INFLUENCE OF DISPERSION PROCESS ON THE CHARACTERISTICS OF PVP-CLAY HYDROGEL

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Abstract: Hydrogel is a hydrophilic material and can be used as wound dressing, since it can be biocompatible, potencial drug delivery system and absorbent of fluids. Hydrogels can be produced by one or more hydrophilic polymers; natural or synthetic. These materials have a three-dimensional network of cross-linked polymer chains, and may be synthetized by gamma radiation that crosslinks and sterilizes the hydrogel, in one step. PVP-clays composites show, through many ways of swellings tests, an increase of fluid absorption properties. These properties can be modified when using a mechanical or sonication dispersion process of clay in water, before polymer mixture preparation. The aim of the present study is to prepare a hydrogel with PVP-clay containing poly (N-vinyl-2-pyrrolidone), poly (ethylene glycol), Agar and Laponite clay processed by gamma radiation. The influence of clay dispersion process, clay/polymer ratio in the hydrogel and type of sample (dried or not) were investigate according to the methodology of gel fraction, swelling tests, Scanning electronic microscopy (SEM). According to the results of water swelling, the clay sonication process is more effective than mechanical dispersion, however, if the sample was dried in stove before the swelling test, the results were similar, probable owing to morphology modification promoted by the stove drying process.

Keywords: Hydrogel, Clay, Poly(N-vinyl-2-pyrrolidone), Laponite.

1. INTRODUCTION

Wound dressing are used during the regeneration of dermal and epidermal regions of tissues living, due to your repairing process in injuries such as wounds and burns. These applications are part of biomaterial technology field, and basically study and design new materials with good biocompatibility, high hydrophilicity, physical barriers, bactericidal and regenerative effect [1,2].

These materials are obtained from many ways and by different compounds, polymers show one of the best options for such purposes. One polymeric system very used to this application are the hydrogels, that are defined by many ways for researchers as crosslink network hydrophilic polymers, but the more interesting characteristics of these polymeric systems is the water swollen without lost of their integrity [3].

In recent studies showed that the addition of clay in polymers can modify the property of this material. In hydrogel area, this form of composite is recently investigated from many researches, and is being observed that the hydrogel based on polymer/clay formulation improves mechanical properties and water swelling [4,5].

Hydrogels are produced through the crosslink of hydrophilic polymers in aqueous solution. This process can be from physical or chemical methods or ionizing radiation. Hydrogel can be classified as physical-gels or pseudo gels, depending on electrostatic forces, hydrogen bonds or chain entanglements and chemical (with covalent bonds) [6].

Radio-induced process to produce hydrogels has shown to be one of best methods in nowadays. In this methodology the material can be cross-linked and sterilized in one-step of process. Hydrogels can be obtained through radiation technique applied in solid polymer, monomers or aqueous solution of polymer. When polymer is solution submitted to high energy radiation as gamma radiation , short-lived reactive species such H, $OH^{\cdot}$, e^{-}_{aq}, are immediately generated and cross-linked networks are obtained [7].

In this work, Laponite RD clay (LP) was used due to vast industries applications such as a rheology modifier and reinforcement additive in products like petroleum, personal care, pharmaceutical, agrochemical, and polymer. This inorganic material is a synthetic clay with a nano size particles of lamellae shaped with a thickness of 1 nm and diameter of 25 ± 2 nm. LP has a chemical formula given by: $Na_{0.7}Si_8Mg_{5.5}Li_{0.3}O_{20}(OH)_4$ [11-13].

