RPE | Radiation Physics & Engineering
A Peer-Reviewed Journal
Published by K.N. Toosi University of Technology
http://rpe.kntu.ac.ir
Research Article

Radiation Physics and Engineering 2024; 5(4):47–51

Synthesis and characterization of carboxymethyl cellulose/acrylic acid superabsorbent hydrogel by gamma irradiation

Mahsa Radmehr[a], Ahmad Poursattar Marjani[a], Azam Akhavan[b,*], Farahnaz Nasiri[b]

[a] *Department of Organic Chemistry, Faculty of Chemistry, Urmia University, Urmia, Iran*
[b] *Radiation Applications Research School, Nuclear Science and Technology Research Institute, Tehran, Iran*

HIGHLIGHTS

- Synthesis of Carboxymethyl Cellulose/Acrylic acid by gamma irradiation.
- Irradiation dose of 20 kGy can be considered suitable for the preparation of CMC/AAc.
- CMC/AAc SAPs synthesized with irradiation method may be used in medical applications specially in baby diapers.

ABSTRACT

In this study a super absorbent polymer (SAP) based on acrylic acid (AAc) and carboxymethyl cellulose (CMC), as an environmentally friendly material, was prepared using gamma irradiation. Gamma radiation was applied to synthesize CMC/AAc SAPs in the range of 5 to 20 kGy absorbed doses. Fourier Transform Infrared (FT-IR) spectroscopy was used to determine the polymerization and grafting monomer to CMC in SAP formation. The effect of radiation dose, CMC concentration on the gel content, swelling behavior and absorption under load (AUL) in water and saline solution were investigated. Based on the results with increasing irradiation dose from 10 to 20 kGy the water and saline solution absorption of the SAP decrease in SAPs containing 1 and 2% CMC, but increases in SAP containing 0.5% CMC. Also, by raise in the irradiation dose from 10 to 20 kGy AUL decreases. The results suggest that 0.5% CMC/AAc SAPs synthesized using the irradiation method may be suitable for medical applications.

KEYWORDS

Super absorbent polymer
Carboxy methyl cellulose
Gamma irradiation
Acrylic acid

HISTORY

Received: 24 July 2024
Revised: 28 August 2024
Accepted: 13 September 2024
Published: Autumn 2024

1 Introduction

Superabsorbent polymers (SAP) are three-dimensional, hydrophilic functional polymeric network systems that can absorb large amounts of water even under high pressure or temperature (Esposito et al., 1996). SAPs are widely used in various applications such as drug delivery, hygiene, foods, cosmetics, and agriculture (Zhou et al., 2011). In the health care products, the water absorption capacity is a very important parameter. This parameter is a function of the network structure, crosslinking density, hydrophilicity, and ionization of the functional groups (Hariharan and Peppas, 1993). To prepare this kind of products generally functional monomers such as acrylic acid, methacrylic acid, acrylamide, hydroxymethyl acrylamide, diacetone acrylamide are used because of their hydrophilicity and ionization of the functional groups (Zhang et al., 2021). The network structure is also related to hydrogel preparation method. Hydrogels can be prepared by various methods including chemical and radiation induced crosslinking. Ionizing radiation is a very convenient technique for the crosslinking and preparation of SAPs. An initiator, catalyst, and cross-linker are not required in radiation processing. The main advantage of this method is easy process control (Pérez-Álvarez et al., 2019). Rosiak and Ulanski provided an inclusive investigation of the synthesis of hydrogels through the irradiation of homopolymers in aqueous environments (Rosiak and Ulański, 1999). Numerous initial studies have been conducted on the radiation-induced synthesis of pure poly (acrylic acid) hydrogels. Furthermore, the radiolysis mechanism of poly (acrylic acid) in water has been thoroughly investigated. These studies mostly focused on the reaction mechanisms involved in the crosslinking and degradation processes of poly (acrylic acid) due to irradiation (Rosiak and Ulański, 1999).

