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SYNTHESIS, CHARACTERIZATION AND SWELLING STUDY OF PGMA HYDROGEL BASED ON POLY (GLYCIDYL METHACRYLATE)

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ABSTRACT

The PGMA hydrogel studied in this work was prepared by physical cross-linking of poly (glycidyl methacrylate) (PGMA) at 50-55°C without cross-linking agent. The PGMA was synthesized by ring opening polymerization of glycidyl methacrylate (GMA) in presence of Maghnite-H^+ as an catalyst at room temperature. The PGMA hydrogel synthesized was characterized by FT-IR, by X-ray diffraction (XRD), by scanning electron microscope (SEB) and by swelling measurements. The results obtained by X-ray diffraction, showed that the PGMA hydrogel formed by two structures, a crystalline structure and an amorphous structure. Scanning electron microscopy (SEM) analysis indicated that a porous structure of PGMA hydrogel. The equilibriums water content (EWC) obtained were 74.81% at 20°C, 79.38% at 40°C and 85.81% at 60°C.

Keywords: Hydrogel; physically cross-linking; poly (glycidyl methacrylate); swelling study.

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1. INTRODUCTION

Polymers and copolymers materials based on glycidyl methacrylate are recently widely used in different domains, some polymers and copolymers can be converted by a simple reaction to give new materials such as hydrogels and nanocomposite materials. hydrogels are very interesting materials and they are used in pharmaceutical, biomedical and agriculture applications.

The glycidyl methacrylate (GMA) is a methacrylic monomer, is a very important monomer, and it is used in synthesis of several polymers and copolymers [1-5]. Methacrylic monomers or macromonomers are also widely used for the synthesis of hydrogels. In this sense, the pH sensitive hydrogel particles was synthesized from polyethylene glycol dimethacrylate (PEGDMA) and methacrylic acid (MAA) by free radical polymerization [6] also, lenses were synthesized using the 2-hydroxy-ethyl methacrylate and methacrylic acid, other lenses were made from vinyl pyrrolidone and methyl methacrylate [7]. Indeed, the soft contact lenses synthesized from 4-t-butyl, 2-hydroxycyclohexyl methacrylate, methacryloamino-4-t-butyl-2-hydroxycyclohexane, 4-t-butyl, 2-hydroxycyclopentyl methacrylate combined with 2-hydroxy-ethyl methacrylate or N-vinyl pyrrolidone [8].

Because of their excellent water retention properties, recently hydrogels are widely used in Pharmaceutical [9] and biomedical [10] applications, they are also used in agriculture [11] to store water near the roots of plants [12] and they are used as hygienic products [13], Indeed, the hydrogels are hydrophilic macromolecules [14], It can be prepared by chemical or physical cross-linking [15]. Chemically cross-linked networks are obtained using cross-linking agents as well as épichlorhydrine [16], N,N'-methylenebisacrylamide [17], dimethacrylate monomers such as (ethylene, diethylene, triethylene and tetra ethylene) glycol dimethacrylate [15]. Hydrogels prepared without crosslinking agents or by physical crosslinking are formed by hydrogen bonds between the macromolecular chains. In this context, a hydrogen bond is found between the oxygen of the polyethylene glycol and the carboxylic group of the poly (acrylic acid) or poly (methacrylic acid) to form hydrogels or complexes [18].

The swelling property of hydrogels is a very important parameter, and hydrogels are

considered very interesting materials when they have absorbed a significant amount of water or other liquid. The increase in sorption capacity is related to the ionic monomers inside the polymer matrix [19]. Also, other parameters influencing the swelling of the hydrogels are the temperature, the pH of the swelling medium and the structure of the absorbed molecule.

In this present work, we were interested in the synthesis and characterization of hydrogel based on poly (glycidyl methacrylate) in two steps, firstly by ring opening polymerization of epoxide of glycidyl methacrylate (GMA) [20] at room temperature, using Maghnite-H^+ as an catalyst with continuous stirring. The second step in our work is to transform the poly (glycidyl methacrylate) (PGMA) into a hydrogel by a physical cross-linking reaction by increasing the temperature of the reaction mixture to 50-55°C with continuous stirring until the total cross-linking of PGMA. Techniques of analysis, infrared spectroscopy FT-IR, x-ray diffraction (XRD) and scanning electron microscopy (SEM) were used for the characterization of PGMA hydrogel. A study of the swelling behavior is performed to know the amount of water and other solvents absorbed by PGMA hydrogel.

