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Hydrogel composite of poly(vinylalcool) with unmodified montmorillonite

Fatiha Reguieg[ab*], Nabahat Sahli[a] and Mohamed Belbachir[a]

[a] Laboratory of Polymer Chemical, Department of Chemistry, Faculty of Exact and Applied Sciences, University of Oran1 Ahmed Benbella, 31100 Oran, Algeria
[b] Preparatory School in Sciences and Technology. Oran, Algeria

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A B S T R A C T

Crosslinked poly(vinylalcohol) (PVA) hydrogel composites based on algerian hydrophilic natural Na-montmorillonite (Na-MMT) nanoclay named Maghnite-Na (Mag-Na) were prepared in aqueous media, without utilization of chemical crosslinking agents, by repeated cycles of freezing and thawing. The morphology of hydrogel composites and their swelling in water at different amount of Mag-Na were investigated. The characterization of obtained hydrogel composites by X-ray diffraction (XRD) showed a remarkable increase of the basal distance of Mag-Na in PVA hydrogels. Therefore, Intercalated and exfoliated morphology was observed for prepared composites hydrogels of PVA. The infra-red (FTIR) characterization results showed that some interactions have been developed between the hydroxyl groups of PVA chains and Mag-Na in composite hydrogels. Introducing Mag-Na into PVA hydrogel affected their swelling. Increased amount of Mag-Na decreased the equilibrium degree of swelling and equilibrium water content.

1. Introduction

Hydrogels are three-dimensional cross-linked polymer network that can respond to the fluctuations of the environmental stimuli. These materials can incorporate large quantum of biological fluids and swell. When swelled, they are soft and rubbery and resemble the living tissue, exhibiting excellent biocompatibility.[1]

Poly(vinyl alcohol) (PVA) is a water soluble polymer of great importance because of its many appealing characteristics specifically for various pharmaceutical and biomedical applications. PVA hydrogels possess an elastic or rubbery nature structure and high degree of swelling in water or biological fluids.[2]

PVA hydrogels have been applied in different biomedical application sites such as contact lenses, the lining for artificial hearts, wound dressing, drug delivery applications and biomaterials implants.[3]

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* Corresponding author.
E-mail address: fatiha_reguieg@yahoo.fr (F. Reguieg)

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Hydrogel nanocomposites on the basis of nanometer-thin layered materials, like sodium montmorillonite (Na-MMT), have attracted strong interest in today's materials research, as it is possible to achieve impressive enhancements of material properties compared to the pure hydrogels. Mixed with clay, PVA hydrogel have excellent mechanical properties and thermal stability.[4] Because of their biocompatibility, PVA composites hydrogels have been used extensively in the medical field: joint replacement, cartilage replacement, controlled drug delivery, wound dressing as it can prevent loss of body fluid, permeable to oxygen and be a barrier against bacteria.[5]

Sodium montmorillonite (Na-MMT) is natural clay occurring 2:1 phyllosilicate, capable of forming stable suspensions in water. This hydrophilic character of MMT, due to the presence of sodium cation in the clay galleries, also promotes high dispersion of these inorganic crystalline layers in water-soluble polymers such as poly(vinyl alcohol),[6] poly(ethylene oxide). [7, 8] and poly(1,3-dioxolane)[9]

Maghnite is Algerian montmorillonite sheet silicate clay with very high cation exchange property.[10] Its structure is octahedral layers comprise between two tetrahedral layers. Between two successive sheets, there is an interlayer space which contains exchangeable cations (**Fig. 1**).

Maghnite, which has a high ratio of silicium and aluminium[10] (**Table1**), is used in several scientific field, as non-toxic catalyst for the polymerization of different monomers,[11, 12] and as nanofiller for the synthesis of polymer/clay and hydrogels/clay nanocomposites.[13, 14] nanocomposite based on Maghnite clay exhibit improved mechanical, thermal, barrier and flame retardant properties in comparison with unfilled polymer or hydrogel.[15]

Table 1. Chemical composition of the Maghnite[10]

Species	SiO_2	Al_2O_3	Fe_2O3	Na_2O	K_2O	CaO	MgO	TiO_2	SO_3	As
%(W/W)	69.39	14.67	1.16	0.5	0.79	0.3	1.07	0.16	0.91	0.05

