Investigation of Swelling, Morphological, and Thermal Properties of Superabsorbent Carrageenan-Based Hydrogel

G.O. AKALIN

Abstract— In this study, carrageenan/acrylic acid-co-itaconic acid (C/(A-co-I)) hydrogel was prepared with two-step method. Swelling tests of hydrogel were conducted against time, temperature, and pH. The prepared hydrogel showed high swelling values. The chemical structure of the hydrogel was examined via FTIR (Fourier Transformed Infrared Spectroscopy) analysis. SEM (Scanning Electron Microscope) analysis of the hydrogel was performed to examine its morphological characteristics. It has been proven that hydrogel has a porous and layered structure. Thermal stability of the hydrogel was also analyzed using TGA (Thermogravimetric Analysis). Based on the results obtained, it can be said that the synthesized hydrogel is superabsorbent.

Keywords— Carrageenan, hydrogel, swelling, superabsorbent.

I. INTRODUCTION

The rapid pace of industrial growth has led to significant environmental problems, including pollution of the air, soil, and water [1]. Superabsorbents, with their extraordinary ability to absorb and retain large amounts of water and pollutants, offer a promising solution to this problem. Innovative technologies employing superabsorbents must be developed and utilized to effectively reduce pollutant discharge and mitigate their impact on ecosystems. Hydrogels are among the materials employed for this purpose. Due to their inherent structure, superabsorbents are widely used in applications requiring significant moisture retention and control, such as in agricultural soils, wound dressings, and personal hygiene products. Their hydrophilic nature allows hydrogels to swell [2]. The swelling properties of hydrogels can vary based on their contents, as well as factors such as pH and temperature. [2].

Acrylic acid (A) is a vinyl monomer known for its hydrophilic nature and pH sensitivity, widely utilized in the synthesis of superabsorbent hydrogels [3]. Sometimes, using a single monomer in hydrogels does not yield optimal swelling properties; hence, acrylic acid is frequently copolymerized with other monomers. Copolymerization can improve the characteristics of hydrogels. Itaconic acid (I), a non-toxic monomer derived from microbial fermentation of renewable non-petroleum sources, also has hydrophilic properties [3]. This monomer, similar to acrylic acid, can significantly enhance the swelling capacity of hydrogels [3]. Carrageenan (C) is a polysaccharide derived from red seaweed through an alkali extraction method [1]. It can be classified into various subtypes [1]. This study utilized the kappa subtype. Carrageenan's key properties, such as its hydrophilicity, biodegradability, environmental friendliness, and biocompatibility, make it a valuable component for synthesizing superabsorbent [1]. The aim of this study is to prepare the superabsorbent carrageenan/acrylic acid-co-itaconic acid (C/(A-co-I)) hydrogel. The swelling behavior were investigated against time, pH and temperature. Morphological and thermal properties were also researched.

II. EXPERIMENTAL

A. *Hydrogel Preparation*

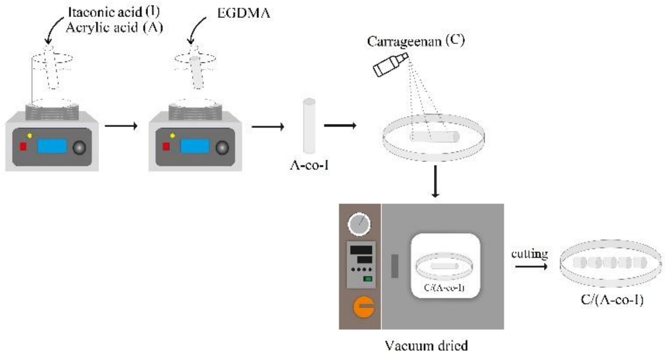
The hydrogel preparation method consists of two stages. The first stage is the preparation of the copolymerization method. This method has been performed according to the literature [2]. Solutions of 5 ml (10 M) itaconic acid (Sigma-Aldrich) and 5 ml (10 M) acrylic acid (Sigma-Aldrich) monomers were prepared and added to glass tubes. After the tubes were placed in a hot water bath, 400 µl of EGDMA (Sigma-Aldrich) was added as a cross-linker for copolymer formation. $(NH_4)_2S_2O_8/Na_2S_2O_5$ (0.05g/0.05g) were utilized as an initiators [2]. The synthesized A-co-I copolymer was removed from the tube. The process has advanced to the second stage. This stage is the spraying and vacuum drying method. 5% carrageenan solution was sprayed onto the copolymer surface using a spray technique and then vacuum-dried at 30°C. C/(A-co-I) hydrogel was kept for 12 h. After the hydrogel was cut into several pieces.

