Konya Mühendislik Bilimleri Dergisi, c. 11, s. 2, 439-448, 2023
Konya Journal of Engineering Sciences, v. 11, n. 2, 439-448, 2023
ISSN: 2667-8055 (Electronic)
DOI: 10.36306/konjes.1218991

INVESTIGATION OF PHYSICOCHEMICAL AND THERMAL PROPERTIES OF CLAY-HYDROGEL COMPOSITES

[1] **Firdevs ÇİRLİ**, [2*] **Gülcihan GÜZEL KAYA**, [3] **Hüseyin DEVECİ**

Konya Technical University, Engineering and Natural Sciences Faculty, Chemical Engineering Department, Konya, TÜRKİYE
[1] firdevscirli@gmail.com, [2] ggkaya@ktun.edu.tr, [3] hdeveci@ktun.edu.tr

Highlights

- Hydrogel composites were synthesized by free radical solution polymerization.
- Hydrogel composites were pH and temperature responsive materials.
- Sepiolite addition increased thermal stability of the hydrogel network.

***Corresponding Author:** Gülcihan GÜZEL KAYA, ggkaya@ktun.edu.tr

Konya Mühendislik Bilimleri Dergisi, c. 11, s. 2, 439-448, 2023
Konya Journal of Engineering Sciences, v. 11, n. 2, 439-448, 2023
ISSN: 2667-8055 (Electronic)
DOI: 10.36306/konjes.1218991

INVESTIGATION OF PHYSICOCHEMICAL AND THERMAL PROPERTIES OF CLAY-HYDROGEL COMPOSITES

[1] Firdevs ÇİRLİ , [2*] Gülcihan GÜZEL KAYA , [3] Hüseyin DEVECİ

Konya Technical University, Engineering and Natural Sciences Faculty, Chemical Engineering Department, Konya, TÜRKİYE
[1] firdevscirli@gmail.com, [2] ggkaya@ktun.edu.tr, [3] hdeveci@ktun.edu.tr

(Received: 14.12.2022; Accepted in Revised Form: 23.02.2023)

ABSTRACT: Hydrogels are cross-linked polymeric networks which retain large amounts of water. The hydrogels with response capability to various stimuli such as pH and temperature have received great attention in many fields. In this study, hydrogels were synthesized by free radical solution polymerization through optimization of acrylamide/sodium acrylate mole ratio and ethylene glycol dimethacrylate content. With the addition of sepiolite as filler into the hydrogel network which had highest swelling percent, hydrogel composites were obtained. In the presence of 10 wt% sepiolite, maximum swelling percent was determined as approximately 10600%. Swelling properties of the hydrogel composite including 10 wt% sepiolite was investigated depending on pH, salt effect and temperature. With increasing pH value, swelling percent of the hydrogel composite showed an increase. At high temperatures, the hydrogel composite exhibited higher swelling percent. Swelling tests in 0.1 M NaCl, $CaCl_2$ and $FeCl_3$ solutions revealed that the lowest swelling percent was observed in 0.1 M $FeCl_3$ solution. Fourier transform infrared spectroscopy (FTIR) analyses verified successfully preparation of the hydrogel composites. Regular layers of the sepiolite in the hydrogel network which made water diffusion easily were shown by scanning electron microscopy (SEM) analyses. Thermogravimetric analyses (TGA) indicated that thermal stability of the hydrogel network was increased with the addition of sepiolite.

Keywords: *Sepiolite, Hydrogel, Swelling Ratio, Thermal Properties*

1. INTRODUCTION

Hydrogels are three dimensional polymer networks consisting of hydrophilic functional groups that make hydrogels water swelling materials. Swelling properties of hydrogels change depending on cross-linking degree, chemical composition, type of solvent and external stimulus [1]. Physically cross-linked hydrogels have reversible swelling ability under various stimuli such as pH, temperature, pressure, light, magnetic and electric field [2]. pH responsive hydrogels consist of ionizable pendant groups which alter hydrogel charge in case of pH changes. Formation of electrostatic interactions or repulsion forces in hydrogel network results in swelling or shrinkage of hydrogels, respectively [3]. Temperature responsive hydrogels are classified into two groups: (1) negative temperature responsive hydrogels which swell at temperatures below lower critical solution temperatures and (2) positive temperature responsive hydrogels which swell at temperatures above upper critical solution temperatures [4].

Hydrogel composites have received great attention in water treatment, biosensors, drug delivery, tissue engineering and implant industry [5]. In general, hydrogel composites have been prepared by four different methods: (1) gel formation in filler suspension, (2) in situ filler growth after gel formation, (3) filler impregnation after gel formation and (4) gel formation in the presence of filler as matrix or cross-linker [6]. To enhance mechanical properties, adsorption capacity, stimuli responsive ability, thermal stability and adhesion properties of hydrogel network, many fillers including carbon nanotubes, graphene, metals, metal oxides and clays have been used [7]. Recently, clays such as kaolin, bentonite, montmorillonite and sepiolite have been utilized in the preparation of hydrogel composites for different

---

*Corresponding Author:** Gülcihan GÜZEL KAYA, ggkaya@ktun.edu.tr applications in literature studies. Yilmaz, et al. [8]) prepared pH responsive poly(acrylamide-*co*-methacrylic acid) hydrogels including kaolin and investigated swelling behavior of the hydrogel composites in different pH values. Khan, et al. [9]) examined pharmaceutical contaminant removal capacity of montmorillonite-poly(methacrylic acid) hydrogel nanocomposites. Peighambardoust, et al. [10]) studied on dye removal performance of montmorillonite-carboxymethyl cellulose-*g*-polyacrylamide hydrogel nanocomposite. Thakur, et al. [11]) utilized xanthan gum-*cl*-poly(itaconic acid)-bentonite hydrogel nanocomposites for drug release. Saraydın, et al. [12]) prepared *N*-isopropyl acrylamide-itaconic acid-acrylamide hydrogels including sepiolite for enzyme immobilization.