Todays, superabsorbents specially with healthcare and medical applications are prepared with a natural poly-

*Corresponding author: azakhavan@aeoi.org.ir

https://doi.org/10.22034/rpe.2024.469540.1227

mer, such as cellulose, chitosan, starch, carrageenan and alginate due to their non-toxic nature and biocompatibility (Hien et al., 2005). CMC, a linear glycosidic macromolecule is the most popular and the cheapest cellulose ether that can also be used for this purpose. Several investigations have explored the swelling characteristics of CMC/AAc hydrogels that are cross-linked through chemical methods (Yu et al., 2014; Suo et al., 2007). But little work has been published on gel properties of radiation crosslinked of CMC/AAc SAP (Fekete et al., 2016). Furthermore, in above reports, irradiation conditions, radiation source, concentration of AAc solutions were different from each other. Obviously mentioned terms have the influence on the structure and subsequently swelling properties of the prepared hydrogels. Hence in this study we synthesized a biodegradable SAP by substituting a part of the acrylic acid content with CMC in various concentrations and irradiation conditions, different from the previous studies. The obtained hydrogels were characterized according to the gel content and swelling behavior. The structure of superabsorbents were determined by FT-IR spectroscopy.

2 Experimental

2.1 Materials

CMC (99.5% purity) was obtained from Sigma-Aldrich Co. AAc (99.5% purity) was acquired from Merck and kept in refrigerator prior to application. Sodium hydroxide (NaOH, 84%) was also obtained from Merck for the purpose of neutralization. Additionally, sodium chloride (NaCl) was purchased from Merck. Distilled water served as the medium for the polymerization and swelling experiments. All reagents utilized were of analytical grade and were employed without further purification.

2.2 Method

The CMC/AAc samples were poured in 20 ml vials. Irradiations were performed within a g-irradiation system using 60Co source (Gammacell-220), at a dose rate of 2.52 kGy.h^{-1} calibrated by Fricke dosimeters.

2.3 Preparation of SAPs

A beaker containing CMC (0.5%, 1%, and 2% wt) was combined with distilled water and stirred for one hour at ambient temperature. Next, a partially neutralized solution of acrylic acid was prepared, using NaOH for neutralization and mixed with CMC solution (15% AAc). The resulting mixture was transferred into glass test tubes, sealed, and subjected to gamma irradiation at 5, 10, 15, and 20 kGy absorbed doses. The resultant CMC/AAc SAPs, formed in a cylindrical configuration, was cut into small pieces and, after drying, was grinded.

Figure 1: AUL tester.

2.4 Characterization

2.4.1 Free swelling capacity (FSC)

The swelling capacity was measured using a free absorption measurement test conducted in both deionized water and a physiological saline solution (0.9% sodium chloride), employing the tea bag method. A sample of 0.1 g (W_1) of the superabsorbent material was immersed in 500 g of either deionized water or saline solution for a duration of thirty minutes, allowing the sample to achieve equilibrium swelling. Next, the bag was removed from the liquid, and excess fluid was eliminated by hanging the bag for a predetermined period before weighing it (W_2). A control bag, empty of the sample, experienced the same procedure and was weighed as well (W_0). The absorption capacity, or equilibrium swelling (g.g^{-1}), was determined using the following equation:

$$FSC = \frac{W_2 - W_0}{W_1} \quad (1)$$

2.4.2 Absorption under load (AUL)

To measure the absorbency under load (AUL) of SAPs, specifically the absorption rate of a 0.9% sodium chloride solution subjected to a pressure of 0.3 psi, a glass strainer with a diameter of 80 mm and a height of 7 mm was positioned within a Petri dish. The filter was secured to the end of a glass cylinder, which had an inner diameter of 63 mm, an outer diameter of 67 mm, and a height of 50 mm, using a metal fastener (Fig. 1). Subsequently, 0.5 grams of the superabsorbent material was regularly spread within the cylinder. A Teflon piston, also with a diameter of 63 mm, was then placed on the superabsorbent particles to maintain the specified pressure of 0.3 psi. Following this setup, saline solution was introduced into the Petri dish until the filter was fully submerged. To mitigate evaporation of the saline solution and to maintain its concentration, the entire apparatus was covered. After a duration of 60 minutes, the swollen superabsorbent sample was weighed, and the AUL value was calculated using