A schematic representation of the preparation of C/(A-co-I) hydrogel is given in Scheme 1. The photo of dried and swollen of cut C/(A-co-I) hydrogel is given Fig. 1.

Manuscript received 31 July, 2024.

G.O. Akalin, Aksaray University, Department of Medical Services and Techniques, Vocational School of Health Services, 68100, Aksaray, Turkey

https://doi.org/10.17758/EARES17.EAP0824604



Scheme 1. Schematic representation of the preparation of C/(A-co-I) hydrogel

Fig. 1. The dried (left) and swollen (right) cut C/(A-co-I) hydrogel

B. Water absorption experiments

To measure the water absorption capacity of C/(A-co-I) and (A-co-I) samples, the percentage swelling values of the hydrogels in water were determined under different pH, temperature and time conditions [5]. Swelling tests were performed gravimetrically. In the initial stage, dried samples were placed in distilled water at room temperature to allow swelling. At regular intervals, the swollen gels were removed from the water, blotted dry with filter paper, weighed, and then returned to the same bath [2]. This procedure continued until each sample reached a stable weight. Equation (1) was used for determining the swelling (%):

$$Swelling\ (\%) = \frac{Ww - Wd}{Wd} \tag{1}$$

where W_w represents the wet weight of the sample, and W_d is the dry weight prior to swelling. The swelling period for all samples was roughly 24 h.

To explore how pH affects swelling behavior, dried hydrogels were immersed in phosphate buffer solutions (PBS) with pH values ranging from 2 to 12 during the second stage [2]. Room temperature and a swelling period of 24 hours were consistently maintained. Once swollen, the samples were taken out of the buffer solutions, dried with filter paper, and weighed. Equation (1) was used to calculate the swelling (%).

The effect of temperature on swelling behavior was examined in the final phase by placing dried samples in distilled water at temperatures between 4°C and 50°C [2]. After a 24-hour period, the swollen samples were removed, dried with filter paper, and weighed. Equation (1) was employed to determine the swelling (%).

C. ATR-FTIR Analysis

C/(A-co-I) and A-co-I samples were positioned to cover the laser for ATR-FTIR analysis (FTIR Shimadzu IR-Prestige 2) [4,6]. By securely fastening the device with its clip, complete interaction between the infrared beams from the laser and the sample was ensured. The spectra of samples were recorded.

D. TGA Analysis

A Shimadzu DTG 60 H analyzer was used to perform thermogravimetric analysis of C/(A-co-I) and A-co-I hydrogels under a dynamic nitrogen atmosphere. To generate TGA and DTA curves, the dried hydrogels were subjected to heating from 0 to 900 °C at a rate of 10 °C/min. [6].

E. SEM Analysis

Surface analysis was determined using a HITACHI SU500 SEM device. Prior to placement in the SEM device, C/(A-co-I) hydrogel was lyophilized. The dry hydrogel was first swollen, then the swollen hydrogel was kept at -80°C for 24 hours before being placed in a freeze-dryer (Christ Alfa2-4LD Plus) for freeze-drying. The lyophilized hydrogel was coated with gold using a sputter coater, then placed on SEM stubs. The images of hydrogel was recorded at 3.0 and 5.0 kV voltage.

III. RESULTS AND DISCUSSION

Fig. 2 represents the variation of swelling (%) with time at room temperature. By examining the swelling behavior of the hydrogel samples over time, it was observed that both samples reached equilibrium in approximately 24 hours. The C/(A-co-I) sample exhibited a swelling value nearly three times greater than that of the A-co-I sample. This indicates that the incorporation of carrageenan into the structure positively influenced the swelling capacity. Carrageenan, a sulfonated biopolymer with ionic groups, is known to enhance swelling [7]. According to the literature, the ionic sulfate anions present in carrageenan content can increase the swelling value [7]. In other words, the increasing presence of anionic groups in structure can enhance the swelling values [7].