2. RESULTS AND DISCUSSION

2. 1. Characterization of PGMA hydrogel

2. 1. 1. FT-IR spectral analysis

The FT-IR spectrum of poly (glycidyl methacrylate) hydrogel obtained is in good agreement with PGMA hydrogel chemical structure. The carbonyl group (C=O) and (C-O) bands, are observed respectively at 1725 and 1152 cm^{-1}. The C–H symmetric and asymmetric stretching due to the (-CH_3 and –CH_2-) groups were observed between 2960 and 2900 cm^{-1}. A wide band is observed at 3450cm^{-1} due to the hydroxide group (O-H). The band of the epoxy group (asymmetric stretching 760 cm^{-1}) was disappeared because of ring opening polymerization and the peak associated to C=C double bond was not observed about 1650 cm^{-1}, this may be because of the crosslinking of poly (glycidyl methacrylate).

2. 1. 2. X-ray diffraction (XRD) analysis

The X-ray diffraction analysis (XRD) of PGMA hydrogel (Figure 1) give a three peaks, one with a strong broad slope around 2θ = 18.38° this peak corresponds to a d-spacing = 4.82A°

and indicating the amorphous structure [21]. Two weak peaks were observed around 2θ = 30.39° with a d-spacing = 2.94A° and around 2θ = 42.15° with a d-spacing = 2.14A°, they are indicates the presence of a crystalline structure.

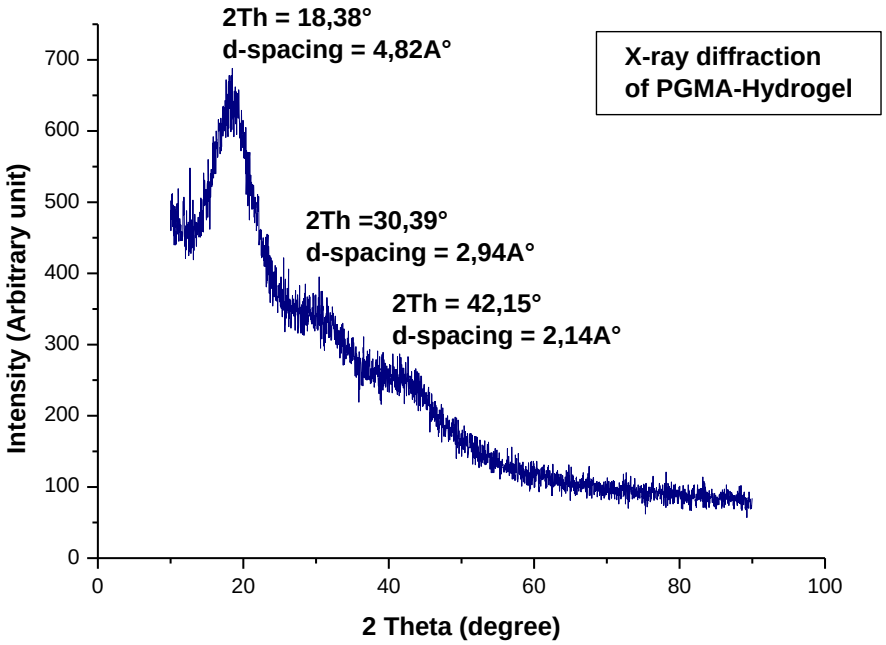

Fig.1. X-ray diffraction (XRD) of PGMA hydrogel

2. 1. 3. Scanning electron microscopy (SEM) analysis

The analysis by SEM allowed us to know the surface morphology of PGMA hydrogel. Figure 2 (A) (30µm, 3000x) showed that the PGMA hydrogel as different particles, the size of each is varied between 8.147-32.48µm. Figure 2 (B) (10µm, 3000x), showed that the morphology of the PGMA hydrogel surface is not uniform with cavities and pores. Figure 2 (C) (4 µm, 20000x) and Figure 2 (D) (30 µm, 3000x) showed that the pore sizes of PGMA hydrogel in the range of 3,694 to 4,954µm (3694 to 4954nm), it is termed macroporous hydrogel [22].