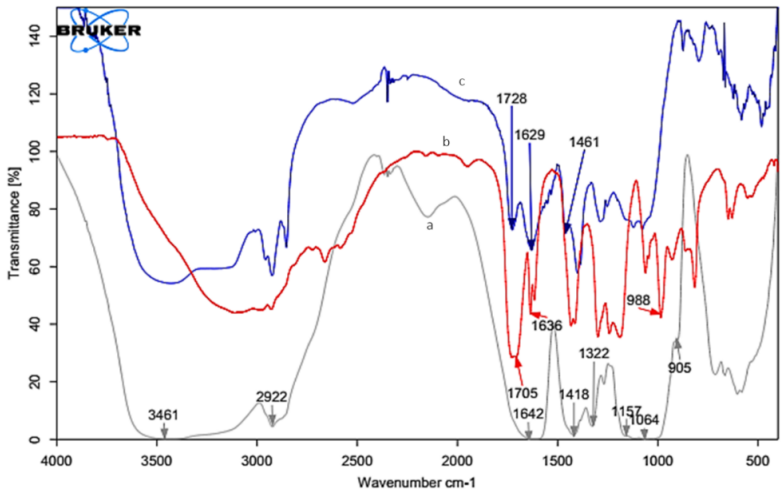

Figure 2: FT-IR spectra of CMC powder (a), Acrylic Acid (AAc) (b), and SAP from CMC/AAc(c).

Eq. (2) (Zohourian and Kabiri, 2008):

$$AUL = \frac{W_2 - W_1}{W_1} \tag{2}$$

where W_1 and W_2 are the weights of dried hydrogel and swollen hydrogel.

2.4.3 Determination of Gel Fraction

The SAP samples, which had reached a constant weight (W_i), were submerged in distilled water for a duration of 24 hours. Following this immersion, the samples were taken out of the distilled water and subsequently dried in a vacuum oven until a constant weight (W_1) was achieved. The gel fraction was then determined using the following calculation:

$$\text{Gel fraction}(\%) = \frac{W_1}{W_i} \times 100 \tag{3}$$

where W_1 is the weight of the dry sample after extraction in water, and W_i is the initial weight of the dry sample.

2.4.4 FT-IR spectroscopic analysis

The vibrational spectra were obtained using a Fourier Transform Infrared Spectrometer (FT-IR), TENSOR 27 model from Brucker, Germany. KBr disks prepared by combining KBr with a fine powder of the SAPs. The measurements were conducted across a frequency range of 500 to 4000 cm^{-1}.

3 Results and discussion

3.1 FT-IR Spectra of SAP and Identification

FT-IR spectroscopic analysis was employed to explain the characteristics of the samples. The FT-IR spectrum of pure CMC powder, AAc, and CMC/AAc has been presented in Fig. 2. Pure CMC had absorption bands related to O-H stretching at 3461 cm^{-1}, -CH_2^- stretching on anhydroglucose units at 2922 cm^{-1}, C=O carbonyl stretching in the anhydroglucose unit of the cellulose at 1642 cm^{-1}, C-OH in in-plane bending at 1418 cm^{-1}, OH bending vibration at 1322 cm^{-1}, C=O stretching from an asymmetric oxygen bridge at 1157 cm^{-1}, and ring stretching at 905 cm^{-1} (Fig. 2-a). These values were consistent with those reported by Rim Dusit et al. (Rimdusit et al., 2008) and Wang et al. (Wang et al., 2004). As shown in Fig. 2-c. the characteristic absorption bands of CMC at 1064 and 1157 cm^{-1} were obviously weakened after the reaction in the CMC/AAc composite hydrogel. Figure 2-b illustrates the spectra of AAc. The peak assigned to the vibration of H in C=C-H at 988 cm^{-1} is very clear, however, it disappears in the spectrum of the CMC/AAc showing that polymerization has occurred. Also, the peaks appeared at the 1636 and 1705 cm^{-1}, are assigned to C=C and C-O vibrations in AAc. In Fig. 2-c the new band at 1728 cm^{-1} (C=O stretch of COOH groups) showed the C=O stretch of the carbonyl group of polyacrylic acid, which was not present in the CMC spectrum. Also, in Fig. 2-c the band shift towards a less obvious wavenumber at 1629 cm^{-1} (which was at 1642 cm^{-1} for CMC) indicates the formation of copolymer hydrogels. These results also indicate that AAc monomers were grafted onto the CMC backbone.