Sepiolite ($Mg_8Si_{12}O_{30}(OH)_4(H_2O)_4.8H_2O$) is an abundant and low-cost clay consisting of two dimensional tetrahedral layers in addition to octahedral layers. Owing to discontinuity of octahedral layers, internal channels are formed in sepiolite structure that provides synergistic effects on its sorption ability [13]. Sepiolite has high surface area as well as 320 $m^2\ g^{-1}$ with surface functional groups. The active groups like Si-OH and -OH on the sepiolite surface increase compatibility between sepiolite and polymer matrix [14].

In this study, acrylamide-sodium acrylate hydrogels were synthesized by free radical solution polymerization. Optimum acrylamide-sodium acrylate molar ratio was determined depending on swelling tests in water through tea-bag method. Different amount of sepiolite was added to optimized monomer solution to prepare sepiolite-acrylamide-sodium acrylate hydrogel composites. Swelling properties of the hydrogel composites were examined as a function of pH and temperature. Their swelling ratio was also investigated in various saline solutions. Characterization of the samples was conducted by FTIR, SEM and TGA analyses to show the effect of sepiolite addition on the properties of acrylamide-sodium acrylate hydrogels.

2. EXPERIMENTAL

2.1. Materials

Acrylamide as monomer was purchased from Merck. Sodium acrylate as monomer, ammonium persulfate as initiator, ethylene glycol dimethacrylate as cross-linker and *N,N,N′,N′*-tetramethylethylenediamine as accelerator were purchased from Sigma-Aldrich. NaCl, $CaCl_2$ and $FeCl_3$ were obtained from Sigma-Aldrich to prepare saline solutions. The chemicals were used without further purification. Sepiolite was utilized as filler in the preparation of hydrogel composites.

2.2. Preparation of hydrogel composites

Acrylamide-sodium acrylate hydrogels were synthesized by free radical solution polymerization. First, acrylamide solution was prepared in distilled water, and then sodium acrylate was added with different mole ratio (acrylamide/sodium acrylate: 1-1; 1-2; 1-3; 2-1; 3-1). For cross-linking, ethylene glycol dimethacrylate (different content: 0.05 mL; 0.10 mL; 0.20 mL; 0.40 mL) was mixed with the monomer solution in the flask equipped with reflux condenser. The solution was stirred with 100 μL *N,N,N′,N′*-tetramethylethylenediamine at about 50 °C after the addition of 0.01 g ammonium persulfate into the solution. The gelation was observed in a short time. Gel washing with distilled water three times was carried out at ambient conditions followed by gel drying at 50 °C.

To prepare hydrogel composites, different weight percent of sepiolite (1 wt%; 3 wt%; 5 wt%; 10 wt%) was added to solution after the incorporation of ethylene glycol dimethacrylate. Gel washing and drying steps were applied as mentioned above.

2.3. Swelling tests

Swelling tests of the hydrogel composites were conducted using tea-bag method in distilled water at room temperature. Moreover, swelling properties of the hydrogel composites were investigated at different pH values (pH 2; pH 7; pH 9), in various salt solutions (0.1 M NaCl; 0.1 M $CaCl_2$; 0.1 M $FeCl_3$) and at different temperatures (25 °C; 30 °C; 40 °C; 50 °C). For swelling test, the tea-bag with dry hydrogel composite was dipped in distilled water or other solutions. At certain times, the tea-bag with wet hydrogel composite was wiped using a filter paper to remove excess liquid on the tea-bag and weighed. The swelling percent (S, %) was calculated using Eq. (1) [15]:

$$S\,(\%) = \frac{W_1 - W_0}{W_0}\, x\, 100 \qquad (1)$$

where W_1 (g) and W_0 (g) is weight of the tea-bag with wet and dry hydrogel composite, respectively.

2.4. Characterizations

Chemical structure of the hydrogel composites were examined by Fourier transform infrared spectroscopy (FTIR) analyses on Bruker Vertex 70 spectrometer. Morphological characterization of the hydrogel composites were carried out through scanning electron microscopy (SEM) analyses by SM Zeiss LS-10 equipment. Before SEM analyses, surface of the hydrogel composites was coated with gold layer. Thermal properties of the hydrogel composites were investigated by thermogravimetric analyses (TGA) with heating rate of 10 °C min^{-1} by METTLER STAR SW thermal analyzer.