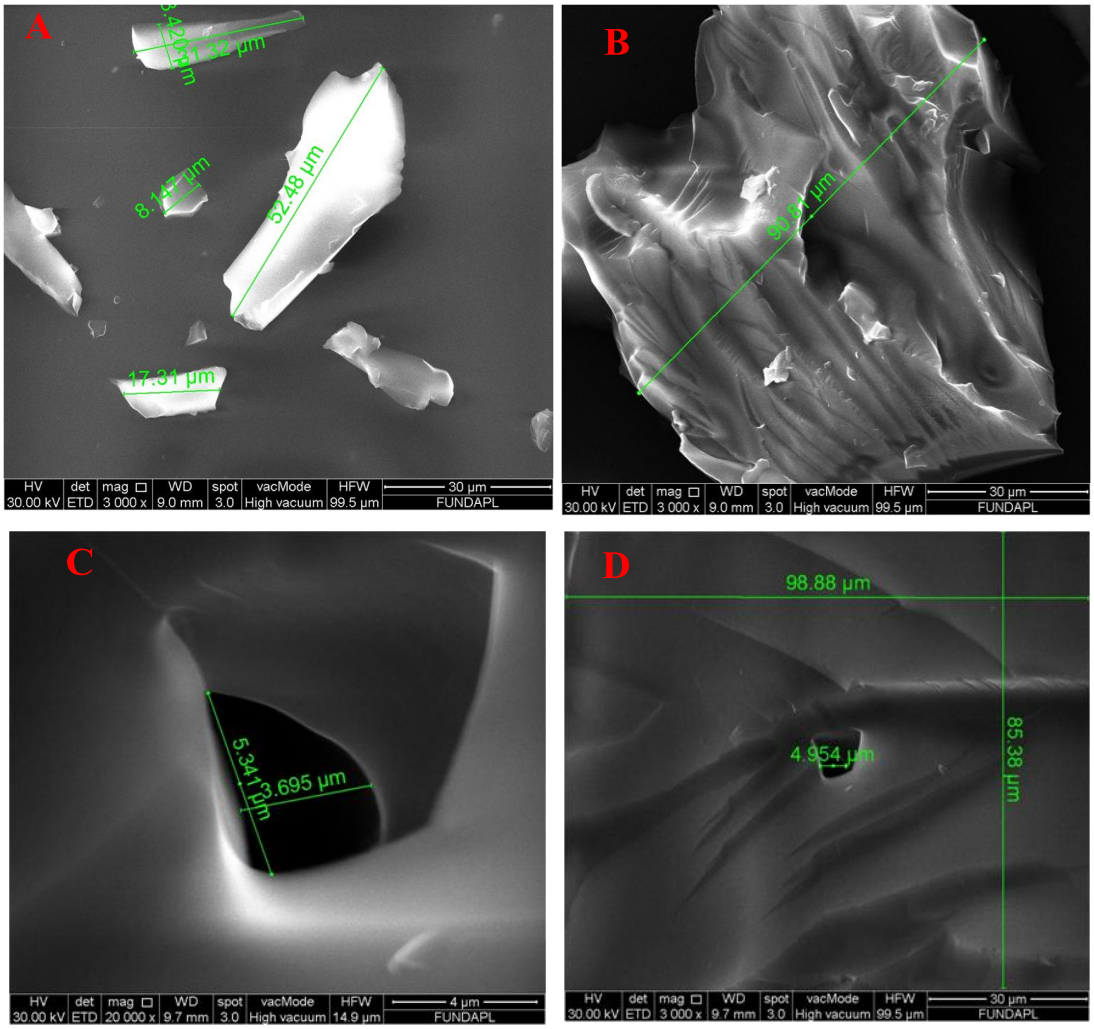

Fig.2. (A); SEM images of PGMA hydrogel particle, (B); SEM images Roughness of PGMA hydrogel, (C); SEM images of pore size of PGMA hydrogel, (D);SEM images of pore size of PGMA hydrogel

2. 1. 4. Hydrogel swelling kinetics

In this first part, we studied the equilibrium solvent content (ESC) of PGMA hydrogel samples by different solvents (water, acetone, hexane, THF and acetonitril) at 25°C. The ESC was evaluated by measuring the amount of solvent absorbed by PGMA hydrogel until saturation. The equilibrium solvent content (ESC) behavior of PGAM hydrogel samples is shown in Figure 3. The equilibrium water content is 75.6%, it is a very important percentage. Indeed, PHEMA contact lenses in the fully hydrated state can contain between 38 to 40% water [10]. Equilibrium water content is very high compared to other organic solvents, such

as acetone (EAC = 68.96%, hexane (EHC = 57.89%), THF (ETC = 53.33%) and finally the acetonitril has an equilibrium acetonitril content equal 35.12%. The inflated of the PGMA hydrogel by a large amount of water is explained by that the hydrogel is hydrophilic material, it is also ionic, and it can form hydrogen bonds with water.

