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INFLUENCE OF GAMMA IRRADIATION DOSE AND CONCENTRATION OF LAPONITE CLAY ON POLY (N-VINYL-2-PYRROLIDONE) HYDROGELS

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ABSTRACT

Hydrogels are polymeric biomaterials widely used in biomedicine and defined as an insoluble system of one or more crosslinked hydrophilic polymers, capable of absorbing large amounts of fluids without losing their physical integrity. Composed by one three-dimensional network of crosslinked polymer chains they can be synthesized by various physical and chemical methods including radiation. One of these methods is the gamma irradiation process, which forms the crosslinked network and sterilizes the material in a single step. In the biomedical field one of hydrogels applications is the transdermal dressings, these systems have an impact of great value in the treatment of wounds, as they can protect regions injured by burns, cuts and even chronic wounds. The association of clay to hydrogels promotes a modification of properties of these materials, such as swelling and gel fraction. Thus, the objective of this work was to evaluate the swelling properties and gel fraction of hydrogels based on polymer formulation of poly (N-vinyl-2-pyrrolidone), poly (ethylene glycol), agar containing nano-clay laponite RD in Different concentrations (0, 0.01, 0.1, 0.5, 1, 2, 5, 10, 20%). The materials were mixed by stirring and heating and then processed by gamma radiation from Co-60 at doses of 10, 25, 50 and 70 kGy. To evaluate the gel fraction, the membranes were immersed in water for 3 weeks. The swelling was evaluated after 48 hours of immersion in distilled water at room temperature. It was observed that as the clay concentration increases regardless of the irradiation dose the amount of gel fraction decreased and the amount of water absorption increased.

1. INTRODUCTION

Hydrogels are formed by one or several polymeric, natural and or synthetic components, which are interconnected by three-dimensional networks. They have a high degree of flexibility that is very similar to natural living tissues. Their structure is composed of polymers which have hydrophilic groups such as -OH, -COOH, $-CONH_2$, $-SO_3H$, amines and R_4N^+, which provide the ability to swell in the presence of water or biological fluids, storing them between the spaces of the macromolecules, without losing their physical integrity. In the equilibrium state of swelling the water fraction contained in the material is much larger than the polymer fraction that provides a low interface energy when in contact with body fluids these characteristics promote to the hydrogels an excellent biocompatibility. Poly (N-vinyl-2-pyrrolidone) (PVP) is a widely used polymer as a biomaterial [1-4].

This polymer was developed 70 years ago by Prof. Dr. Walter Reppe at BASF, where he patented it. The initial application of PVP was in the replacement of blood plasma, being widely used in World War II. Gradually, applications have been found in different industries such as pharmaceuticals, cosmetics, detergents and textiles. PVP is a white hydrophilic powder with amorphous molecular structure, has no crystalline melt, but only a glass transition temperature which may vary from 110 - 180 ° C. In the industry PVPs of molecular weights of about 2,000 to 2,500,000 g/mol are available depending on the degree of polymerization [5].

PVP is capable of forming strong hydrogen bonds, PVP dissolves in water and in many polar solvents such as methanol, ethanol, glycol, glycerol, N-methylpyrrolidone (NMP), dimethylformamide (DMF) and dimethylacetamide (DMAC). PVP can also be associated and complexed to polar surfaces and inorganic structures such as PVP-iodine used in the medical treatment of wounds [5].

Hydrogels can be synthesized by various physical crosslinking techniques such as heating / freezing cycles of polymer solutions, ionic interactions, hydrogen bonding and heating maturation inducing aggregation; And can be crosslinked by chemical crosslinking techniques such as crosslinking agents, catalysts, UV light, and ionizing radiation through high energy sources such as gamma rays [1-2].

Ionizing radiation in gamma source, high energy electromagnetic wave from nuclear origin, is a technique that provides greater practicality by crosslinking and sterilizing polymeric membranes in a single step radiation. The most commonly used sources of ionizing radiation are those of ^{60}Co and ^{137}Cs that emit gamma radiation, ^{60}Co is produced from ^{59}Co in nuclear reactors by neutron capture, and is the more used source due to the higher energy intensity of its gamma emissions (higher radiation penetration power) relative to ^{137}Cs. [6].