3. RESULTS and DISCUSSIONS

3.1. Swelling properties

Swelling percent of the hydrogels with different acrylamide/sodium acrylate mole ratio is shown in Figure 1a. It was clear that swelling percent of the hydrogel significantly increased with increasing sodium acrylate mole ratio. Optimum acrylamide/sodium acrylate mole ratio was determined as 1-3. In the presence of high mole of sodium acrylate in the hydrogel network, hydrophilicity of the hydrogel increases due to $–COO^-$ functional groups belonged to sodium acrylate monomer. An increase in hydrophilic groups of hydrogel structure provides to increase swelling percent [16].

Swelling percent of the hydrogel with 1-3 acrylamide/sodium acrylate mole ratio as a function of ethylene glycol dimethacrylate content is shown in Figure 1b. The highest swelling percent was indicated as about 10000% in the case of using 0.05 mL ethylene glycol dimethacrylate. The swelling percent of the hydrogel decreased, while ethylene glycol dimethacrylate content was increasing. It can be explained with possible formation of highly cross-linked hydrogel networks. Generally, high cross-linking in hydrogel structure behaves as a barrier against water diffusion; so swelling ratio of hydrogels can significantly decreases [17].

Swelling percent of the hydrogels with 1-3 acrylamide/sodium acrylate mole ratio and 0.05 mL of ethylene glycol dimethacrylate is shown depending on amount of sepiolite in Figure 2. In general, incorporation of optimum amount of sepiolite into hydrogel network has synergistic effects on the swelling properties of hydrogels due to internal channels of sepiolite as well as its –OH functional groups. However, more sepiolite in hydrogel network acts as a cross-linker that increases cross-linking density leading to decrease water diffusion [18]. An increase in swelling percent of the hydrogel was observed with increasing amount of sepiolite in this study. And also, an increase in amount of sepiolite provided fast reaching to equilibrium swelling point. For example, the hydrogel composite including 1 wt% sepiolite reached to equilibrium swelling point in ~500 min; whereas, the hydrogel composite reached to equilibrium swelling point in ~350 min in case of 10 wt% sepiolite addition.

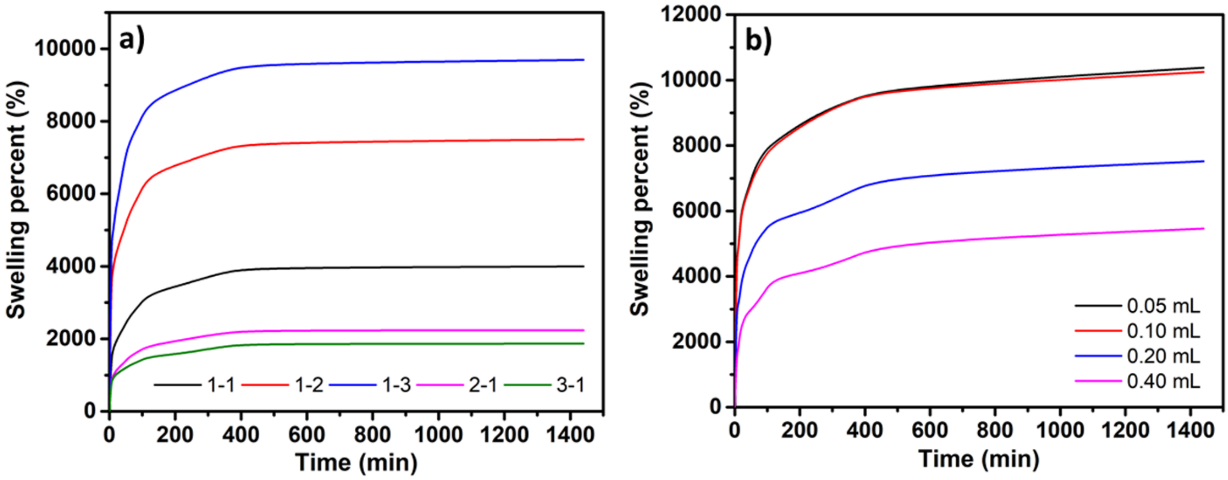

Figure 1. Swelling percent of the **a)** hydrogels with different acrylamide/sodium acrylate mole ratio and **b)** hydrogels with different content of ethylene glycol dimethacrylate in water

