
ICAMS 2016 – 6th International Conference on Advanced Materials and Systems

**RADIATION SYNTHESIS AND CHARACTERIZATION OF
POLY(ACRYLAMIDE-CO-ACRYLIC ACID) HYDROGELS USED FOR THE
ABSORPTION OF HEAVY METALS**

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The purpose of the paper is to present the synthesis and characterization of hydrogels prepared by free-radical copolymerization of acrylamide and acrylic acid in aqueous solutions using potassium persulfate as initiator and trimethylolpropane-trimethacrylate as crosslinker, via radiation technique. The influence of the absorbed dose on the swelling properties, diffusion coefficient and network parameters of hydrogels was investigated. The swelling of hydrogels loaded with metal cations (copper, chromium) was investigated.

Keywords: hydrogels, heavy metals, electron beam

INTRODUCTION

Hydrogels are three-dimensionally cross-linked hydrophilic polymers capable of swelling and retaining huge volume in the swollen state, even under pressure. These macromolecule networks can absorb water, many hundreds of times than their dried weight. Due to their unique characteristics like hydrophilicity, swelling in aqueous media, non-soluble nature in aqueous fluids and ionic aspects, they are applied in biomedicine, bioengineering, pharmaceutical, food industry or agriculture (Karadag *et al.*, 2000; Bardajee *et al.*, 2008; Saraydin *et al.*, 2000). The various techniques adopted for hydrogels preparation are the physical and chemical cross-linking, the grafting polymerization and the radiation cross-linking (Said *et al.*, 2004; Fei *et al.*, 2000; Liu *et al.*, 2002). The initiation of chemical reactions by using radiation is increasingly used for novel hydrogels obtaining. The radiation technique is more preferable than the chemical one, because of the advantages offered by the gently control of cross-linking level through the variation of the absorbed dose. It is a simple additive-free process which is happening at any temperature, the reactions such as polymerization, cross-linking and grafting can be easily controlled and the treatment can be limited to a specific area (Karadag *et al.*, 2004). The processing of materials by irradiation with accelerated electrons removes many drawbacks of the conventional technologies, because ionizing radiation initiates polymerization without thermal input from the outside, due to free radicals that are formed at the interaction with the monomers and especially with the solvent (water in this case). So, a good solution to produce polymeric materials is to use ionizing radiation and especially electron beams, which direct their energy in the entire volume of the monomeric solutions to be irradiated.

The purpose of this study is to present the synthesis and characterization of some hydrogels prepared by free-radical copolymerization of acrylamide and acrylic acid in aqueous solutions using potassium persulfate as initiator and trimethylolpropane trimethacrylate as cross-linker. The free-radical copolymerization was realized by electron beam irradiation in the dose range of 2.4 to 7.2 kGy in atmospheric conditions

and at room temperature. The cross-linker was used in conjunction with the radical cure systems in order to improve physical properties of the final product. The obtained hydrogels were investigated through swelling and diffusion experiments. The heavy metals (Cu^{2+} and Cr^{6+}) removal was evaluated at room temperature.

EXPERIMENTAL

Materials

The materials used for the obtaining of hydrogels are shown in Table 1: acrylamide (AMD) and acrylic acid (AA) as co-monomers, potassium persulfate (PP) as initiator and trimethylolpropane trimethacrylate (TMPT) as cross-linker. All reagents were obtained from LACHEMA, Germany and were used directly, without purification.

Preparation and Irradiation of the Samples

Two different types of aqueous solutions based on acrylamide and acrylic acid for the irradiation experiments were prepared: (a) the first type based on AMD (5 mol/L), AA (0.5 mol/L), PP (3.7×10^{-3} mol/L) and TMPT (2.95×10^{-3} mol/L) - noted H-TMPT-1 and (b) the second type on AMD (5 mol/L), AA (0.5 mol/L), PP (3.7×10^{-3} mol/L) and TMPT (5.90×10^{-3} mol/L) - noted H-TMPT-2. The solutions were placed in polyvinylchloride (PVC) containers of 3 cm diameter and irradiated in atmospheric conditions and at room temperature of 25°C with 2.4 kGy, 4.8 kGy and 7.2 kGy. After irradiation, the obtained hydrogels were cut into pieces of 3 ± 4 mm length, dried in air for 3 days and in a laboratory oven at 50°C for 12 hours to constant weight and then stored in desiccators. The dried hydrogels were used to determine the swelling, diffusion and network parameters.