The formation of hydrogels from the technique of ionizing radiation is due to the result of mutual recombination of macroradicals. The ionizing radiation can be applied to dry solid polymer, aqueous polymer and monomer. The irradiation of solid state polymers presents some difficulties such as the lack of macroscopic homogeneity of the hydrogels and requires higher doses of irradiation compared to the synthesis in aqueous solution of the polymers and lastly present difficulties for the removal of the present oxygen, which promotes unwanted reactions [1].

Irradiation of polymers in aqueous solution, eq. 1, promotes chemical changes precisely by the indirect action of radiation, this process is initiated through the radiolysis of water, which when exposed to ionizing radiation of high energy, generates reactive species that interact with the polymer in solution [7-8].

$$H_2O^{\text{Radiação Ionizante}} = {}^{\bullet}OH;\ H^+;\ {\cdot}e^-_{(aq)} \tag{1}$$

Poly (N-vinyl-2-pyrrolidone) (PVP) in aqueous solution, under ionizing radiation, is influenced mainly by the action of the hydroxyl radicals ● OH being negligible the influence of e- (aq) (Species produced in the radiolysis of water). The probable structures of the PVP radicals obtained by the abstraction of hydrogen by the hydroxyl radicals (● OH) are shown in Fig. 1 [8].

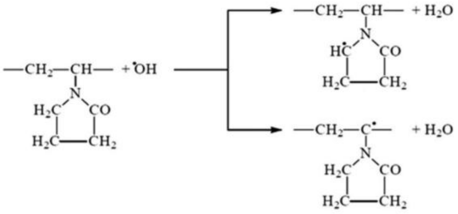

Figure 1: Macroradicals generated during irradiation of dilute aqueous PVP solution[8]

The addition of clays to organic compounds has been the subject of numerous researches, due to a type of interaction in which the interlamellar space can be occupied by polymeric materials or organic compounds. This system can be applied in biomaterials, engineering polymers, packaging, agricultural materials, dental polymers and dressings for wound treatments. This mixture gives to this system an increase of mechanical properties, and physical-chemical properties [9-12].

Clays can be defined as natural or synthetic, earthy, fine-grained material which when moistened with water exhibits plasticity. They consist of clay minerals that have lamellar layers formed by silicon (or aluminum) tetrahedra and oxygen, and lamellae formed by octahedra of aluminum (magnesium, iron or lithium) oxygen and hydroxyl. The clays are classified by the type of cation present in the octahedral lamella [13].

In definition nanostructured materials are those having nanoscale elements added to a matrix like nanotubes, nano spheres, nano sheets, these have at least one size less than 100 nanometers. This mixture can enhance physical-chemical and mechanical properties of this material relative to pure material. The application of nano-clays to polymers has been of scientific interest in recent years, including layered silicates (clays), which are widely used in nanostructured polymers [14].

The Laponite Clay (LP) is a nano synthetic clay of approximately 25 nm in diameter and 0.92 nm thick, classified as a hectorite clay, is highly hydrophilic and forms gel when in aqueous solution. It is composed of an octahedral sheet of magnesium oxide and lithium between two tetrahedral sheets of silicon oxide, has an Na + ion between its lamellae. This clay frequently used as a rheology modifier in polymers, cosmetics and pharmaceuticals is represented chemically according to the formula: Na + 0.7 [(Si8Mg5.5Li0.3) O20 (OH) 4] -0.7 [17].

A number of commercial formulations using Laponite involve multicomponent clay blends with various polymers. The addition of these polymers also modifies the interactions between the particles and the properties of the resulting materials. It can also be observed the modification of mechanical and rheological properties in systems containing Laponite in conjunction with the polymer [15].

During the wound healing process, the immune system also produces exudate, which results from the death of bacteria and neutrophils associated with polar fluids. This product can disrupt the healing process, so it is important that dressings have the ability to absorb fluids. In order for there to be an adequate use of the dressing it is essential to exhibit mechanical properties such as tensile strength and compression, as they will undergo such stresses when applied to some part of the body with wounds [16].

