Afyon Kocatepe Üniversitesi Fen ve Mühendislik Bilimleri Dergisi

Afyon Kocatepe University Journal of Science and Engineering

AKÜ FEMÜBİD **23** (2023) 045701 (984-990) AKU J. Sci. Eng. **23** (2023) 045701 (984-990)

DOI: 10.35414/ akufemubid.1247090

Araştırma Makalesi/Research Article

Characterization of Stimuli-Responsive Acrylamide/Sodium Methacrylate/Kaolin Semi-Interpenetrating Polymer Network Composite Hydrogels

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Geliş Tarihi: 03.02.2023 Kabul Tarihi: 31.07.2023

Keywords

Composite hydrogel; Semi-interpenetrating; Swelling properties; Stimuli-responsive

Abstract

With the advantages of their self-healing, stimuli-response ability, water sorption capacity and shape memory, hydrogels have been commonly utilized. However, new strategies have been developed to enhance mechanical and thermal properties of hydrogels in addition to increase their water sorption. In this study, stimuli-responsive acrylamide/sodium methacrylate based hydrogels were synthesized with the optimization of sodium methacrylate amount by free radical polymerization. With the incorporation of optimum amount of polyethylene glycol 400 (PEG-400) into the hydrogel network, semi-interpenetrating polymer network (semi-IPN) hydrogels were prepared. With the addition of kaolin, swelling properties of the semi-IPN composite hydrogels were investigated in water under the effect of different pH and temperature. Maximum swelling percent of the semi-IPN composite hydrogels was determined as 24214% at pH 7 and 25 °C. Fourier transform infrared spectroscopy (FTIR) analyses revealed that hydrogel samples were successfully synthesized. Morphological structure of hydrogel samples was examined by scanning electron microscopy (SEM) analyses. Both of the water motion through the hydrogel layered structure and water diffusion into the pores made the semi-IPN composite hydrogel more swollen material compared to the acrylamide/sodium methacrylate based hydrogel.

Uyarı-Cevap Akrilamid/Sodyum Metakrilat/Kaolin Yarı-İç İçe Geçmiş Polimer Ağ Kompozit Hidrojellerinin Karakterizasyonu

Anahtar kelimeler

Kompozit hidrojel; Yarı-iç içe geçmiş ağ; Şişme özellikleri; Uyarı-cevap

Öz

Kendi kendini onarma, uyarı-cevap yeteneği, su sorpsiyonu kapasitesi ve şekil hafızası avantajları ile hidrojeller yaygın bir şekilde kullanılmaktadır. Ancak hidrojellerin su sorpsiyonuna ek olarak mekanik ve termal özelliklerini de geliştirmek amacıyla yeni stratejiler geliştirilmiştir. Bu çalışmada sodyum metakrilat miktarının optimizasyonu yapılarak serbest radikal polimerizasyonu ile akrilamit/sodyum temelli uyarı-cevap hidrojelleri sentezlenmiştir. Hidrojel ağına optimum miktarda polietilen glikol 400 (PEG-400) eklenmesi ile yarı-iç içe geçmiş polimer ağ (semi-IPN) hidrojelleri hazırlanmıştır. Kaolin ilavesi ile semi-IPN kompozit hidrojellerinin farklı pH ve sıcaklık etkisi altında şişme özellikleri incelenmiştir. Semi-IPN kompozit hidrojelinin pH 7 ve 25 °C'de maksimum şişme yüzdesi 24214% olarak belirlenmiştir. Fourier dönüşümlü kızılötesi spektroskopisi (FTIR) analizleri hidrojel örneklerinin başarılı bir şekilde sentezlendiğini ortaya çıkarmıştır. Hidrojel örneklerinin morfolojik yapısı taramalı elektron mikroskobu (SEM) analizleri ile incelenmiştir. Hem hidrojelin tabakalı yapısında suyun ilerleyişi hem de suyun gözeneklere difüzyonu, semi-IPN kompozit hidrojelini akrilamit/sodyum metakrilat temelli hidrojel ile karşılaştırıldığında daha çok şişen bir malzeme yapmıştır.