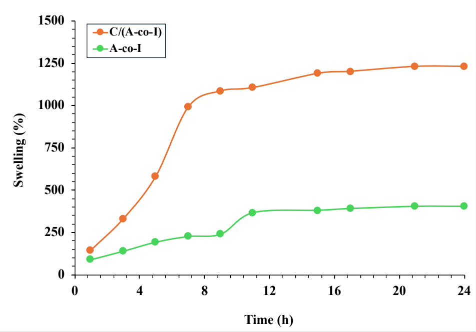


Fig. 2. The swelling (%) with time

Fig. 3 illustrates the variation in swelling (%) values with pH. When examining the swelling values, it was found that as the pH rose, the swelling values also increased. The least swelling was detected in acidic conditions, while the greatest swelling was recorded in alkaline conditions. In an acidic environment, the enhanced formation of hydrogen bonds among hydroxyl groups in the structure may result in more compact networks, leading to reduced swelling [8]. Hence, the swelling value may have diminished under acidic conditions. In an alkaline environment, the swelling may have increased due to the repulsion between ionized groups following ionization [8].

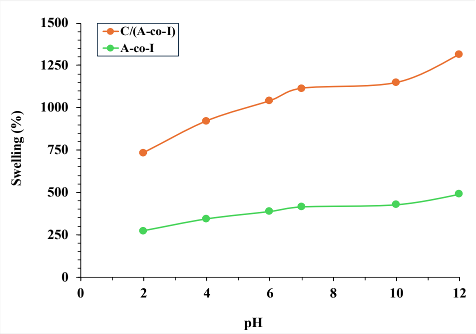


Fig.3. The swelling (%) with pH

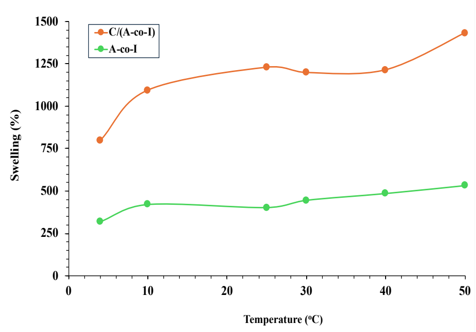


Fig. 4. The swelling (%) with temperature

Fig. 4 shows the change in swelling (%) values with temperature. As the temperature increases, the swelling values of the hydrogels increase. When the temperature rises, the polymer chains can become more mobile, causing the hydrogel network to expand or relax. This relaxation facilitates easier penetration of the solution into the hydrogel, which can enhance the diffusion rate [9]. Consequently, the swelling values may also increase correspondingly with the heightened diffusion.

Fig. 5 shows the FTIR spectra of C/(A-co-I) and A-co-I samples. Although the peaks are mostly similar, there are some minor differences. A broad absorption band in the range of 3000 to 3500 cm^{-1} is indicative of the stretching vibration of the hydroxyl group [3]. However, there is band broadening between 2300-4000 cm^{-1} in C/(A-co-I) hydrogel. This can be attributed to the increase in the -OH group in the structure with the addition of carrageenan. The findings align with the literature. According to literature, the broad band at nearly 3600–3200 cm^{-1} was also observed due to O-H stretching in the polysaccharide [10]. In both spectra, the characteristic -C-O vibration of itaconic acid can be represented by the bands at 1714 and 1695 cm^{-1} [1]. According to the literature, the characteristic peaks of carrageenan at nearly 1228, 1033, 924, and 848 cm^{-1} corresponded to sulfate ester, glycosidic linkage, 3,6-anhydro-D-galactose, and D-galactose-4-sulfate groups, respectively [10, 11]. The stretching vibration of the -C-O-C- band is likely related to the peak observed around 1068–1035 cm^{-1} [3]. Additionally, C-H stretching, bridge C-O stretching, and C-O stretching are indicated by the peaks near 2927 cm^{-1}, 1188 cm^{-1}, and 970 cm^{-1}, respectively [1]. These findings show that the presence of carrageenan in the structure was successfully proven.