Experimental Installation and Sample Irradiation

Experiments were carried out with an experimental installation consisting mainly of the following units: an electron linear accelerator (ALIN-10) of 6.23 MeV energy and 75 mA peak current of the electron beam and an irradiation chamber containing the samples of monomer solution. The optimum values of the EB peak current I_{EB} and EB energy E_{EB} to produce maximum output power P_{EB} for a fixed pulse duration t_{EB} and repetition frequency f_{EB} are as follows: $E_{EB} = 6.23$ MeV, $I_{EB} = 75$ mA, $P_{EB} = 164$ W ($f_{EB} = 100$ Hz, $t_{EB} = 3.5$ μ s). The EB effects are related to the absorbed dose (D) expressed in Gray or J kg^{-1} and absorbed dose rate (D^*) expressed in Gy s^{-1} or $\text{J kg}^{-1} \text{s}^{-1}$.

RESULTS AND DISCUSSION

Network Studies

One of the most important structural parameters for the characterization of the cross-linked polymers is M_c , the average molar mass between cross-links, which is directly related to the cross-link density. The swelling equilibrium is widely used to determine M_c . According to the theory of Flory and Rehner for a perfect network, M_c is calculated using the following relation (Karadag *et al.*, 2001):

$$M_c = -V_1 d_p \frac{v_s^{1/3} - v_s / 2}{\ln(1 - v_s) + v_s + \chi v_s^2} \quad (1)$$

where V_1 is the molar volume of the solvent (in this case water: $18 \text{ cm}^3 \text{ mol}^{-1}$), d_p is the polymer density (1.106 g cm^{-3}), v_s is the volume fraction of the polymer in the swollen gel (cm^3) and is equal to $1/S$, χ is the Flory–Huggins interaction parameter between the solvent and polymer.

The value of χ is calculated as follows (Yiamsawas *et al.*, 2007; Ding *et al.*, 1991; Karadag *et al.*, 1997):

$$\chi = 0.431 - 0.311v_s - 0.036v_s^2 \quad (2)$$

The cross-link density, q , is defined as being the mole fraction of the cross-linked units.

$$q = \frac{M_0}{M_c} \quad (3)$$

where M_0 is the molecular weight of the repeating units from polymer and is calculated using the following relation (Yiamsawas *et al.*, 2007; Karadag *et al.*, 1997).

$$M_0 = \frac{(m_{AMD} \times M_{AMD}) + (m_{AA} \times M_{AA}) + (m_{TMPT} \times M_{TMPT})}{m_{AMD} + m_{AA} + m_{TMPT}} \quad (4)$$

where m_{AMD} , m_{AA} and m_{TMPT} are the masses of acrylamide, acrylic acid and cross-linker (TMPT) expressed in grams and M_{AMD} , M_{AA} and M_{TMPT} are the molar masses of acrylamide, acrylic acid and TMPT expressed in g mol^{-1} .

Another parameter used for cross-link density characterization is ν_e which represents the number of elastically effective chains totally included in a network per volume unit and it is calculated with the following relation:

$$\nu_e = \frac{d_p N_A q}{M_0} \quad (5)$$

where N_A is the Avogadro number.

The values of parameters M_c , q and ν_e were calculated as above and are listed in Table 1.

Table 1. The variation of the number-average molar mass between cross-links ($M_c/\text{g mol}^{-1}$), cross-link density (q) and number of elastically effective chains (ν_e) with the amount of TMPT and absorbed dose

| TMPT (mol/l) | Absorbed dose (kGy) | | |
|-----------------------|---------------------|------------------------|---------|
| | 2.4 | 4.8 | 7.2 |
| | | $M_c \times 10^{-3}$ | |
| 2.95×10^{-3} | 449 717 | 309 883 | 184 895 |
| 5.90×10^{-3} | 994 785 | 498 836 | 235 255 |
| | | $q \times 10^7$ | |
| 2.95×10^{-3} | 1.597 | 2.318 | 3.885 |
| 5.90×10^{-3} | 0.729 | 1.453 | 3.082 |
| | | $\nu_e \times 10^{14}$ | |
| 2.95×10^{-3} | 2.459 | 3.569 | 5.982 |
| 5.90×10^{-3} | 1.112 | 2.217 | 4.701 |

From the Table 1 it is observed that the number-average molar mass between cross-links of hydrogels has increased with the increasing of the amount of cross-linker (TMPT) but has decreased with the increasing of absorbed dose. The values of the cross-link density and number of elastically effective chains are inversed due to the value of number-average molar mass between cross-links. The increasing of the amount of cross-linker decreases the cross-linking density, because the hydrogels obtained are not stiff. Increasing the cross-linker concentration increases the M_c between the two main backbones. A large value of M_c indicates long chains between the two backbones. The obtained results show that the M_c values are affected by the absorbed dose. The increasing of absorbed dose leads to the decreasing of M_c , since the hydrogel becomes more and more dense.