1. Introduction

Hydrogels are defined as hydrophilic polymer network which swells in water or various biological fluids. Cross-linked structure of hydrogels provides insolubility in aqueous media (Laftah *et al.* 2011). Without using a cross-linker, physically cross-linked hydrogels are synthesized by hydrogen bonds, self-assembly of polymers, crystallization, ionic interactions and protein interaction. Through covalent bonding between polymer chains, energy radiation and free radical polymerization, chemically cross-linked hydrogels are synthesized (Hennink and van Nostrum 2012). Depending on preparation methods, hydrogels are separated into four groups: homo-polymers, co-polymers, semi-interpenetrating networks (semi-IPN) and interpenetrating networks. Semi-IPN hydrogels consist of one linear polymer penetrated into another cross-linked structure. Semi-IPN make hydrogels rapid responsive materials to various stimuli (Ullah *et al.* 2015).

Stimuli-responsive hydrogels are promising materials for drug delivery, biotechnology and biomedical applications (Hoffman 2012). Against to physical stimuli (temperature, pressure, mechanical stress, electrical and magnetic field) and chemical stimuli (pH, chemical agents and ionic parameters), stimuli-responsive hydrogels can show changes including swelling, shrinkage or discoloration. Moreover, dual responsive hydrogels which respond to two stimuli are another smart hydrogels (Khan *et al.* 2016).

With the advantages of their self-healing, stimuli response ability, water sorption capacity and shape memory, hydrogels have been commonly utilized. However, new strategies have been developed to enhance mechanical and thermal properties of hydrogels in addition to increase their water sorption (Mahinroosta *et al.* 2018). Preparation of composite hydrogels with the combination of hydrogel network and filler including metals, metal oxides, clays and carbon based materials is one of the most effective strategies to obtain hydrogel networks with better properties (Hu *et al.* 2022, Sivakumar and Lee 2022). Composite hydrogels are generally prepared by five methods: (1) hydrogel synthesis in a filler suspension, (2) filler impregnation into hydrogel network, (3) dual synthesis of functional filler and hydrogel network, (4) hydrogel synthesis in the presence of filler as cross-linker and (5) hydrogel synthesis through cross-linking of polymers, filler and other precursors *(*Pereira *et al.* 2021).

Incorporation of clays such as montmorillonite, bentonite, mica etc. into hydrogel structure is a significant approach to improve mechanical properties, thermal stability and swelling capacity (Shirsath *et al.* 2013). Kaolin consisting of tetrahedral silicon and octahedral alumina flakes is a cheap and abundant natural material which is generally evaluated in ceramic, dye, paper industry and waste treatment (Pourjavadi *et al.* 2007a, Sirousazar *et al.* 2012). Kaolin represents good surface activity which provides easy surface modification or functionalization (Huang *et al.* 2022).

This study focused on synthesis of stimuli-responsive semi-IPN hydrogels including kaolin as a filler. In the first stage, acrylamide/sodium methacrylate based composite hydrogels were prepared by free radical polymerization. In the second stage, swelling properties of the composite hydrogels were examined in distilled water. At different pH and temperature, their swelling percent was also investigated to reveal stimuli response properties of the composite hydrogels. Structural and morphological characteristics of the composite hydrogels were determined in the last stage.

2. Materials and Method

Kaolin ($Al_2Si_2O_5(OH)_4$) obtained from Industrial Minerals Industry, Turkey was used as filler. Acrylamide (monomer), sodium methacrylate (monomer), *N*,*N*-methylenebisacrylamide (cross-linker), *N*,*N*,*N*',*N*'-tetramethylethylenediamine (accelerator) and ammonium persulfate (initiator) were purchased from Sigma-Aldrich. Polyethylene glycol 400 (PEG-400) obtained from Sigma-Aldrich was used in the formation of semi-IPN.

2.1 Preparation of semi-IPN composite hydrogels

Acrylamide/sodium methacrylate hydrogels were

firstly synthesized using free radical polymerization technique. Acrylamide solution was mixed with sodium methacrylate (1, 5 and 10 wt%) at 40 °C. With the addition of 0.01 g cross-linker, 0.01 g initiator and 100 µL accelerator, the monomer solution was stirred under the reflux condenser. Reaction between initiator and accelerator results in the formation of sulfate and hydroxyl radicals which initiate polymerization (Dragan and Apopei 2011). Following to cross-linking, gel formation was seen at approximately 50 °C. To remove impurities and unreacted precursors, the gel was washed, and then dried until the constant mass at 50 °C.

To synthesize acrylamide/sodium methacrylate semi-IPN hydrogels, PEG-400 (0.45, 0.90 and 1.35 mL/g) was added to monomer solution and gel was formed with the same method as mentioned above.