2. MATERIAL AND METHODS

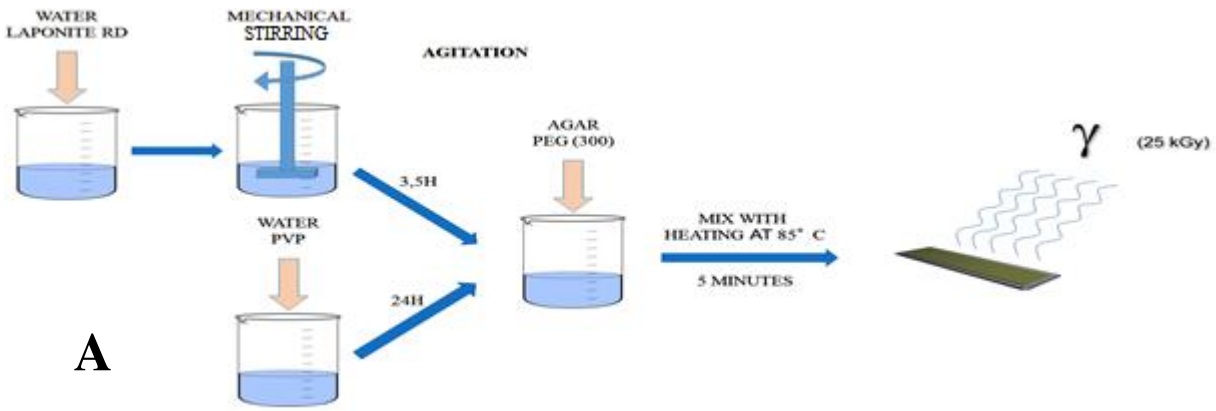
In this present work, the Nano composites were processed by gamma irradiation, and the LP was dispersed in water before the addition on hydrogel solution by two different processes: mechanical stirring examples of (Fig. 1) and sonification examples (Fig. 2. They were characterized by maximum swelling: from the dry membrane and from membrane as recently synthetized. The water swelling was determinated as the fraction gel after 3 weeks.

2.1 Material

Poly (*N*-vinyl-2-pyrrolidone) (PVP) provided by Êxodo Científica, poly (ethylene glycol) (PEG) provided by BRENNT AG, Agar provided by OXOID and Laponite RD Clay provided by BYK Aditives & Instruments.

2.1 Syntheses of hydrogel

To synthesize Nano-composites membranes of hydrogel/clay, three stages were established: LP dispersed, polymers/clay mixture and cross-linked by gamma radiation. To dispersed LP was put in becker with water and after was used two methods different to disperse, mechanical stirring (during 3,5 hours) showed in Figure 1a and sonification (during 30 minutes) showed in figure 1b. The solution was deposited in thermoformed molds of polyethylene terephthalate (PET) and irradiated at 25 kGy.



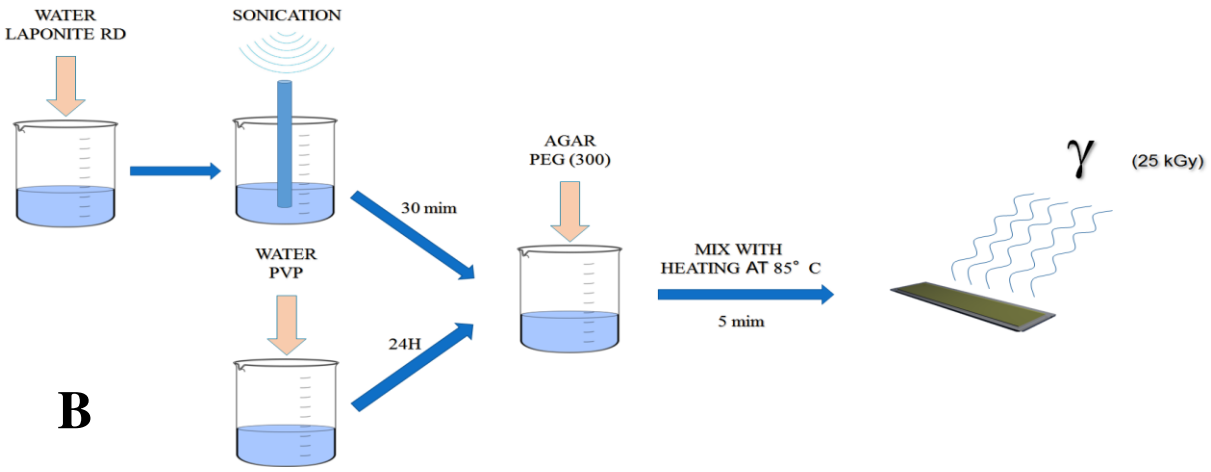


Figure 1: Route 1 of hydrogel prodution (A), Route 2 of hydrogel prodution (B).