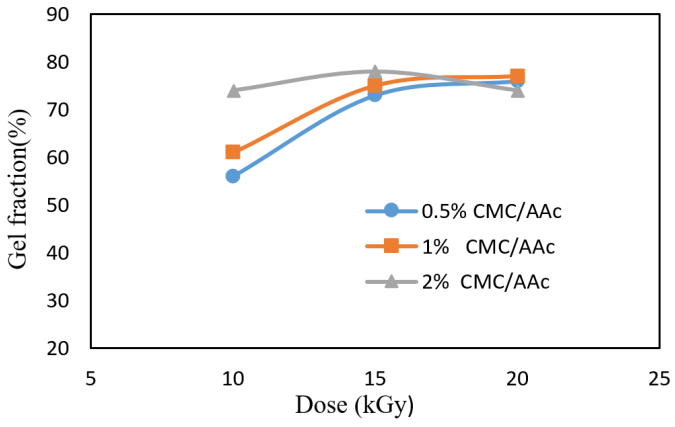

Figure 3: Effect of absorbed dose and concentration of CMC on the gel fraction of CMC/AAc SAP.

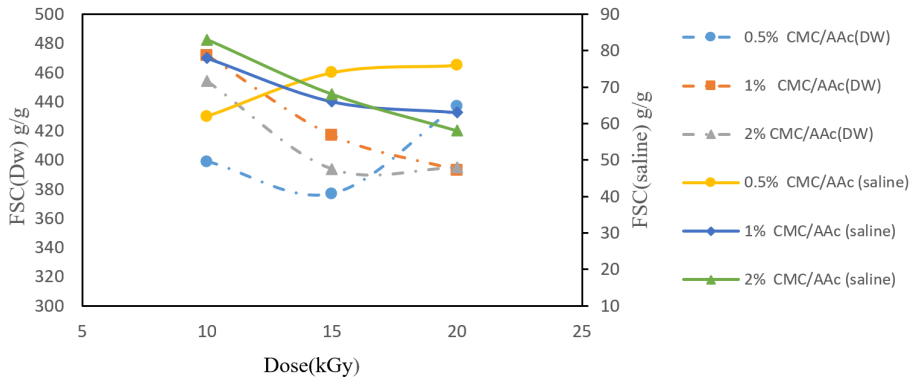

Figure 4: Effect of absorbed doses and CMC content on SAPs water absorption.

3.2 Gel fraction of SAP

The gel fraction of CMC/AAc SAPs prepared at the various irradiation doses with different concentrations of CMC was shown in Fig. 3. In the absorbed dose of 5 kGy, a viscose liquid was formed indicating that gelation was not occurred. With increasing absorbed dose, the gel fraction of SAP increases and the maximum value is obtained at 15 kGy and after that, it levels off. In addition, the gel fraction increases from 73 to 78% following the variation of the CMC concentration from 0.5 to 2% at an absorbed dose of 15 kGy. In fact, when an aqueous solution of CMC/AAc is irradiated with gamma rays, free radicals are generated on the CMC and AAc. Random reactions of these radicals lead to formation of a graft copolymer of CMC and AAc. When the irradiation dose increases beyond a certain value, the polymer chains become more cross-linked, and a gel-like material is obtained. As the concentration of CMC increases, a slight increase is observed in gel fraction due to the presence of more CMC leading to more cross-linking phenomena (Rosiak and Ulański, 1999).