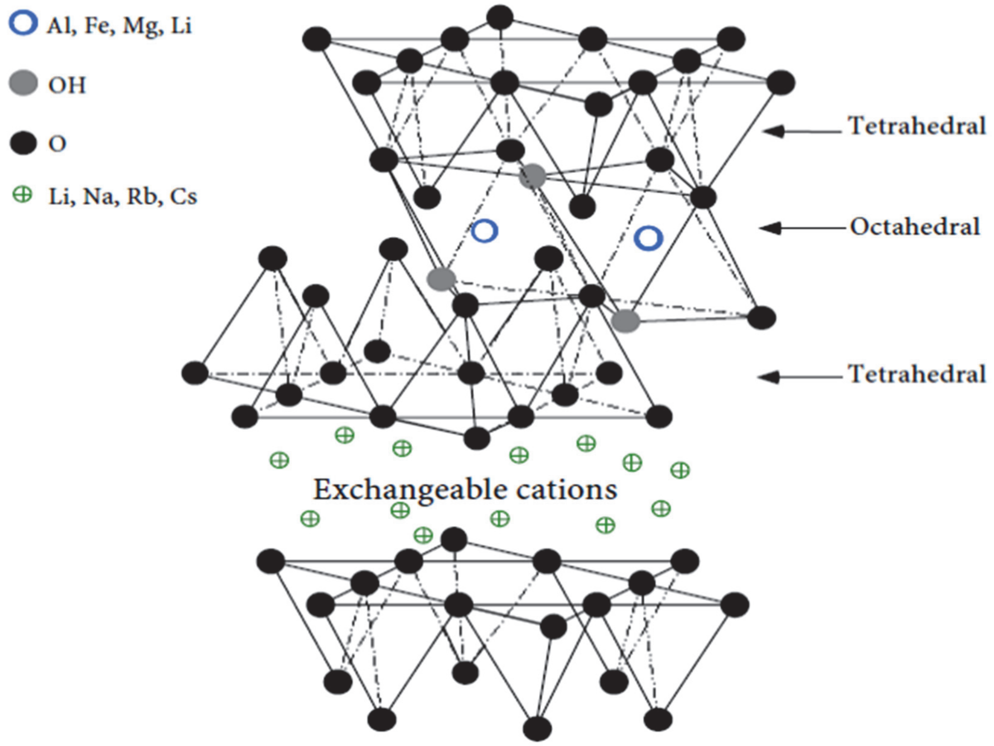

Fig. 1. The Maghnite structure

Crosslinking in hydrogels occurs by chemical or physical means depending on the polymer properties and experimental conditions. A chemical process is utilized to prepare a chemical hydrogel using chemical crosslinking agents.

In physical hydrogels, the crosslinking is achieved via utilizing physical processes such as association, aggregation, crystallization, complexation, and hydrogen bonding.
Crystallization by Freezing-thawing is one of the effective physical methods to produce the PVA hydrogel composites. By repeated freezing-thawing process, the PVA hydrogels formed are non-toxic and strong. This preparation method of nanocomposite hydrogels is safer in the absence of co-solvent and chemical crosslinking agents.[16, 17]

In the most research work, PVA is mixed with an organically modified montmorillonite which has hydrophobic environment.[17, 18] However PVA is an hydrophilic polymer and it can be blended with unmodified montmorillonite which has an hydrophilic environment for the synthesis of hydrogels nanocomposites hydrogels, and this is our objective in this present work. Consequently, series of freeze-thawed Poly(vinylalcohol) (PVA) composite hydrogels were prepared using the Algerian hydrophilic montmorillonite-Na nanoclay called Maghnite-Na (Mag-Na).[10] The effect of Mag-Na quantity on the morphology and swelling behavior of nanocomposite hydrogels were investigated.

2. Results and discussion

2.1. Structure of PVA/Mag-Na hydrogel composites

2.1.1. X-ray Diffraction (XRD)

The DRX profiles of Mag-Na and PVA hydrogel composites are shown in **Fig. 2**. For the Mag-Na, typical peak of Na-MMT is shown at around $2\theta=5,5°$, which represents the (d001) spacing at 15A°. In the XRD profile of PVA hydrogel composite with 1, 5 and 7% of Mag-Na, the typical Mag-Na peak initially at $2\theta=5,5°$ was disappeared which indicate that were strong increase in the interlayer spacing of Mag-Na. It could be concluded that the chains of PVA has intercalated between silicate layers during the freezing-thawing process.