With the incorporation of kaolin (0.01, 0.02 and 0.04 g) into monomer solution, acrylamide/sodium methacrylate/kaolin composite hydrogels were prepared with the same method as mentioned above. Before the kaolin addition into the monomer solution, kaolin dispersion was provided in the 5 mL of distilled water for 30 min using ultrasonic bath.

Lastly, acrylamide/sodium methacrylate/kaolin semi-IPN composite hydrogels were prepared with the combination of optimum amount of PEG-400 (1.35 mL/g) and kaolin (0.04 g) with the same method as mentioned above.

2.2 Characterization of semi-IPN composite hydrogels

Fourier transform infrared spectroscopy (FTIR) spectra (4000-400 cm^{-1}) were recorded by Bruker Vertex 70 spectrometer. Scanning electron microscopy (SEM) analyses of the thin gold layer coated samples were conducted by SM Zeiss LS-10 equipment.

2.3 Swelling study of semi-IPN composite hydrogels

Swelling properties of the samples were studied with gravimetric method. Dried sample was dipped in distilled water (about pH 7) at 25 °C. Swollen sample was withdrawn from the water and excess water on the sample surface was removed using filter paper at certain time intervals. After weighing the swollen sample, swelling percent (S%) of the sample was calculated by Eq. (1) (Sujan *et al.* 2020):

$$S\ (\%) = \frac{m_1 - m_0}{m_0}\ x\ 100 \qquad (1)$$

where m_1 and m_0 shows the swollen and dry sample mass, respectively.

Furthermore, the swelling capacity of the samples was studied under the effect of different pH (2, 5 and 9) and temperature (40 and 60 °C).

3. Results and Discussion

Figure 1 shows swelling behaviour of the acrylamide/sodium methacrylate hydrogels depending on sodium methacrylate ratio. While using low content of sodium methacrylate, lower swelling percent of the hydrogel was observed. With increasing amount of sodium acrylate, synergistic effects on the swelling behaviour of the hydrogels were determined. Maximum swelling percent was 18165% in the presence of 10 wt% sodium methacrylate. The ionic groups in the sodium methacrylate (-COONa) led to the formation of hydrophilic groups, which increases both the swelling capacity and swelling rate of the hydrogels. Moreover, an increase in the ionic groups by the completely ionization of the salt groups makes hydrogel chains flexible which are effective in more water uptake (Murali Mohan *et al.* 2005, Üzüm and Karadağ 2011).

Influence of PEG-400 on the water uptake of the acrylamide/sodium methacrylate semi-IPN hydrogels including 10 wt% sodium methacrylate is shown in Figure 2. It was clear that the swelling percent of the semi-IPN hydrogels reached to approximately 32630% with the incorporation of 1.35 mL/g PEG-400 in 1440 min. An increase in the swelling percent of the semi-IPN hydrogels was contributed to acting of PEG-400 molecules like a pore-forming agent. Formation of porous structure of hydrogels provides easy water diffusion into the hydrogel network which

increases swelling capacity (Dogu and Okay 2006). And also, hydrophilic groups of PEG-400 molecules tend to combine with water molecules that affects swelling behaviour of hydrogels positively (Xu *et al.* 2016).

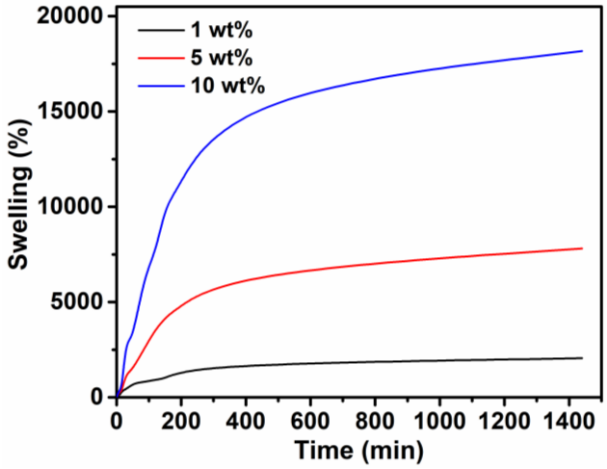

Figure 1. Swelling of the acrylamide/sodium methacrylate hydrogels as a function of sodium methacrylate ratio