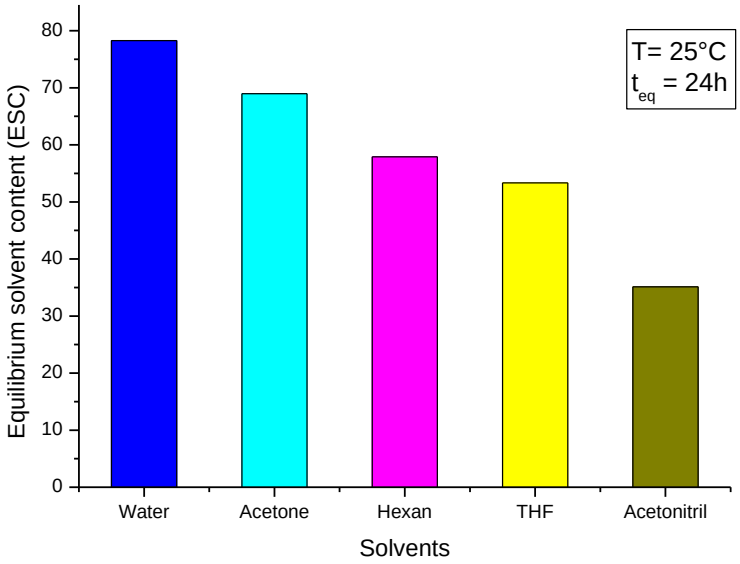

Fig.3. Equilibrium solvent content of the PGMA hydrogel

In the second part, we studied the variation of swelling behavior of PGMA hydrogel as a function of time (min) at three temperatures 20, 40 and 60°C. The results found are shown in Figure 4. After (50mn) of immersion in distilled water, the PGMA hydrogel was completely swollen for the three temperatures. In addition, the swelling content of our hydrogel is influenced by the increase in temperature. The equilibrium water content (EWC) values are as follows: 74.81% at 20°C, 79.38% at 40°C and 85.81% at 60°C.

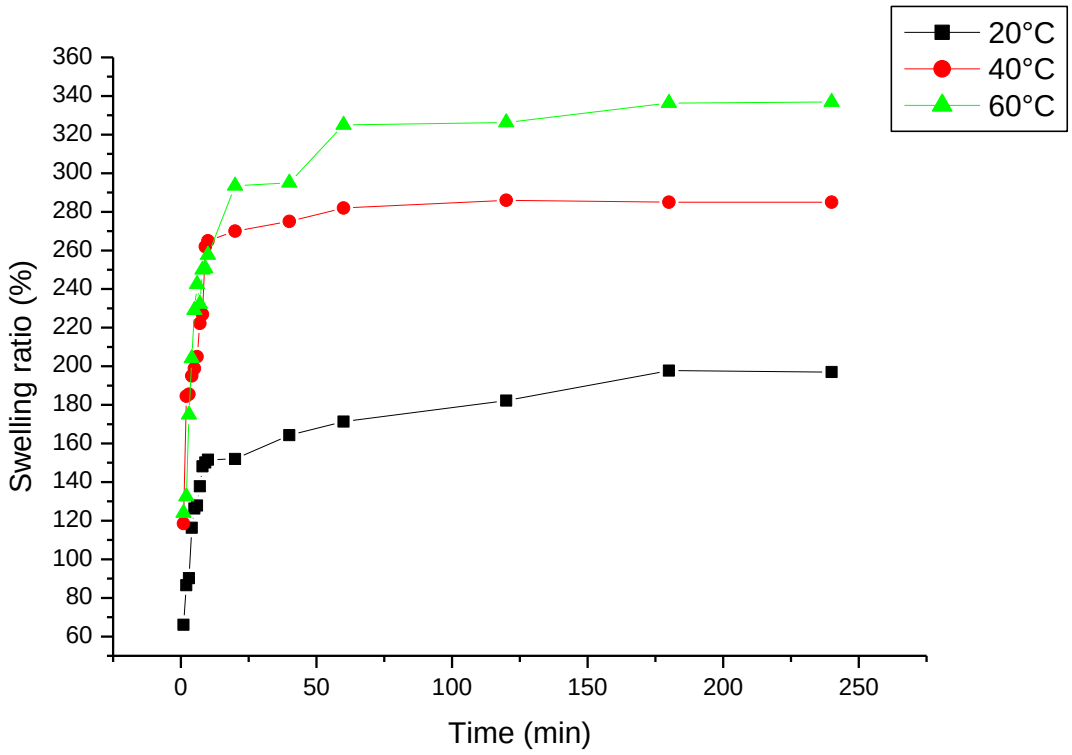

Fig.4. Swelling behavior of the PGMA hydrogel in distillate water

3. EXPERIMENTAL

3.1. Materials

Glycidyl methacrylate (GMA) (Sigma-Aser) was purified by a column chromatography to remove the inhibitor, Sulfuric acid (98%, d = 1.84) (Sigma-Aldrich), solvents: acetone, hexane, THF, acetonitril (Sigma Aldrich) were used as received. Raw-Maghnite: Algerian montmorillonite clay was procured from "BENTAL" (Algerian Society of Bentonite).