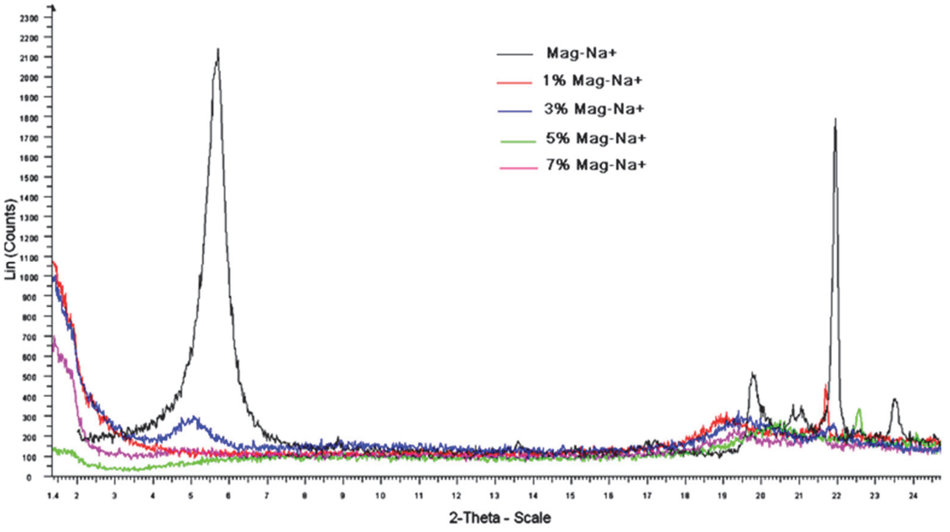

Fig. 2. XDR pattern of Mag-Na and hydrogel composite PVA/Mag-Na

2.1.2 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra shown in **Fig. 3** were obtained for pure Maghnite-Na, pure PVA hydrogel and hydrogel composites of PVA/Mag-Na. For the final product of hydrogel composite of PVA/Mag-Na, the bands at around 500 and 1000 cm^{-1} corresponding to the SiO stretching vibration of clay are due to the presence of the Mag-Na in the PVA/Mag-Na hydrogel composite. The OH stretching bands of the Mag-Na initially at around 3650 cm^{-1} was shifted to lower wave number and combined with the OH streching bands of the PVA (3500-3000 cm^{-1}). This combination led to a broader hydroxyl stretching band. This broader band notes that incorporation of Mag-Na into PVA developed some interactions between the OH groups of PVA and Mag-Na.

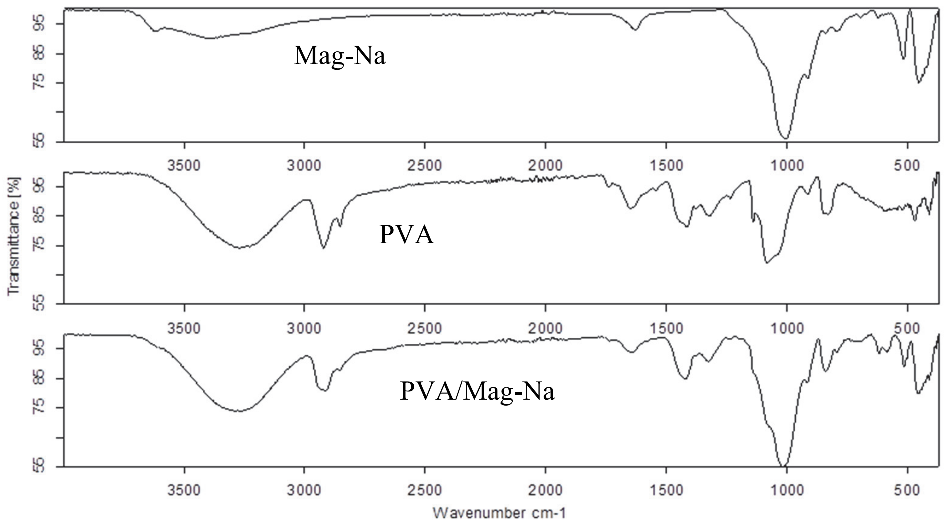

Fig. 3. FTIR spectrum of Mag-Na, PVA and hydrogel composite PVA/Mag-Na

2.2 Swelling and water content measurement

The swelling behavior of PVA hydrogels prepared by freezing-thawing technique was examined in distilled water. **Fig. 4** shows the equilibrium swelling rate measured at different times, for different amounts of Mag-Na. Significant absorption of water at the beginning is observed in gels and maximum swelling equilibrium is reached after 72 hours of contact with distilled water.