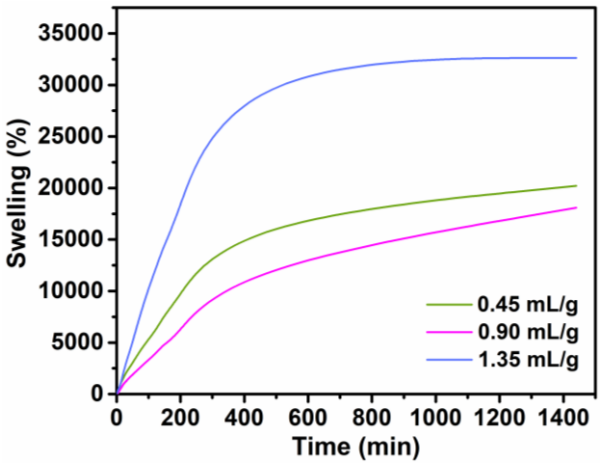

Figure 2. Swelling of the acrylamide/sodium methacrylate semi-IPN hydrogels including 10 wt% sodium methacrylate depending on PEG-400 content

Swelling behaviour of the acrylamide/sodium methacrylate composite hydrogels including 10 wt% sodium methacrylate was investigated as a function of kaolin content (Figure 3). In case of using higher kaolin content, higher swelling percent of the composite hydrogels was specified. Depending on kaolin content and hydrogel structure, swelling behaviour of hydrogels can change. Optimum amount of kaolin addition generally increases swelling capacity of hydrogels owing to functional groups of kaolin such as -OH groups and its layered structure which facilitates water diffusion (Dai and Huang 2017, Kaşgöz *et al.* 2008). However, a decrease in swelling capacity of hydrogels can be determined that is explained with two reasons: (1) acting of kaolin as a cross-linker and (2) restriction of polymer chain growth (Pourjavadi *et al.* 2008, Pourjavadi *et al.* 2007b). Kaolin incorporation into the hydrogel structure improved water uptake of the composite hydrogel in this study. The swelling percent of the composite hydrogel including 0.04 g kaolin was specified as about 36000%.

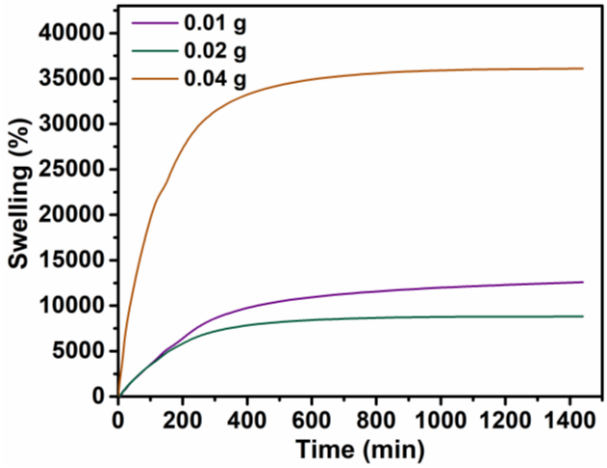

Figure 3. Swelling of the acrylamide/sodium methacrylate/kaolin composite hydrogels including 10 wt% sodium methacrylate depending on kaolin content

After optimizing amount of PEG-400 and kaolin, swelling behaviour of the acrylamide/sodium methacrylate/kaolin semi-IPN composite hydrogels including 10wt% sodium methacrylate was examined at different pH values. It was observed that the swelling percent of the semi-IPN composite hydrogels was lower at pH 2 than other pH values (Figure 4). At low pH, polymer chains connected each other by hydrogen bonding inhibited water uptake. Moreover, no significant impacts of -COOH groups in non-ionic form belonged to the semi-IPN composite hydrogel structure on the swelling capacity were specified. At pH 7, the semi-IPN composite hydrogels represented the highest swelling percent. An increase in the swelling capacity from pH 2 to pH 7 was contributed to $-COO^-$ anionic groups originated

from ionization of -COOH groups (Kalagasidis Krušić *et al.* 2012). Electrostatic repulsion forces between the $-COO^-$ groups promoted relaxation of polymer network leading high water diffusion into the polymer network (Murali Mohan *et al.* 2006). It was seen that swelling percent of the semi-IPN composite hydrogels decreased at high pH values. A decrease in the swelling percent of the semi-IPN composite hydrogels resulted from weak hydrogen bonding between polymer network and water molecules that caused release of water (Mohan *et al.* 2005).