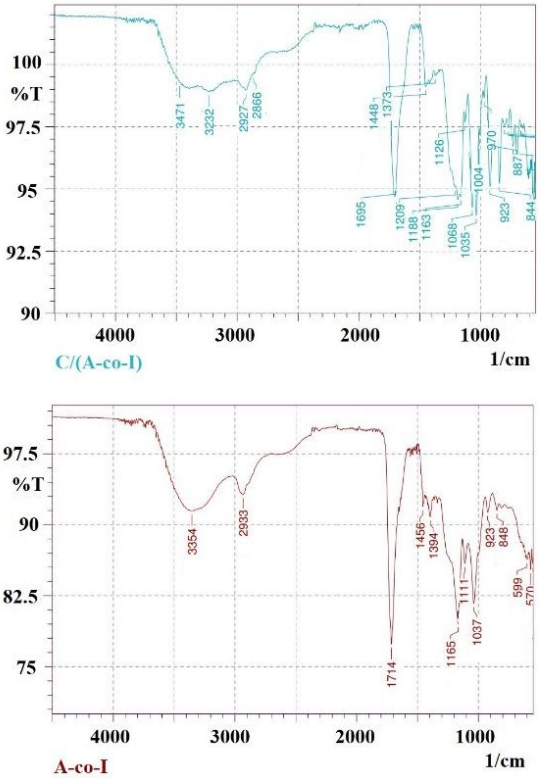


Fig. 5. The FTIR spectra of C/(A-co-I) and A-co-I

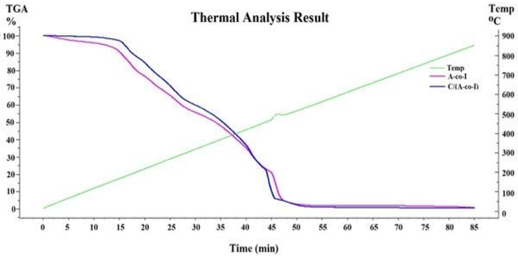


Fig.6. The TGA curves of C/(A-co-I) and A-co-I

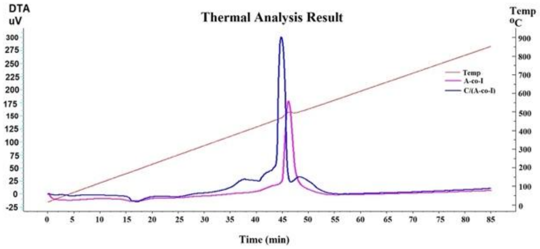
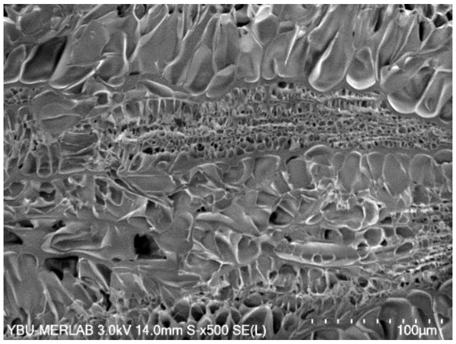