2.2 Gel fraction analyses

The gel fraction is the insoluble fraction of the cross-linked polymer, while the sol-fraction is related to the soluble fraction after extraction operation [14]. To determine the gel fraction, the samples were dried in stove for 12 hours, weighted, after that, they were submersed in water for 3 weeks. After extraction, the samples were removed and dried in stove at 50°C for 12 hours and weighted as dried samples. The fraction gel was calculated following equation 1, where the Wi is a mass before extraction and Wf is the mass after extraction.

Equation to determination gel fraction (1):

$$\text{Fraction gel } \% = [Wf / Wi] \times 100 \quad (1)$$

2.3 Swelling

The swelling was determined by submersion of the hydrogel in dry state (dried in stove at 50 °C during 12 hours) and hydrogel from membrane as recently synthetized, in water for 72 hours. The swelling of dried samples was measured after period of one hour up to 15 h and after 24, 48 and 72 h while for recently synthetized were determined each hour for period up to 10 h and after 24, 48 and 72 hours. the swelling was calculated following the equation 2, where W(g) is the initial mass and W(s) is the swollen state:

Equation to determination maximum swelling (2):

$$\text{Swelling } \% = [W(g - s)/W(s)] \times 100 \quad (2)$$

3. RESULTS AND DISCUSSIONS

In Figure 2 was shown a Nano composite by hydrogel/clay membrane.

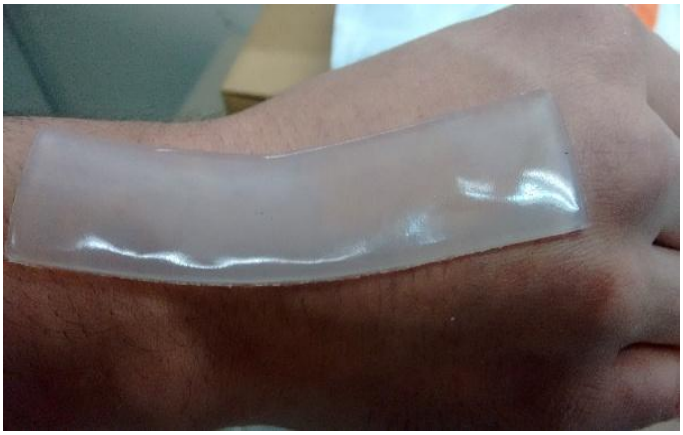


Figure 2: Hydrogel/clay membrane.

3.1 Gel fraction results

Gel fraction quantified the cross-linked fraction of the polymeric system hydrogel. On gel fraction analyses of Nano composites prepared by mechanical clay disperson different results were obtained. At low clay content, the gel content increased related to hydrogel without clay, while increasing clay content the gel decreases. Nano composites prepared by clay sonification result in gel fraction lower than the hydrogel without clay except for the concentration of 20% of clay in which gel fraction turns to the hydrogel without clay value. The results and standard deviation of gel fraction was showed in Table 1:

Table 1: Gel Fraction results.

LP porcentage %	Mechanical stirring	Standard Deviation	Sonification	Standard Deviation
0%	94.12	0.51	94.12	0.51
1%	97.08	0.54	92.29	1.01
2%	98.26	0.35	91.91	0.65
5%	92.61	0.23	93.89	0.84
10%	92.79	0.49	92.44	0.63
20%	94.20	0.42	94.18	0.30

3.2 Swelling results (dried hydrogels)

The swelling graphic of the hydrogels from the dried state are shown in figure 3. The swelling curves demonstrated a similar profile where all masses were stabilized around 24 hours. Hydrogels with 20% of clay presented the smaller swelling in both methods of clay dispersion. It was observed that for all concentrations of clay/polymer (except 20 %) the swelling were higher than the hydrogel without clay. In mechanical stirring process, the concentrations 5 and 1% of clay had the largest swelling content and in sonification process was 2% of clay.