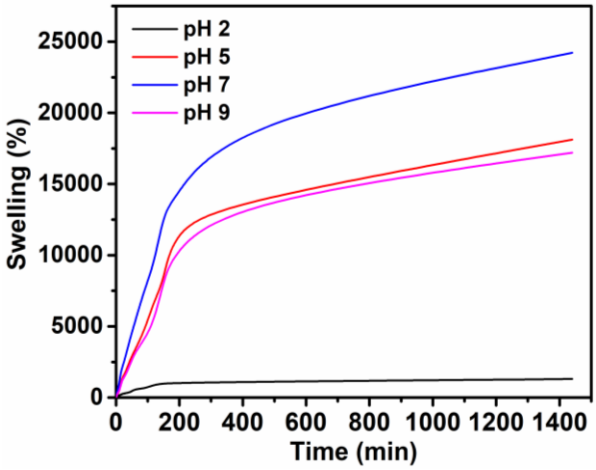

Figure 4. Swelling of the acrylamide/sodium methacrylate/kaolin semi-IPN composite hydrogels including 10 wt% sodium methacrylate at different pH

Swelling behaviour of the acrylamide/sodium methacrylate/kaolin semi-IPN composite hydrogels including 10wt% sodium methacrylate is shown at different temperature in Figure 5. An increase in temperature caused adverse effects on the swelling properties of the semi-IPN composite hydrogels. The hydrophilicity of the semi-IPN composite hydrogels may decrease with increasing temperature, as a result of disruption of hydrogen bonding (Boztepe *et al.* 2020). Furthermore, water release generally tends to prevail over water retention in case of high temperature (Tanan *et al.* 2019).

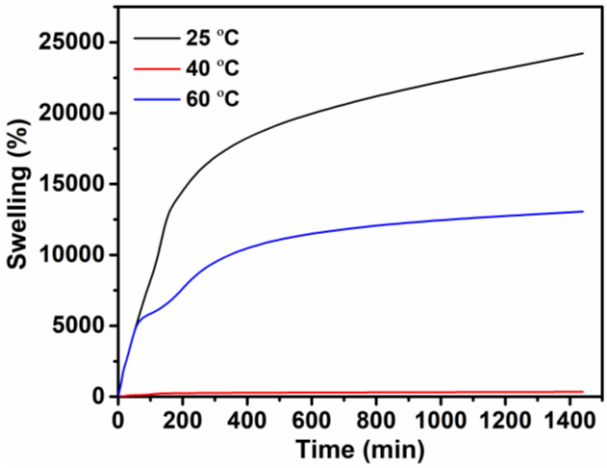

Figure 5. Swelling of the acrylamide/sodium methacrylate/kaolin semi-IPN composite hydrogels including 10 wt% sodium methacrylate at different temperature

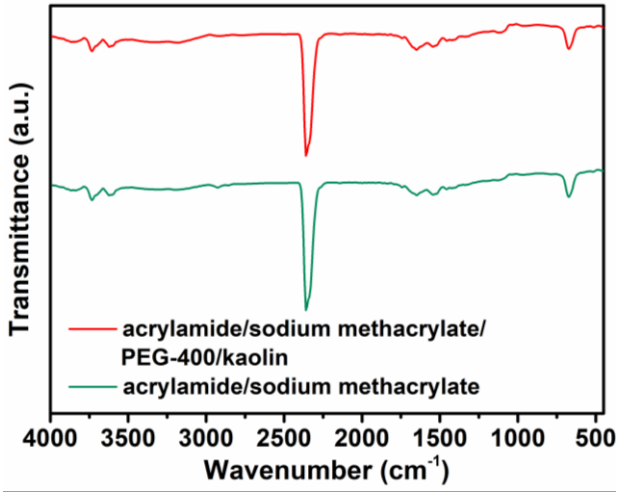

Figure 6. FTIR spectra of hydrogel samples

Figure 6 shows FTIR spectrum of the acrylamide/sodium methacrylate hydrogel including 10 wt% sodium methacrylate and acrylamide/sodium methacrylate/kaolin semi-IPN composite hydrogel including 10 wt% sodium methacrylate. The peaks at about 3600 cm^{-1} and 3700 cm^{-1} were contributed to -OH stretching vibrations. The broad band with low intensity centered at 3170 cm^{-1} was associated with N-H stretching vibrations. The peaks originated from C-H asymmetric and symmetric stretching vibrations were observed at 2920 cm^{-1} and 2850 cm^{-1}, respectively (Wang *et al.* 2022). The peak at 1741 cm^{-1} was attributed to C=O bonding of sodium methacrylate. C=O bonding belonged to acrylamide resulted in formation of peak at 1653 cm^{-1}. The peaks at 1533 cm^{-1} and 1439 cm^{-1} were

assigned to -COO^- asymmetric and symmetric stretching vibrations, respectively. The peaks contributed to C-O stretching vibrations at 1103 cm^{-1} and C-H bending vibrations at 673 cm^{-1} were determined (Üzüm and Karadağ 2012). Adsorption of CO_2 molecules in the atmosphere caused a peak appearance at 2347 cm^{-1}.