Fig.7. The DTA curves of C/(A-co-I) and A-co-I

Fig. 6 and Fig. 7 display TGA and DTA curves againts the time and temperature of samples. Thermal treatment of a substance can lead to changes in its physico-chemical characteristics, such as breakdown, phase shifts, structural alterations, and variations in volume [3, 12]. As illustrated in Fig. 6, the breakdown of both C/(A-co-I) and A-co-I samples took place in four distinct stages as the temperature ranged from 0-900°C. Thermal decomposition occurred later in the C/(A-co-I) compared to the A-co-I. The first weight loss (up to nearly 15 min for A-co-I and up to nearly 20 min for C/(A-co-I)) can be attributed to the evaporation of moisture from the samples. The initial degradation of the C/(A-co-I) sample took slightly longer. The second phase of weight loss occurring in approximately 20-30 min may be associated with the breaking of single bonds like C-O, -C–O–C etc. [3]. In the third and fourth stages, the weight loss observed between 300–430°C (approximately 30-42 min) and 430-550°C (approximately 42-55 min) may be attributed to the thermal decomposition of carboxyl groups and the breaking of hydrogel chains, respectively [3]. In the DTA curves, both samples showed similar thermal behavior and exhibited three smaller peaks and a distinct maximum peak around 498-500°C. The smaller peaks are not very prominent because they are overshadowed by the maximum peak. This exothermic peak is higher in the C/(A-co-I) compared to A-co-I, indicating a more pronounced exothermic reaction during the thermal process. This may suggest that this sample releases more energy or undergoes more significant phase changes.In contrast, the peak height in the other sample (A-co-I) is slightly lower and broader, indicating a more gradual or less energetic reaction. In Fig. 8, the SEM images of the C/(A-co-I) hydrogel clearly show that the surface is not uniform (homogeneous) and consists of different regions. In some areas, the porosity is smaller, while in others it is larger. When examining the images, especially in Fig. 8(a) and Fig. 8(b), it can be observed that the surfaces are layered in certain regions. This layering can be explained by the spray method applied during the preparation. The surface application might have led to the formation of a layered structure.



A

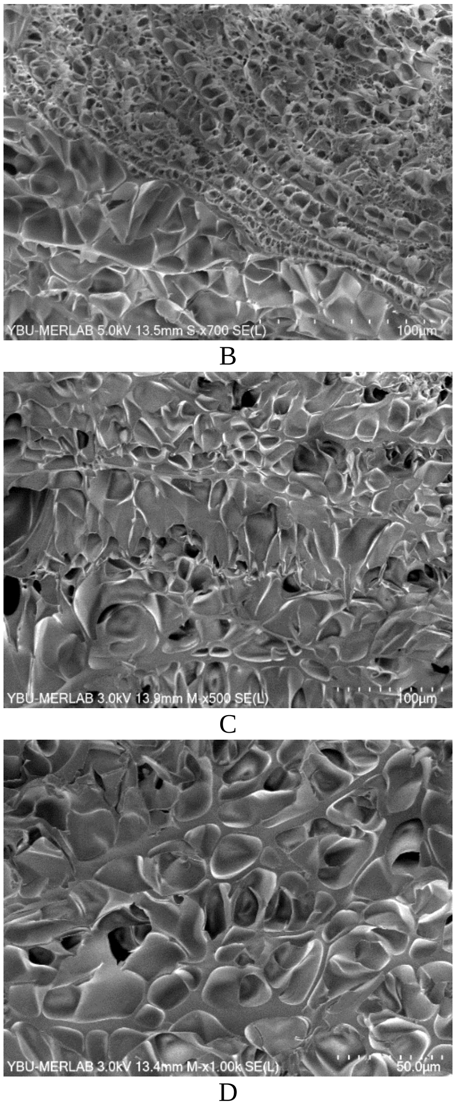


Fig.8. SEM images of C/(A-co-I) hydrogel

IV. CONCLUSION

In this study, carrageenan/acrylic acid-co-itaconic acid (C/(A-co-I)) hydrogel was prepared using a two-step synthesis method. Its properties were investigated by comparing it with the A-co-I copolymer. Due to the significant differences between the two samples, carrageenan is an important component of the C/(A-co-I) hydrogel, which can also be referred to as a carrageenan-based hydrogel. The swelling behavior of the carrageenan-based hydrogel, assessed across variations in time, temperature, and pH, revealed high swelling values, indicating its superabsorbent properties. FTIR analysis confirmed the chemical structure, while SEM analysis illustrated its porous and layered morphology.Additionally, the thermal stability was verified by TGA analysis. These findings suggest that the hydrogel may be highly effective as a superabsorbent in various fields (agricultural, biomedical, and environmental). Future research can further improve the properties of this hydrogel and explore its use in various application areas, thus realizing its full potential.