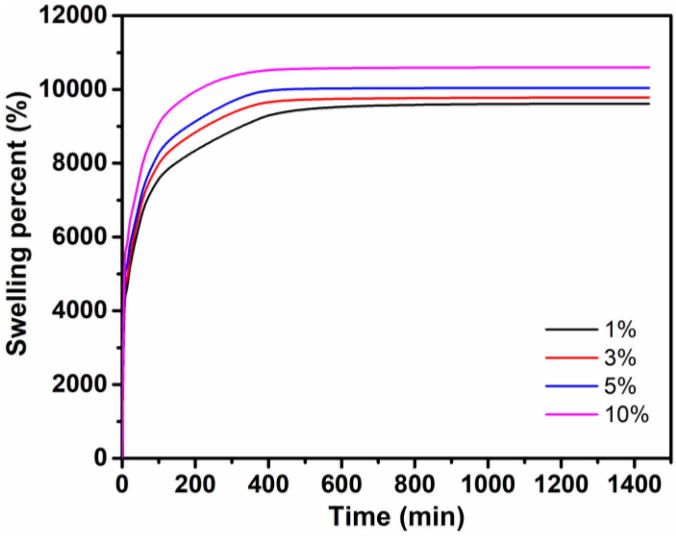

Figure 2. Swelling percent of hydrogel composites in water

Swelling percent of the hydrogel composite including 10 wt% sepiolite at different pH values is shown in Figure 3a. It was obvious that the lowest swelling percent of the hydrogel composite was observed at pH 2. At low pH, $-COO^-$ functional groups belonged to hydrogel networks tend to form hydrogen bonding that restricts their swelling [19]. With increasing pH, swelling percent of the hydrogel composite showed an increase. It was contributed to a decrease in interactions between $-COO^-$ groups at high pH values. Relaxation of hydrogel network chains makes diffusion of water molecules into hydrogel network easily which increases swelling percent of hydrogel [20].

It is known that osmotic pressure difference between salt solution and hydrogel network is one of the main factors affecting swelling capacity of hydrogel in salt solutions. Generally, shrinkage of hydrogels is determined depending on a decrease in the osmotic pressure difference which causes screening effect of cations belonged to the salt solutions. Also, complexation between cations with high ionic charge and carboxylate groups is too easy that limits relaxation of hydrogel network chains [21, 22]. Swelling percent of the hydrogel composite including 10 wt% sepiolite in different salt solutions with same concentration is shown in Figure 3b. Swelling percent of the hydrogel composite in NaCl and $CaCl_2$ solutions was almost same with its swelling percent in water. However, swelling capacity of the hydrogel composite significantly decreased in $FeCl_3$ solution. Compared to Na^+ and Ca^{2+} ions, complexing ability of Fe^{3+} ions with $-COO^-$ groups is high that decreased water diffusion into the hydrogel composite structure.

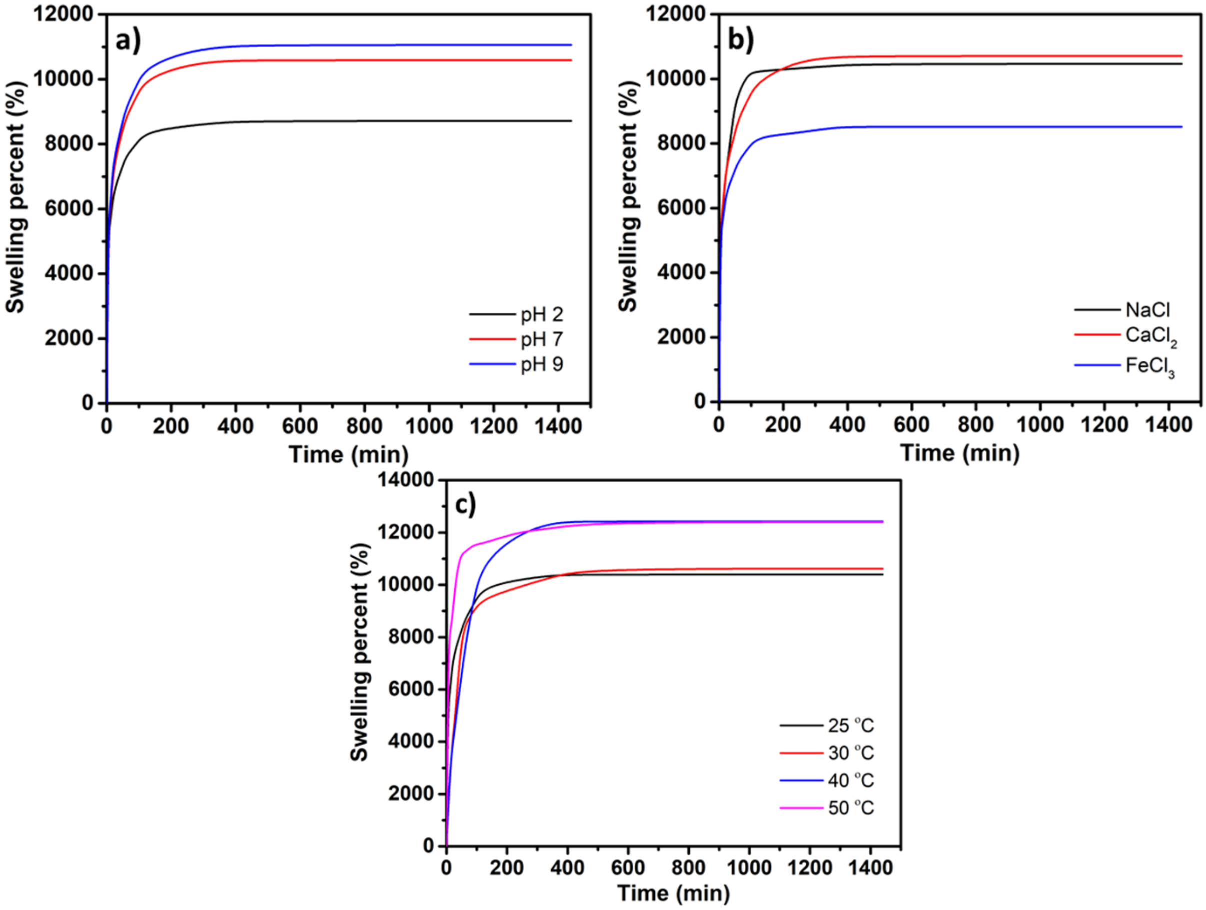

Figure 3. Swelling percent of the hydrogel composite including 10 wt% sepiolite under the effect of different **a)** pH values, **b)** salt solutions and **c)** temperatures