SEM images of the acrylamide/sodium methacrylate hydrogel including 10 wt% sodium methacrylate and acrylamide/sodium methacrylate/kaolin semi-IPN composite hydrogel including 10 wt% sodium methacrylate are shown in Figure 7. The acrylamide/sodium methacrylate hydrogel had regular layered structure which provides water uptake easily (Nie *et al.* 2015). However, the semi-IPN composite hydrogel consisted of porous structure as well as layers. Porosity of the semi-IPN composite hydrogel due to PEG molecules promoted higher water diffusion. In other words, both of water motion through the layers and water diffusion into the pores made the semi-IPN composite hydrogel more swollen material (Huang *et al.* 2013, Wang *et al.* 2012).

4. Conclusion

Acrylamide/sodium methacrylate hydrogels were synthesized as a function of sodium methacrylate ratio using free radical polymerization technique. In case of 10 wt% sodium methacrylate, the swelling percent was specified as 18165% in water at room temperature. The semi-IPN hydrogels were prepared with the incorporation of optimum amount of PEG-400. The swelling percent of the semi-IPN hydrogels including 1.35 mL/g PEG-400 reached to 32630%. Kaolin was used as a filler for composite hydrogels and an increase in the water uptake of the composite hydrogels were observed with increasing amount of kaolin.

Stimuli-responsive properties of the semi-IPN composite hydrogel were examined under the influence of pH and temperature. Maximum swelling percent of the semi-IPN composite hydrogel was observed at pH 7. Moreover, the swelling percent of the semi-IPN composite hydrogel decreased with increasing temperature.

Characteristic chemical bonding of the samples was investigated by the FTIR analyses. SEM images supported higher swelling percent of the semi-IPN composite hydrogel than that of the acrylamide/sodium methacrylate hydrogel. Combination of water motion through the hydrogel layers and water diffusion into the hydrogel pores improved swelling capacity of the semi-IPN composite hydrogel.

The promising results showed that semi-IPN composite hydrogels were stimuli-responsive materials and can be utilized in many engineering fields and biomedical applications.

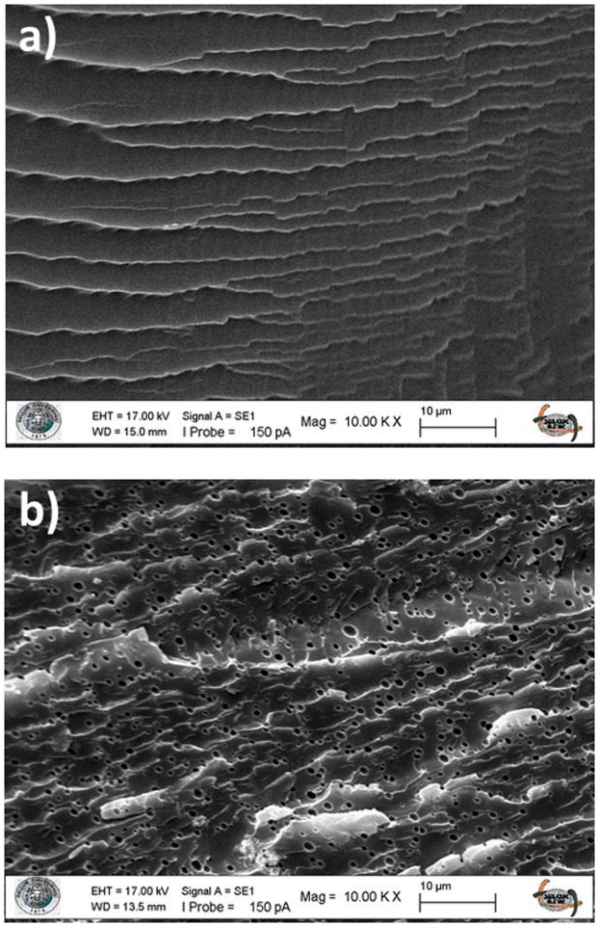

Figure 7. SEM image of the **a)** acrylamide/sodium methacrylate hydrogel and **b)** semi-IPN composite hydrogel including 10 wt% sodium methacrylate

Acknowledgement

This study was supported by the Konya Technical University Coordinationship of Scientific Research Projects with the grant number 191016039.

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