficient method, which enables energy and time saving resulting in hydrogels with desired morphology. Swelling behavior was investigated at physiological conditions, considering the application of acrylate hydrogels as suberabsorbents in hygine products. Swelling ratio increases with increasing in acrylic acid amount in hydrogel composition. Regression analysis has been proved as a fast and simple method for determination of swelling kinetics, by assumption the function of empirical dependence.

LITERATURE

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