Swelling percent of the hydrogel composite including 10 wt% sepiolite as a function of temperature is shown in Figure 3c. The temperature rising up to 40 °C provided to increase swelling capacity of the hydrogel (~12000%) that was attributed to relaxation of hydrogel network chains as well as strong interactions of water molecules with –OH and $-COO^-$ functional groups of hydrogels [23, 24]. In case of 50 °C, a slight decrease in swelling percent of the hydrogel composite was identified. At high temperatures, water release can be dominant which decreases swelling capacity of hydrogels.

3.2. FTIR analyses

FTIR spectrum of the hydrogel and hydrogel composite including 10 wt% sepiolite shows successful synthesis of the materials (Figure 4). The peaks between 3400 cm^{-1} and 3600 cm^{-1} indicated –OH stretching vibrations [25]. The broad peaks centered on 3182 cm^{-1} and 3343 cm^{-1} were attributed to N-H stretching vibrations of amide groups [26]. C-H asymmetric stretching vibrations placed in hydrogel network chains and cross-linking points were observed at about 2932 cm^{-1}. The peak at 1663 cm^{-1} was contributed to –OH stretching vibrations [27]. $-COO^-$ asymmetric and symmetric stretching vibrations were determined at 1549 cm^{-1} and 1408 cm^{-1}, respectively [28]. The peak at 1450 cm^{-1} was originated from C-N stretching vibrations which confirm amide groups. The peaks from 1100 cm^{-1} to 1400 cm^{-1} was related to C-N deformation vibrations and CH_2 groups in general [29]. The peak belonged to C-H bending vibrations was specified at 666 cm^{-1}. In spite of similar FTIR spectrum of the hydrogel and hydrogel composite, the peak at 1058 cm^{-1} assigned to Si-O-Si bonds of sepiolite appeared in FTIR spectrum of the hydrogel composite [30].

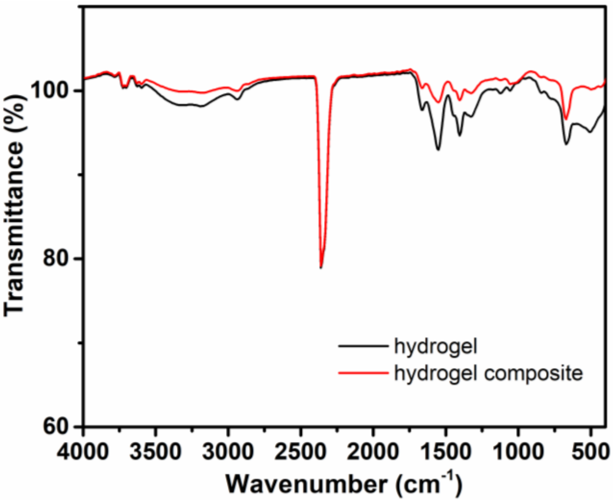

Figure 4. FTIR spectrum of the hydrogel and hydrogel composite including 10 wt% sepiolite

3.3. SEM analyses

SEM image of the hydrogel and hydrogel composite including 10 wt% sepiolite is shown in Figure 5. The hydrogel surface was smoother than that of the hydrogel composite (Figure 5a). In the presence of sepiolite, layered structure of the hydrogel composite with no agglomeration was observed (Figure 5b). Uniform dispersion of sepiolite and its layered structure had synergistic effects on the water diffusion into the hydrogel network. In literature studies, it is indicated that regular layers of clays in a hydrogel network generally increases swelling capacity of hydrogels [31, 32].

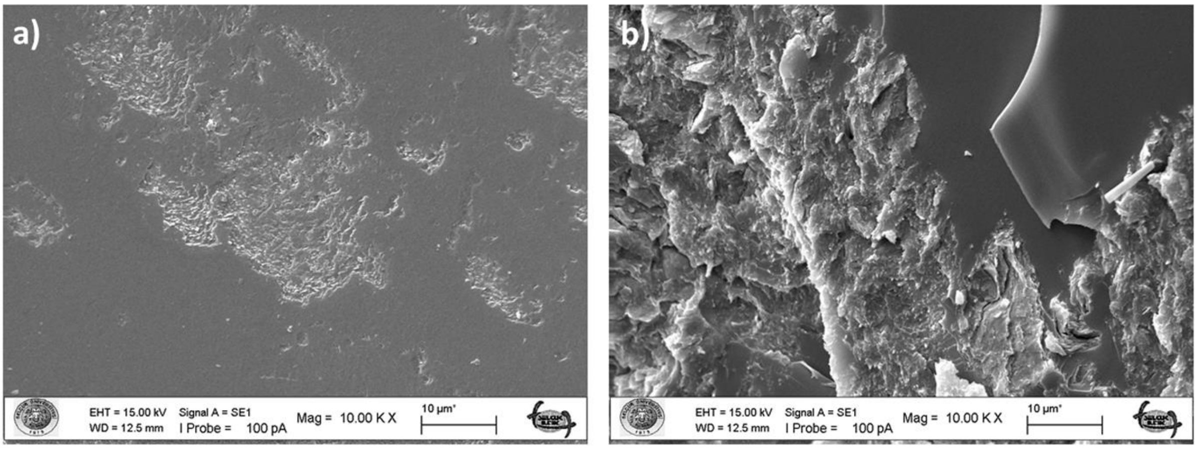

Figure 5. SEM image of the hydrogel and hydrogel composite including 10 wt% sepiolite