REFERENCES

[1] S. Sharma, G. Sharma, A. Kumar, T. S. AlGarni, M. Naushad, Z. A. ALOthman, and F. J. Stadler, "Adsorption of cationic dyes onto carrageenan and itaconic acid-based superabsorbent hydrogel: Synthesis, characterization and isotherm analysis," *Journal of Hazardous Materials*, vol. 421, 126729, pp. 1-16, 2022. https://doi.org/10.1016/j.jhazmat.2021.126729

[2] M. Pulat, and H. Eksi, "Determination of swelling behavior and morphological properties of poly (acrylamide-co-itaconic acid) and poly (acrylic acid-co-itaconic acid) copolymeric hydrogels," *Journal of applied polymer science*, vol. 102, no. 6, pp. 5994-5999, June 2006. https://doi.org/10.1002/app.25182

[3] P. M. Pakdel, S. J. Peighambardoust, N. Arsalani, and H. Aghdasinia, "Safranin-O cationic dye removal from wastewater using carboxymethyl cellulose-grafted-poly (acrylic acid-co-itaconic acid) nanocomposite hydrogel," *Environmental Research*, vol. 212, 113201, pp. 1-17, April 2022.
https://doi.org/10.1016/j.envres.2022.113201

[4] X. Qi, W. Wei, T. Su, J. Zhang, and W. Dong, "Fabrication of a new polysaccharide-based adsorbent for water purification," *Carbohydrate polymers*, vol. 195, pp. 368-377, April 2018. https://doi.org/10.1016/j.carbpol.2018.04.112

[5] Q. Lv, M. Wu, and Y. Shen, "Enhanced swelling ratio and water retention capacity for novel super-absorbent hydrogel," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 583, 123972, pp. 1-10, September 2019.
https://doi.org/10.1016/j.colsurfa.2019.123972

[6] M. Zaltariov, D. Filip, C. D. Varganici, and D. Macocinschi, "ATR-FTIR and thermal behavior studies of new hydrogel formulations based on hydroxypropyl methylcellulose/poly (acrilic acid) polymeric blends," *Cellulose Chemistry and Technology*, vol. 52, no. 7-8, pp. 619-631, August 2018.

[7] G. R. Mahdavinia, G. B. Marandi, A. Pourjavadi, and Kiani, G. "Semi-IPN carrageenan-based nanocomposite hydrogels: synthesis and swelling behavior," *Journal of Applied Polymer Science*, vol. 118, no. 5, pp. 2989-2997, July 2010.
https://doi.org/10.1002/app.32700

[8] H. Hezaveh, and I. I. Muhamad, "Effect of natural cross-linker on swelling and structural stability of kappa-carrageenan/hydroxyethyl cellulose pH-sensitive hydrogels," Korean *Journal of Chemical Engineers*, vol. 29, no. 11, pp. 1647-1655, April 2012. https://doi.org/10.1007/s11814-012-0056-6

[9] A. M. Saeed, "Temperature effect on swelling properties of commercial polyacrylic acid hydrogel beads," *International journal of Advanced Biological and Biomedical Research*, vol. 1, no. 12, pp. 1614-1627, 2013.

[10] L. Zhao, Q. Zheng, Y. Liu, S. Wang, J. Wang, and X. Liu, "Enhanced strength and toughness of κ-carrageenan/polyacrylic acid physical double-network hydrogels by dual cross-linking of the first network," *European Polymer Journal*, vol. 124, 109474, pp. 1-11, January 2020 https://doi.org/10.1016/j.eurpolymj.2020.109474

[11] A. Pourjavadi, A. M. Harzandi, and H. Hosseinzadeh, "Modified carrageenan 3. Synthesis of a novel polysaccharide-based superabsorbent hydrogel via graft copolymerization of acrylic acid onto kappa-carrageenan in air," *European Polymer Journal*, vol. 40, no. 7, pp. 1363-1370, April 2004.
https://doi.org/10.1016/j.eurpolymj.2004.02.016

[12] W. Bessashia, Y., Berredjem, Z. Hattab, and M. Bououdina, "Removal of Basic Fuchsin from water by using mussel powdered eggshell membrane as novel bioadsorbent: Equilibrium, kinetics, and thermodynamic studies," *Environmental research*, vol. 186, 109484, pp. 1-12, July 2020. https://doi.org/10.1016/j.envres.2020.109484