3.3 Water absorption of SAP

The effects of the radiation dose and the concentration of CMC on the water absorption of SAP prepared from CMC/AAc are shown in Fig. 4. The results show that with increasing CMC percent in solutions both the water and saline solution absorption increase due to increasing of hydroxyl groups in the CMC. When the samples are irradiated from 10 to 20 kGy the water and saline solution absorption of the SAP decrease in solutions contain 1 and 2% CMC. This result might be due to the increased cross-linked density with the increase in the irradiation dose. For the solution with 0.5% CMC increasing dose lead to increasing water and saline solution absorption. Measured water and salt absorption were 437 and 76 g.g^{-1} respectively for the 0.5% CMC, which occurred at a dose of 20 kGy. Although gel content at 20 kGy for three samples is almost in the same range the high amount of absorbed water for the sample with the lowest concentration of CMC is may be because of the pores geometry and size related to their specific location in the matrix which is also important in water absorption (Erizal et al., 2015).

3.4 Absorption under load (AUL)

The Absorbency under load (AUL) test measures the capacity of the SAP sample to absorb fluid under specific pressures. Figure 5 displays that by raise in the irradiation dose from 10 to 20 kGy and subsequently content of cross-link density the AUL decreases. Also, the figure shows that with increasing the CMC content the AUL decreases in both 10 and 15 kGy. However, there is no definite trend for the amounts of AUL at 20 kGy. It should be noted that at the dose of 20 kGy, the AUL for 0.5% CMC, which had the best saline solution FSC (76 g.g^{-1}), is 24.6 g.g^{-1}. This amount of AUL is in the range of commercial baby diaper brands, indicating that the prepared CMC/AAc can be used in personal health care products especially in baby diapers (Bachra et al., 2020).

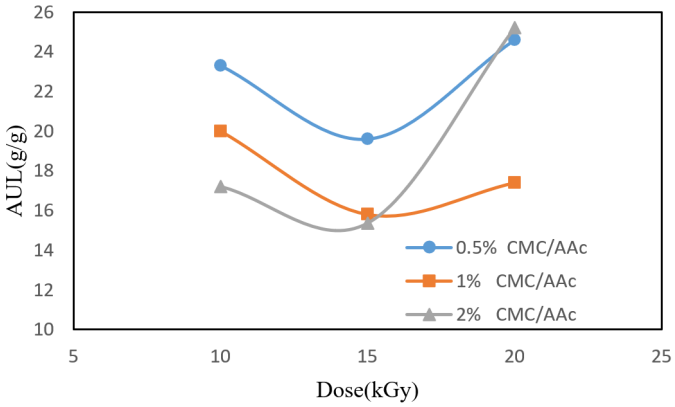

Figure 5: Effect of absorbed dose and concentration of CMC on AUL.

4 Conclusions

CMC/AAc SAPs were synthesized by gamma irradiation technique at different absorbed doses in the range of 5 to 25 kGy. The gel fraction of SAP increases with increasing absorbed dose, and the maximum value is obtained at 15 kGy and after that, it levels off. Gel formation and grafting of AAc on CMC were also confirmed by FT-IR spectroscopy. With increasing irradiation dose from 10 to 20 kGy the water and saline solution absorption of the

SAP decrease in SAPs containing 1 and 2% CMC, but increases in SAP containing 0.5% CMC. Also, by raise in the irradiation dose from 10 to 20 kGy AUL decreases. It should be noted that at the dose of 20 kGy, the AUL for 0.5% CMC is 24.6 $g.g^{-1}$. This amount of AUL is in the range of commercial baby diaper brands. Therefore, gamma irradiation technique is a suitable method to synthesize CMC/AAc SAP for biomedical applications.

Conflict of Interest

The authors declare no potential conflict of interest regarding the publication of this work.