3.4. TGA analyses

TGA curve of the hydrogel and hydrogel composite including 10 wt% sepiolite is shown in Figure 6. Until 200 °C, evaporation of water molecules from the samples resulted in mass loss [33]. The sharp decrease in the TGA curve of the hydrogel was observed at about 315 °C that was related to decomposition of polymeric side chains [29]. The incorporation of sepiolite into the hydrogel network provided to increase decomposition temperatures of the hydrogel network owing to the heat barrier effect of the sepiolite. The residue of the hydrogel at 600 °C was increased by 5% in the presence of sepiolite. Many studies in literature also reveal that the addition of clay type fillers has positive effects on the thermal stability of a hydrogel network [34-36].

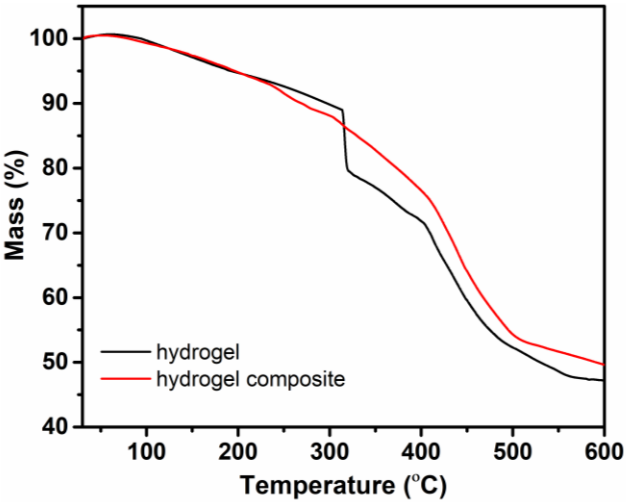

Figure 6. TGA curve of the hydrogel and hydrogel composite including 10 wt% sepiolite

4. CONCLUSIONS

In this study, the hydrogels were synthesized by free radical solution polymerization. First, the effect of acrylamide/sodium acrylate mole ratio and ethylene glycol dimethacrylate content on the swelling percent of the hydrogel in water was investigated. The highest swelling percent of the hydrogel was determined in the case of acrylamide/sodium acrylate mole ratio: 1-3 and ethylene glycol dimethacrylate content: 0.05 mL. With the incorporation of different amount of sepiolite (1 wt%; 3 wt%; 5 wt%; 10 wt%) into the hydrogel network, the hydrogel composites were successfully prepared. Swelling percent of the hydrogel increased with increasing amount of sepiolite. Moreover, the hydrogel composite reached to equilibrium swelling point with the 10 wt% sepiolite addition in a shorter time. Different swelling behaviour of the hydrogel composite at various pH values and temperatures showed that the hydrogel composite was pH and temperature responsive material. The lowest swelling percent of the hydrogel composite was identified in $FeCl_3$ solution when compared to NaCl and $CaCl_2$ solutions.

The presence of the characteristic peaks in the FTIR spectrum of the acrylamide-sodium acrylate based hydrogel composite was indication of the successfully preparation of the composite with the combination of hydrogel network and sepiolite. Layered structure of the hydrogel composite with no agglomeration was observed in the SEM image of the hydrogel composite. And also, TGA analyses revealed that sepiolite addition increased thermal stability of the hydrogel network.

The results showed that the hydrogel composite with the advantages such as high swelling percent, pH and temperature responsive ability and high thermal stability can be utilized in various fields such as tissue engineering, drug delivery and biosensors.

Declaration of Ethical Standards

The authors declare that all ethical guidelines including authorship, citation, data reporting, and publishing original research are followed.

Credit Authorship Contribution Statement

Firdevs Çirli: Conceptualization, Investigation, Methodology, Writing-original draft. **Gülcihan Güzel Kaya:** Conceptualization, Methodology, Writing – review & editing. **Hüseyin Deveci:** Conceptualization, Funding acquisition, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Funding / Acknowledgements

This study was supported by the Konya Technical University Coordinatorship of Scientific Research Projects (Grant number: 211016066).

Data Availability

Data will be made available on request.

REFERENCES

[1] W. A. Laftah, S. Hashim, and A. N. Ibrahim, "Polymer Hydrogels: A Review," Polymer-Plastics Technology and Engineering, vol. 50, no. 14, pp. 1475-1486, 2011.

[2] H. Huang, X. Qi, Y. Chen, and Z. Wu, "Thermo-sensitive hydrogels for delivering biotherapeutic molecules: A review," Saudi Pharmaceutical Journal, vol. 27, no. 7, pp. 990-999, 2019.