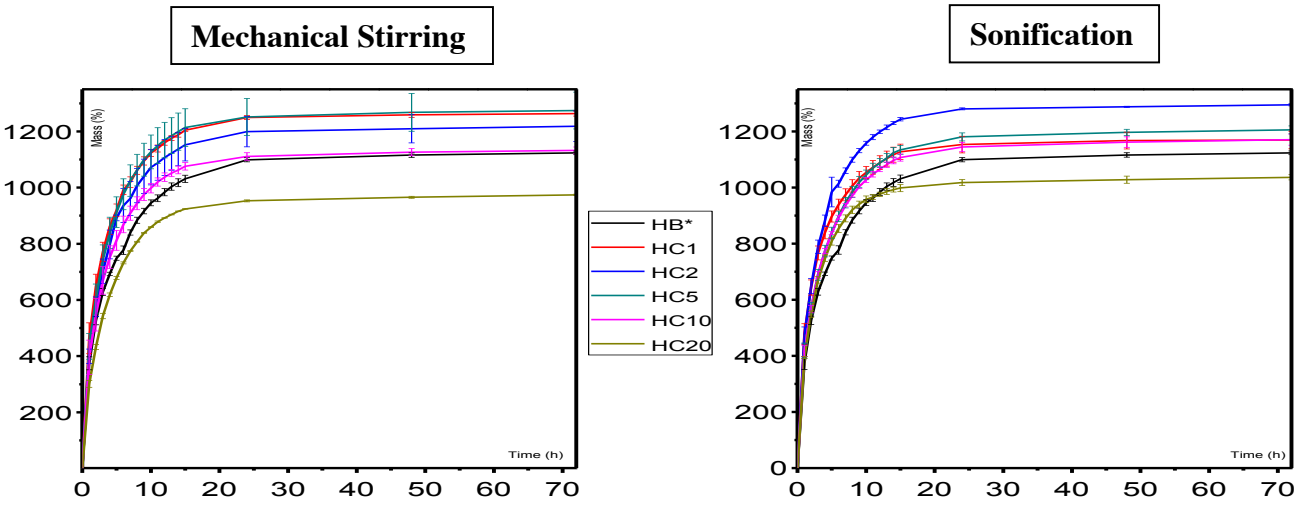


Figure 3: Swelling results by Hydrogels in dry state.

* Where HB is hydrogel without clay, HC1 is the hydrogel with 1%, HC2 is the hydrogel with 2%, HC5 is the hydrogel with 5%, HC10 is the hydrogel with 10% and HC20 is the hydrogel with 20%.

3.3 Swelling results (recently synthetized hydrogels)

The swelling graphic of the hydrogels from the recently synthesized hydrogels are shown in figure 4. All concentrations of clay/polymer showed a higher swelling than the hydrogel without clay. In sonification process was observed that the concentration which promoted the highest result of maximum swelling was 1% of clay, 190% major than the hydrogel without clay. Sonification dispersion process showed that 2,5,10 and 20% promoted an increase of maximum swelling respectively 81, 112, 81 and 56%. In mechanical stirring process the results are closed to the other compared to sonification results. All results were higher than the hydrogel without clay.