3. 2. Synthesis of poly (glycidyl methacrylate) hydrogel

A mixture of 15g (0,1056 mol) of GMA and 3g (20%) of Maghnite-H^+ with continues agitation at room temperature for 96h, the progress of the reaction is controlled by thin-layer chromatography. When the reaction time is finished, 50 ml of acetone was added to the mixture and then filtered to remove the catalyst. The mixture (PGMA and acetone) was heated at 50-55°C during 20mn with continuous stirring. The obtained product was solid semi-transparent. The schematic representation of the PGMA and PGMA hydrogel synthesis is shown in Figure 5.

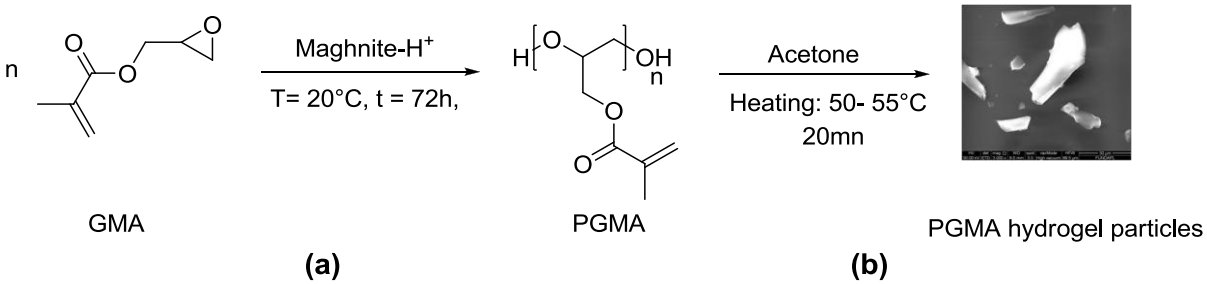

Fig.5. (a); Scheme of synthesis of poly (glycidyl methacrylate) [20], (b); Scheme of synthesis of hydrogel based on poly (glycidyl methacrylate)

3. 3. Measurement of equilibrium solvents content (ESC) and swelling content (SC)

The study of the swelling characteristics of hydrogels is determined by the equilibrium water content (EWC) using relation (1) [10] and by percent mass swelling determined by the relation (2) [23].

$$EWC = \frac{m}{m_{tot}} \times 100\% \quad (1)$$

Where: m is the weight of water in polymer, m_{tot} is the total weight of hydrated hydrogel.

$$\%Swelling = \frac{M_t - M_0}{M_0} \times 100 \quad (2)$$

Where: M_t is the weight of hydrogel at different time-intervals, M_0 is the initial weight of hydrogel.

In the first part of our study, masses of 50mg of PGMA hydrogel are dried then are immersed during a time of 24h in 50 ml of each solvent (water, acetone, hexane, THF and acetonitril). The results obtained are given in Figure 3. in the second part of our study, the PGMA hydrogel swelling kinetics were studied in distilled water (pH = 7) at different temperatures (20, 40, and 60°C) in a time interval of 0-240 min. Masses of 50mg completely dried are immersed in beakers containing 50ml of distilled water in different times. The results of the swelling behavior of PGMA hydrogel by water are given in Figure 4.

3. 4. Characterization

The FT-IR absorption spectrum was recorded by Shimadzu Lab Solutions IR spectrometer. The samples were analyzed by a Philips "X'PERT PRO MPD" diffractometer in the mode θ-θ (Bragg-Brentano) configuration, using a copper anticathode of wavelength λ = 1,54060A°. The PGMA hydrogel images were obtained by SEM quanta 650 at a voltage of 30.00 kV and under high vacuum.

4. CONCLUSION

The PGMA hydrogel was successfully synthesized by physically cross-linked of Poly (glycidyl methacrylate) at 50 to 55°C without cross-linked agent. The analysis by infrared spectroscopy clearly shows the disappearance of epoxide function of glycidyl methacrylate and the appearance of the (O-H) function. Also the disappearance of the carbon-carbon double bond confirms the cross-linking is performed at the double bonds. The X-ray diffraction analysis of PGMA hydrogel confirms the existence of two structures, one crystalline and the other amorphous. Analysis by SEM showed that PGMA hydrogel has a porous structure, pores with a diameter between 3.695 and 4.954um. The resultants of swelling ratio (%) of PGMA hydrogel by water were: 196.98 at 20°C, 285 at 40°C and 336.88 at 60°C.

5. ACKNOWLEDGEMENTS

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