Other important parameters used for the assessment of networks are gel pore size or mesh size (ξ) and porosity (P %). Using the calculated values of number average molecular mass between cross-links, M_c , the mesh size was determined using the following equation (Thakur *et al.*, 2011):

$$\xi = v_s^{-1/3} \sqrt{\frac{2C_n M_c}{M_r}} \quad (6)$$

where v_s is the volume fraction of the polymer in the swollen gel, l is the length of the C-C bond along the polymer backbone (0.154 nm), C_n is the Flory characteristic ratio of the polymer and M_r is the molecular mass of the repeated unit.

The characteristic ratio, C_n , for poly(AMD-co-AA) hydrogels was taken as the weighted average of C_n values for poly(AMD) and poly(AA) chains, according to their molar ratio in the hydrogel (C_n was taken 8.8 and 6.7 for poly(AMD) and poly(AA), respectively).

The porosity P(%) of the obtained hydrogels was determined using the following equation (Karadag *et al.*, 2001):

$$P(\%) = \frac{V_d}{1 - V_d} \times 100 \quad (7)$$

where V_d is the volume ratio of water at equilibrium. The values of the mesh size, (nm) and porosity (P) are shown in Table 2.

Table 2. The variation of mesh size (ξ) and porosity (P) with the amount of TMPT and absorbed dose

| TMPT (mol/l) | Absorbed dose (kGy) | | |
|-------------------------|---------------------|--------|-------|
| | 2.4 | 4.8 | 7.2 |
| | | /nm | |
| 2.95 x 10 ⁻³ | 133.70 | 103.21 | 72.14 |
| 5.90 x 10 ⁻³ | 232.38 | 143.70 | 85.25 |
| | | P(%) | |
| 2.95 x 10 ⁻³ | 98.05 | 97.56 | 96.68 |
| 5.90 x 10 ⁻³ | 98.78 | 98.76 | 97.12 |

As it is presented in Table 2, the mesh size and porosity have increased with the increasing of the amount of cross-linker (TMPT) and have decreased with the increasing of the absorbed dose. The mesh size is related with the space available for transport of a solute or of a solvent in a network. The increasing of the mesh size and

porosity has as a result the increasing of water content in the hydrogel. More than that, from the results it is observed that the degree of cross-linking had a significant influence on the mesh size. Hydrogels having higher degrees of cross-linking have a relatively shorter distance between two cross-linking points and as a result, the mesh sizes and porosity of these hydrogels are lower.

Adsorption of Ions from Aqueous Solutions

The obtained hydrogels have been tested to remove toxic heavy metals from aqueous media, even if their application on large scale may not be a practical solution due to exorbitant costs. The heavy metals (Cu^{2+} and Cr^{6+}) removal was evaluated at room temperature on water samples synthesized from $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.5 wt/vol%) and $\text{K}_2\text{Cr}_2\text{O}_7$ (0.5 wt/vol %).

The adsorption of ions was studied by the following procedure: 0.01 g of dry hydrogel was introduced in 5 mL of aqueous solution containing Cu^{2+} or Cr^{6+} ions for 72 h. Then, the gel was removed from the solution and the ions retention was monitored by UV-VIS absorption spectrophotometry. The heavy metals adsorption performance is presented in terms of “adsorption efficiency” and was calculated as follows:

$$E(\%) = \frac{C_0 - C_1}{C_0} \times 100 \quad (8)$$

where C_0 is the initial heavy metals concentration (Cu^{2+} and Cr^{6+}), C_1 is the heavy metals concentration after adsorption.

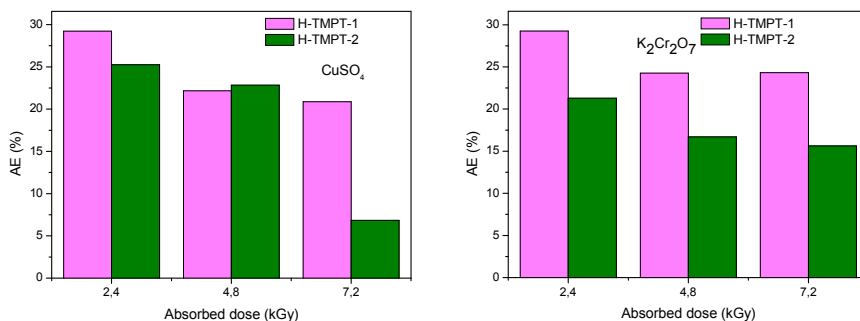


Figure 1. Heavy metals removal efficiency (%) as a function of electron beam dose (kGy)

In Figure 1 the heavy metals removal is represented depending on the absorbed dose used for the hydrogels obtaining. It is observed that the heavy metals adsorption performance decreases with the increasing of the absorbed dose. Thus, low radiation doses leads to the obtaining of efficacious hydrogels for heavy metals removal. This is related with the decrease of mesh size () and porosity (P) due to the increase of degree of cross-linking when the radiation dose has increased. The mesh size and porosity are related with the space available for transport of the liquid in the polymeric network, so their decreases indicate that the hydrogels present modest possibilities of water adsorption.