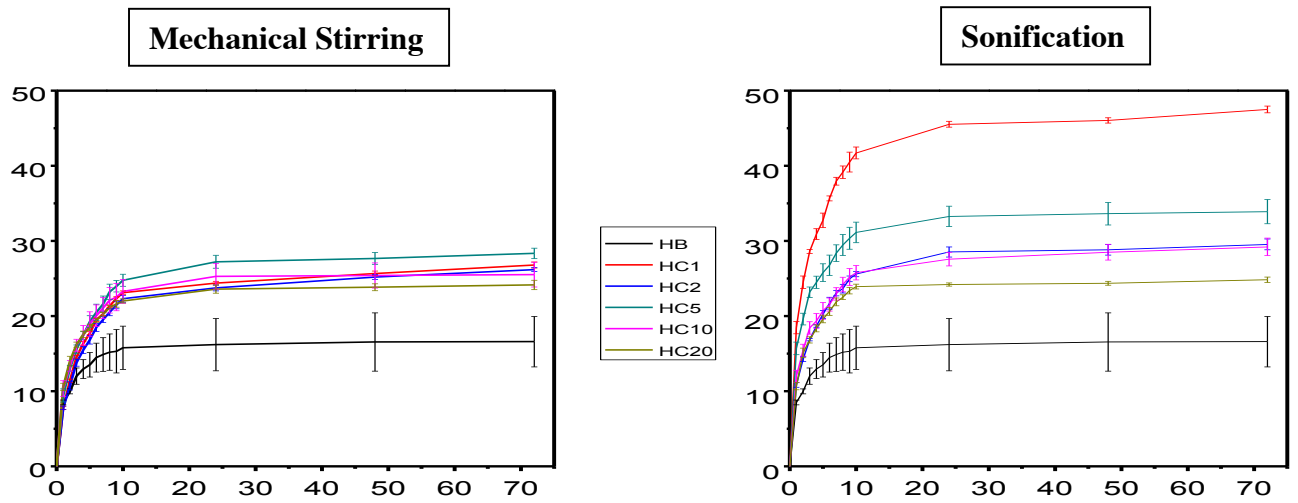


Figure 4: Swelling results by Hydrogels recently synthetized (without drying).

* Where HB is hydrogel without clay, HC1 is the hydrogel with 1%, HC2 is the hydrogel with 2%, HC5 is the hydrogel with 5%, HC10 is the hydrogel with 10% and HC20 is the hydrogel with 20%.

3.4 Scanning electronic microscopy and Energy Dispersive Spectroscopy.

The micrograph and energy dispersive spectroscopy of the surface of Nano composite polymer/clay morphology showed in figure 5. The clay is evident in the image of the hydrogel. In energy dispersive spectroscopy was detected a peak corresponding to silicon attributed to silicon oxide of the clay, as by orange points in the micrograph.

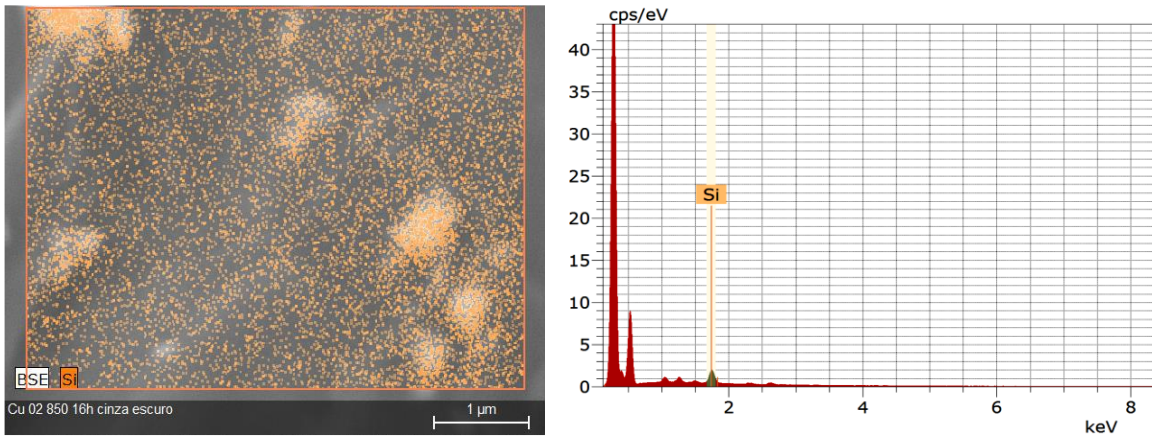


Figure 5: Micrograph and energy dispersive spectroscopy of the hydrogel surface.

4. CONCLUSIONS

In this work were analyzed the differences on properties of hydrogel/clay nanocomposites in relation to the hydrogel without clay under mechanical or sonification process. Considering the hydrogels recently synthesized, it was observed in the swelling tests that the nanocomposite had higher swelling than the hydrogel without clay and under sonification the 1% of clay hydrogel had a gain of 190% of higher swelling than the hydrogel without clay. When the hydrogels are dried the differences on swelling are the minimum. Probably the network morphology was disrupted and the differences between the processes mechanical and sonification were lost.

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