References

Bachra, Y., Grouli, A., Damiri, F., et al. (2020). A new approach for assessing the absorption of disposable baby diapers and superabsorbent polymers: A comparative study. *Results in Materials*, 8:100156.

Erizal, E., Abbas, B., Sukaryo, S. G., et al. (2015). Synthesis and Characterization Superabsorbent Hydrogels of Partially Neutralized Acrylic Acid Prepared Using Gamma Irradiation: Swelling and Thermal Behavior (Indonesian Journal of Chemistry). *Indonesian Journal of Chemistry*, 15(3):281–281.

Esposito, F., Del Nobile, M. A., Mensitieri, G., et al. (1996). Water sorption in cellulose-based hydrogels. *Journal of applied polymer science*, 60(13):2403–2407.

Fekete, T., Borsa, J., Takács, E., et al. (2016). Synthesis of carboxymethylcellulose/acrylic acid hydrogels with superabsorbent properties by radiation-initiated crosslinking. *Radiation Physics and Chemistry*, 124:135–139.

Hariharan, D. and Peppas, N. (1993). Modelling of water transport and solute release in physiologically sensitive gels. *Journal of Controlled Release*, 23(2):123–135.

Hien, N. Q., Van Phu, D., Duy, N. N., et al. (2005). Radiation grafting of acrylic acid onto partially deacetylated chitin for metal ion adsorbent. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 236(1-4):606–610.

Pérez-Álvarez, L., Ruiz-Rubio, L., Lizundia, E., et al. (2019). Polysaccharide-based superabsorbents: synthesis, properties, and applications. *Cellulose-Based Superabsorbent Hydrogels*, pages 1393–1431.

Rimdusit, S., Jingjid, S., Damrongsakkul, S., et al. (2008). Biodegradability and property characterizations of methyl cellulose: effect of nanocompositing and chemical crosslinking. *Carbohydrate Polymers*, 72(3):444–455.

Rosiak, J. and Ulański, P. (1999). Synthesis of hydrogels by irradiation of polymers in aqueous solution. *Radiation Physics and Chemistry*, 55(2):139–151.

Suo, A., Qian, J., Yao, Y., et al. (2007). Synthesis and properties of carboxymethyl cellulose-graft-poly (acrylic acid-co-acrylamide) as a novel cellulose-based superabsorbent. *Journal of Applied Polymer Science*, 103(3):1382–1388.

Wang, X.-L., Yang, K.-K., Wang, Y.-Z., et al. (2004). Crystallization and morphology of a novel biodegradable polymer system: poly (1, 4-dioxan-2-one)/starch blends. *Acta Materialia*, 52(16):4899–4905.

Yu, J., Yang, G., Li, Y., et al. (2014). Synthesis, characterization, and swelling behaviors of acrylic acid/carboxymethyl cellulose superabsorbent hydrogel by glow-discharge electrolysis plasma. *Polymer Engineering & Science*, 54(10):2310–2320.

Zhang, W., Wang, P., Liu, S., et al. (2021). Factors affecting the properties of superabsorbent polymer hydrogels and methods to improve their performance: a review. *Journal of Materials Science*, 56:16223–16242.

Zhou, H. Y., Zhang, Y. P., Zhang, W. F., et al. (2011). Biocompatibility and characteristics of injectable chitosan-based thermosensitive hydrogel for drug delivery. *Carbohydrate Polymers*, 83(4):1643–1651.

Zohourian, M. M. and Kabiri, K. (2008). Superabsorbent polymer materials: a review. *Iranian Polymer Journal*.

To cite this article:

Radmehr, M., Poursattar Marjani, A., Akhavan, A., Nasiri, F. (2024). Synthesis and characterization of carboxymethyl cellulose/acrylic acid superabsorbent hydrogel by gamma irradiation. *Radiation Physics and Engineering*, 5(4), 47–51. doi: 10.22034/rpe.2024.469540.1227

DOI: 10.22034/rpe.2024.469540.1227

To link to this article: https://doi.org/10.22034/rpe.2024.469540.1227