CONCLUSIONS

This study was carried out to illustrate the synthesis of poly[acrylamide-co-acrylic acid]-hydrogels using potassium persulfate as initiator and trimethylolpropane-trimethacrylate as cross-linker, via the radiation technique. The obtained hydrogels were investigated through swelling analysis. The number-average molar mass between cross-links of hydrogels increased with the increasing of the amount of cross-linker (TMPT) but decreased with the increasing of absorbed dose. Also, the mesh size and porosity have increased with the increasing of the amount of cross-linker (TMPT) and have decreased with the increasing of the absorbed dose. Hydrogels having higher degree of cross-linking have a relatively shorter distance between two cross-linking points and for this reason, the mesh sizes and porosity of these hydrogels have decreased. Also, the swelling of hydrogels loaded with metal cations (copper, chromium) was investigated. The efficiency in heavy metals adsorption decreases with the increasing of the absorbed dose, because the mesh size (ξ) and porosity (P) are connected in the same way with the absorbed dose.

REFERENCES

- Bardejee, G.R., Pourjavadi, A., Sheikh, N. and Amini-Fazl, M.S. (2008), "Grafting of acrylamide onto kappa-carrageenan via g-irradiation: Optimization and swelling behavior", *Radiation Physics and Chemistry*, 77(2), 131-137.
- Ding, Y.Z., Aklonis, J.J. and Salovey, R. (1991), "Model filled polymers. VI. Determination of the crosslink density of polymeric beads by swelling", *Journal of Polymer Science Part B: Polymer Physics*, 29(8), 1035-1038.
- Fei, B., Wach, R.A. Mitomo, H., Yoshii, F. and Kume, T. (2000), "Hydrogel of biodegradable cellulose derivatives. I. Radiation-induced crosslinking of CMC", *Journal of Applied Polymer Science*, 78(2), 278-283.
- Karadag, E., Saraydin, D. and Guven, O. (1997), "Influence of some crosslinkers on the swelling of acrylamide-crotonic acid hydrogels", *Turkish Journal of Chemistry*, 21, 151-161.
- Karadag, E., Saraydin, D. and Guven, O. (2004), "Water absorbency studies of c-radiation crosslinked poly(acrylamide-co-2,3-dihydroxybutanedioic acid) hydrogels", *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 225(4), 489-496.
- Karadag, E., Saraydin, D., Caldiran, Y. and Guven, O. (2000), "Swelling studies of copolymeric acrylamide/crotonic acid hydrogels as carriers for agricultural uses", *Polymers for Advanced Technologies*, 11, 59-68.
- Karadag, E., Saraydin, D., Sahiner, N. and Guven, O. (2001), "Radiation induced acrylamide/citric acid hydrogels and their swelling behaviors", *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry*, 38(11), 1105-1121.
- Liu, P., Zhai, M., Li, J., Peng, J. and Wu, J. (2002), "Radiation preparation and swelling behavior of sodium carboxymethyl cellulose hydrogels", *Radiation Physics and Chemistry*, 63(3-6), 525-528.
- Said, H.M., Abd Alla, S.G. and El-Naggar, A.W.M. (2004), "Synthesis and characterization of novel gels based on carboxymethyl cellulose/acrylic acid prepared by electron beam irradiation", *Reactive and Functional Polymers*, 61(3), 397-404.
- Saraydin, D., Karadag, E. and Guven, O. (2000), "Relationship between the swelling process and the releases of water soluble agrochemicals from radiation crosslinked acrylamide/itaconic acid copolymers", *Polymer Bulletin*, 45, 287-294.
- Thakur, A., Wanchoo, R.K. and Singh, P. (2011), "Structural Parameters and Swelling Behavior of pH Sensitive Poly(acrylamide-co-acrylic acid) Hydrogels", *Chemical and Biochemical Engineering Quarterly*, 25(2), 181-194.
- Yiamsawas, D., Kangwansupamonkon, W., Chailapakul, O. and Kiatkamjornwong, S. (2007), "Synthesis and swelling properties of poly[acrylamide-co-(crotonic acid)] superabsorbents", *Reactive and Functional Polymers*, 67(10), 865-882.