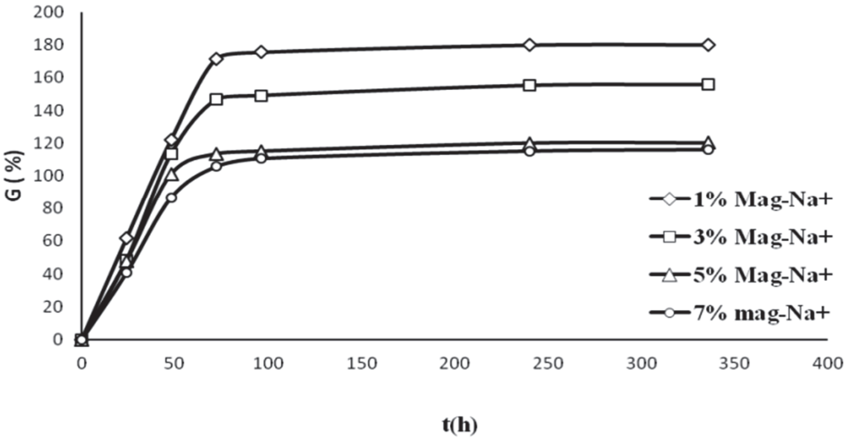

Fig. 4. Swelling kinetic curve of hydrogel composite PVA (10%)/Mag-Na

The effect of the amount of Mag-Na on the equilibrium swelling and the amount of water in the gel is also shown in **Fig. 5** and **Fig. 6**. For the pure hydrogels (0% Mag-Na), the physical network of

PVA/Mag-Na is able to retain between its macromolecular chains up to 200% water of its weight in the dry state for the hydrogel containing 5% PVA, up to 180% water of its weight in the dry state for the hydrogel to 10% PVA and up to 160% water by weight in the dry state for the hydrogel to 15% PVA. Increasing the amount of PVA increases the cristallinity and rigidity of the network then the swelling decreases.

In the presence of the Mag-Na within the network, whatever the content of the PVA hydrogel, we observe a decrease in degree of swelling at equilibrium and the amount of water retained with increasing the amount of Mag-Na. This is often noted in the case of chemical crosslinking where the swelling ratio decreases with increase in the amount of crosslinking agent.[19] It can be deduced that the Mag-Na acts as a crosslinking agent by hydrogen bond with the PVA linear chains during the freezing-thawing process. The amount of water absorbed by the gel is related to the physical crosslinking degree, the hydrophilic character of the Mag-Na and the PVA content as well as the barrier effect of Mag-Na sheets that keep down water molecules from penetrating within the network of PVA/Mag-Na hydrogel composite.