[3] M. Champeau, D. A. Heinze, T. N. Viana, E. R. de Souza, A. C. Chinellato, and S. Titotto, "4D Printing of Hydrogels: A Review," Advanced Functional Materials, vol. 30, no. 31, p. 1910606, 2020.

[4] O. Erol, A. Pantula, W. Liu, and D. H. Gracias, "Transformer Hydrogels: A Review," Advanced Materials Technologies, vol. 4, no. 4, p. 1900043, 2019.

[5] E. Karadağ, H. Ödemiş, S. Kundakçi, and Ö. B. Üzüm, "Swelling Characterization of Acrylamide/Zinc Acrylate/Xanthan Gum/Sepiolite Hybrid Hydrogels and Its Application in Sorption of Janus Green B from Aqueous Solutions," Advances in Polymer Technology, vol. 35, no. 3, pp. 248-259, 2016.

[6] P. Lavrador, M. R. Esteves, V. M. Gaspar, and J. F. Mano, "Stimuli ‐ Responsive Nanocomposite Hydrogels for Biomedical Applications," Advanced Functional Materials, vol. 31, no. 8, p. 2005941, 2020.

[7] S. Rafieian, H. Mirzadeh, H. Mahdavi, and M. E. Masoumi, "A review on nanocomposite hydrogels and their biomedical applications," Science and Engineering of Composite Materials, vol. 26, no. 1, pp. 154-174, 2019.

[8] E. Yilmaz, G. Guzel Kaya, and H. Deveci, "Preparation and characterization of pH-sensitive semi-interpenetrating network hybrid hydrogels with sodium humate and kaolin," Applied Clay Science, vol. 162, pp. 311-316, 2018.

[9] S. A. Khan, M. F. Siddiqui, and T. A. Khan, "Synthesis of Poly(methacrylic acid)/Montmorillonite Hydrogel Nanocomposite for Efficient Adsorption of Amoxicillin and Diclofenac from Aqueous Environment: Kinetic, Isotherm, Reusability, and Thermodynamic Investigations," ACS Omega, vol. 5, no. 6, pp. 2843-2855, 2020.

[10] S. J. Peighambardoust, O. Aghamohammadi-Bavil, R. Foroutan, and N. Arsalani, "Removal of malachite green using carboxymethyl cellulose-g-polyacrylamide/montmorillonite

nanocomposite hydrogel," International Journal of Biological Macromolecules, vol. 159, pp. 1122-1131, 2020.

[11] B. Thakur et al., "Designing of bentonite based nanocomposite hydrogel for the adsorptive removal and controlled release of ampicillin," Journal of Molecular Liquids, vol. 319, p. 114166, 2020.

[12] D. Saraydın, H. N. Öztop, and C. Hepokur, "Nanocomposite smart hydrogel based on sepiolite nanochannels/N-isopropyl acrylamide/itaconic acid/acrylamide for invertase immobilization," Polymer-Plastics Technology and Materials, vol. 60, no. 1, pp. 25-36, 2021.

[13] H. N. Oztop, C. Hepokur, and D. Saraydin, "Acrylamide-sepiolite based composite hydrogels for immobilization of invertase," Journal of Food Science, vol. 74, no. 7, pp. N45-9, 2009.

[14] R. R. Palem et al., "Physicochemical characterization, drug release, and biocompatibility evaluation of carboxymethyl cellulose-based hydrogels reinforced with sepiolite nanoclay," International Journal of Biological Macromolecules, vol. 178, pp. 464-476, 2021.

[15] S. Kordjazi, K. Kamyab, and N. Hemmatinejad, "Super-hydrophilic/oleophobic chitosan/acrylamide hydrogel: an efficient water/oil separation filter," Advanced Composites and Hybrid Materials, vol. 3, no. 2, pp. 167-176, 2020.

[16] E. Karadağ and Ö. B. Üzüm, "A study on water and dye sorption capacities of novel ternary acrylamide/sodium acrylate/PEG semi IPN hydrogels," Polymer Bulletin, vol. 68, no. 5, pp. 1357-1368, 2011.

[17] K. Kabiri, H. Omidian, S. A. Hashemi, and M. J. Zohuriaan-Mehr, "Synthesis of fast-swelling superabsorbent hydrogels: effect of crosslinker type and concentration on porosity and absorption rate," European Polymer Journal, vol. 39, no. 7, pp. 1341-1348, 2003.

[18] F. Santiago, A. E. Mucientes, M. Osorio, and F. J. Poblete, "Synthesis and swelling behaviour of poly (sodium acrylate)/sepiolite superabsorbent composites and nanocomposites," Polymer International, vol. 55, no. 8, pp. 843-848, 2006.

[19] Y. Huang, M. Zeng, J. Ren, J. Wang, L. Fan, and Q. Xu, "Preparation and swelling properties of graphene oxide/poly(acrylic acid-co-acrylamide) super-absorbent hydrogel nanocomposites," Colloids and Surfaces A: Physicochemical and Engineering Aspects, vol. 401, pp. 97-106, 2012.

[20] Y. Bao, J. Ma, and N. Li, "Synthesis and swelling behaviors of sodium carboxymethyl cellulose-g-poly(AA-co-AM-co-AMPS)/MMT superabsorbent hydrogel," Carbohydrate Polymers, vol. 84, no. 1, pp. 76-82, 2011.