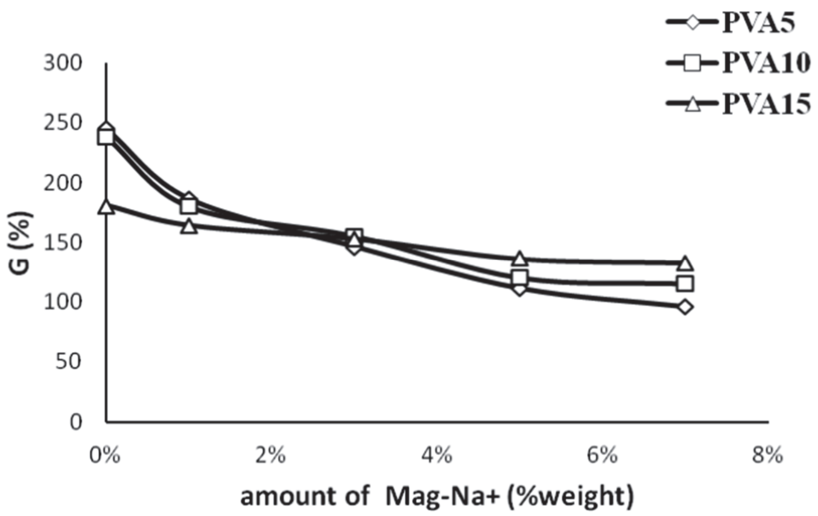

Fig. 5. The swelling of hydrogel composite PVA/Mag-Na

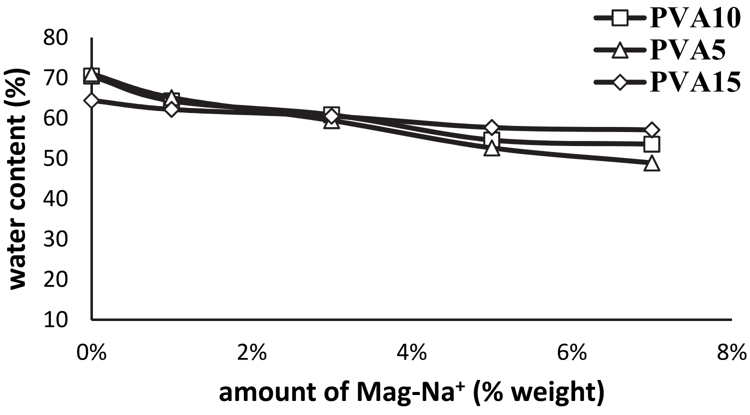

Fig. 6. The water content in hydrogel composite PVA/Mag-Na

3. Conclusion

Composite hydrogels of poly (vinyl alcohol) (PVA) with an unmodified maghnite (Mag-Na) were prepared at different morphologies: exfoliated, intercalated and intercalated-flocculated by freezing-thawing method. The swelling ratio at equilibrium of PVA composite hydrogels decreases with increasing the amount of the maghnite-Na in the hydrogel and increases with increasing PVA content. Increasing the amount of the maghnite in the hydrogel leads to an increase of the network rigidity and a decrease in its swelling. Increasing the PVA content in the hydrogel leads to increased hydrophilicity of the network and its swelling.

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4. Experimental

4.1 Materials

PVA (CAS N° 9902-89-5), having an average molecular weight of 86000 g.mol^{-1} and degree of hydrolysis of 98%, was purchased from aldrich. Algerian montmorillonite clay (Maghnite) used was supplied by a local company (ENOF Maghnia).

4.2 Preparation of Maghnite-Na (Mag-Na)

Maghnite-Na was prepared as follows: crushed raw maghnite (10 g) was dispersed in (250 ml) of NaCl aqueous solution (1M). The mixture was stirred vigorously for 48 hours at room temperature, and then Mag-Na was formed. The separated Mag-Na was washed with large volume of distilled water and filtered several times until the excessive anionic entity (Cl^-) was completed removed. Removing Cl^- ions is tested by introduction of $AgNO_3$ salt, if Cl^- ions are present, AgCl salt precipitates as a white powder. Then, Mag-Na was dried in vacuum oven 100°C. Mag-Na was characterized by XRD and FTIR (see Fig. 2 and Fig. 3).

4.3 Preparation of PVA-Mag-Na composites hydrogels

A series of PVA/Mag-Na hydrogels comoposites were prepared by repeated cycles of freezing and thawing method by using various amount of PVA and Mag-Na following this table:

PVA (% by weight)	5					10					15				
Mag-Na (% by weight)	0	1	3	5	7	0	1	3	5	7	0	1	3	5	7

To prepare each hydrogel, the necessary amount of Mag-Na was stirred with 10 mL of deionized water for 2 hours to gain a desirable Mag-Na suspension. Then, the necessary weight of PVA powder was added gradually to the Mag-Na suspension and the solution was heated at 80°C for 2 hours with stirring to achieve complete dissolution. The obtained aqueous solutions were then poured into moulds and placed at -20°C for 24 hours to produce gel formation. A gel is formed as a consequence of cristallization of PVA molecules. After freezing process, the obtained gels were thawed for 24 hours at room temperature. The freezing-thawing cycles were repeated four times for each solution.

4.4 Structural characterization

Mag-Na, pure PVA hydrogel and all obtained PVA/Mag-Na hydrogel composites were examined using X-ray diffractometry (XRD) and Fourier Transform Infrared spectroscopy (FTIR). X-ray diffraction analysis (XRD) was carried out at room temperature on a Bruker D8 Advance X-Ray diffractometer (40 kV, 30 mA) using CuKα radiation (λ = 0.154 nm) at the rate of 2° min in the 2θ range of 2.0-80°. FTIR analyses were carried out using the PerkinElmer Spectrum Two FT-IR with UATR sampling accessory.

4.5 Swelling and water content measurement

The pre-weighed sample of each hydrogel was immersed into excess of deionized water for five days to extract uncrosslinked species. After this, the samples were dried at room temperature. To swell, the rinsed and dried samples were immersed into excess of deionised water at room temperature until swollen mass showed constant weight. The equilibrium degree of swelling (S%) and equilbrium water content (W%) were calculated respectively as follows :

$$S\% = \frac{Ws - Wd}{Wd} \times 100 \tag{1}$$

$$\mathrm{W}(\%) = \frac{Ws - Wd}{Ws} \times 100 \tag{2}$$

where Ws is the swollen weight of the sample at equilibrium state and Wd is the final dry of the rinsed sample.

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