[21] H. Namazi, M. Hasani, and M. Yadollahi, "Antibacterial oxidized starch/ZnO nanocomposite hydrogel: Synthesis and evaluation of its swelling behaviours in various pHs and salt solutions," International Journal of Biological Macromolecules, vol. 126, pp. 578-584, 2019.

[22] W. Tanan, J. Panichpakdee, and S. Saengsuwan, "Novel biodegradable hydrogel based on natural polymers: Synthesis, characterization, swelling/reswelling and biodegradability," European Polymer Journal, vol. 112, pp. 678-687, 2019.

[23] K. S. V. P. Chandrika, A. Singh, A. Rathore, and A. Kumar, "Novel cross linked guar gum-g-poly(acrylate) porous superabsorbent hydrogels: Characterization and swelling behaviour in different environments," Carbohydrate Polymers, vol. 149, pp. 175-185, 2016.

[24] M. R. Jozaghkar, A. Sepehrian Azar, and F. Ziaee, "Preparation, Characterization, and swelling study of N,N′-dimethylacrylamide/acrylic acid amphiphilic hydrogels in different conditions," Polymer Bulletin, vol. 79, no. 7, pp. 5183-5195, 2022.

[25] Y. M. Mohan, J. P. Dickson, and K. E. Geckeler, "Swelling and diffusion characteristics of novel semi-interpenetrating network hydrogels composed of poly[(acrylamide)- co-(sodium acrylate)] and poly[(vinylsulfonic acid), sodium salt]," Polymer International, vol. 56, no. 2, pp. 175-185, 2007.

[26] Y. M. Mohan, T. Premkumar, D. K. Joseph, and K. E. Geckeler, "Stimuli-responsive poly(N-isopropylacrylamide-co-sodium acrylate) hydrogels: A swelling study in surfactant and polymer solutions," Reactive and Functional Polymers, vol. 67, no. 9, pp. 844-858, 2007.

[27] M. M. Ghobashy et al., "Characterization of Starch-based three components of gamma-ray cross-linked hydrogels to be used as a soil conditioner," Materials Science and Engineering: B, vol. 260, p. 114645, 2020.

[28] J. Zhang, L. Wang, and A. Wang, "Preparation and Swelling Behavior of Fast-Swelling Superabsorbent Hydrogels Based On Starch-g-Poly(acrylic acid-co-sodium acrylate)," Macromolecular Materials and Engineering, vol. 291, no. 6, pp. 612-620, 2006.

[29] F. B. Santos, N. T. Miranda, M. I. R. B. Schiavon, L. V. Fregolente, and M. R. Wolf Maciel, "Thermal degradation kinetic of poly(acrylamide-co-sodium acrylate) hydrogel applying isoconversional methods," Journal of Thermal Analysis and Calorimetry, vol. 146, no. 6, pp. 2503-2514, 2021.

[30] A. Olad, M. Eslamzadeh, and A. Mirmohseni, "Ion crosslinked poly(acrylic acid-co-acrylamide)/poly(vinyl alcohol)/Cloisite 15A nanocomposite hydrogels as potential wound dressing films: Effect of clay content on water absorption kinetic and mechanical properties," Polymer Composites, vol. 40, no. 5, pp. 1762-1773, 2019.

[31] S. Zhumagaliyeva, R. Iminova, G. Kairalapova, M. M. Beysebekov, M. K. Beysebekov, and Z. Abilov, "Composite Polymer-Clay Hydrogels Based on Bentonite Clay and Acrylates: Synthesis, Characterization and Swelling Capacity," Eurasian Chemico-Technological Journal, vol. 19, no. 3, p. 279, 2017.

[32] R. Ianchis et al., "Novel Hydrogel-Advanced Modified Clay Nanocomposites as Possible Vehicles for Drug Delivery and Controlled Release," Nanomaterials (Basel), vol. 7, no. 12, 2017.

[33] S. G. Abd Alla, R. H. Helal, A. A. F. Wasfy, and A. W. M. El-Naggar, "Structure-property and swelling behavior of electron beam irradiated poly(vinyl alcohol)/acrylamide/sodium montmorillonite clay composites," Journal of Applied Polymer Science, vol. 121, no. 5, pp. 2634-2643, 2011.

[34] E. Farid, E. A. Kamoun, T. H. Taha, A. El-Dissouky, and T. E. Khalil, "PVA/CMC/Attapulgite Clay Composite Hydrogel Membranes for Biomedical Applications: Factors Affecting Hydrogel Membranes Crosslinking and Bio-evaluation Tests," Journal of Polymers and the Environment, vol. 30, no. 11, pp. 4675-4689, 2022.

[35] S. Datta Chaudhuri, A. Mandal, A. Dey, and D. Chakrabarty, "Tuning the swelling and rheological attributes of bentonite clay modified starch grafted polyacrylic acid based hydrogel," Applied Clay Science, vol. 185, p. 105405, 2020.

[36] L. Bounabi, N. B. Mokhnachi, N. Haddadine, F. Ouazib, and R. Barille, "Development of poly(2-hydroxyethyl methacrylate)/clay composites as drug delivery systems of paracetamol," Journal of Drug Delivery Science and Technology, vol. 33, pp. 58-65, 2016.