2. MATERIALS AND METHODS

2.1. Hydrogel materials

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

2.2. Method of production of hydrogel membranes

Polymer mixture (PVP 6% / PEG 0.45% / Agar 1.5%) were solubilized by heating and stirring in aqueous medium by adding pre-dispersed clay. This step of the process will give rise to the pseudo gel where there will be only physical bonds between the polymer molecules. The hydrogel membranes were synthesized through the process of ionizing radiation that uses the indirect interaction of gamma radiation. This step of the process will promote the chemical crosslinking of the polymer chains forming covalent bonds between them [18]. The membranes were irradiated by ionizing radiation from ^{60}Co gamma source, model 220 of the CTR - IPEN, circular geometry, operating the dose rate of 5.72 kGy h^{-1}. The radiation absorbed doses were of 10, 25, 50 and 70 kGy.

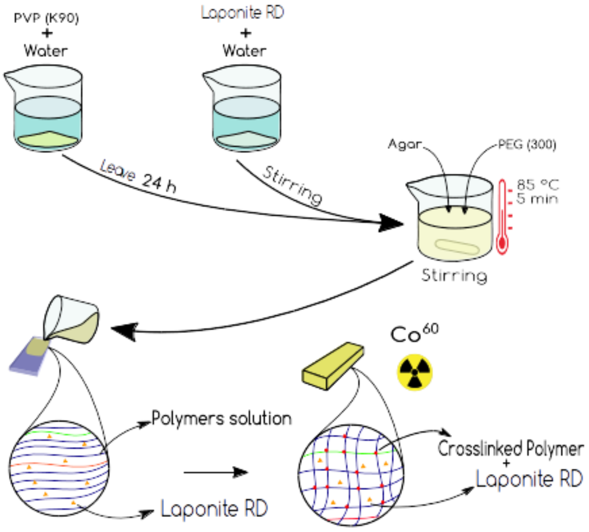

Figure 2: Scheme of formulation, preparation and irradiation synthesis of the hydrogel.

2.3. Gel Fraction

The gel fraction contained in a material is equivalent to the polymer chains of the hydrogel that were interconnected during the crosslinking process [1]. One of the techniques used to evaluate the gel fraction is the measurement of the mass of the insoluble portion of a sample. The technique requires complete dehydrated so that its mass is measured before the analysis (Mi), and then measured after extraction in water for 3 weeks. After extraction the remained material of the crosslinked material is then dried and its mass measured (Mf). The gel fraction is calculated according to equation 2:

$$GelFraction(hydrogel\%) = \frac{Mf}{Mi} * 100 \tag{2}$$

2.4. Sweling

Swelling of the hydrogels will be assessed by subjecting the hydrogel membranes to a buffered saline solution (NaCl 0.9%) pH 6.0. The mass will initially be measured in the sample as such (Mi) and at regular intervals (Mr) after immersion of the membranes in the solution. The analysis will last the maximum time of 72 hours. The degree of swelling will be established by the following equation 3:

$$Swelling\% = \frac{Mr - Mi}{Mi} * 100 \qquad (3)$$

3. RESULTS

3.1. Gel Fraction

Fig. 3 shows the graph of gel fraction where we can relate with the degree of cross-linked of the produced membranes. It can be seen that hydrogel membranes having in their composition from 5% to 20% clay showed a similar and pronounced gel fraction decrease for all irradiation doses. On the other, for lower concentrations (<5%) of clay in the hydrogel membranes, as 0.01; 0.1; 1; 2, the gel fraction values were similar, remaining with approximately 90% gel fraction, except for 10kGy dose where the lower initial result increased up to 5% of clay. This fact allow us to propose that the laponite clay in quantity higher than 5%, that means ratio clay : polymer of 1:1, can reduce the degree of crosslinking of the polymer matrix, this phenomenon may be linked to the difficulty to crosslink the polymer higly absorbed in the clay surface.

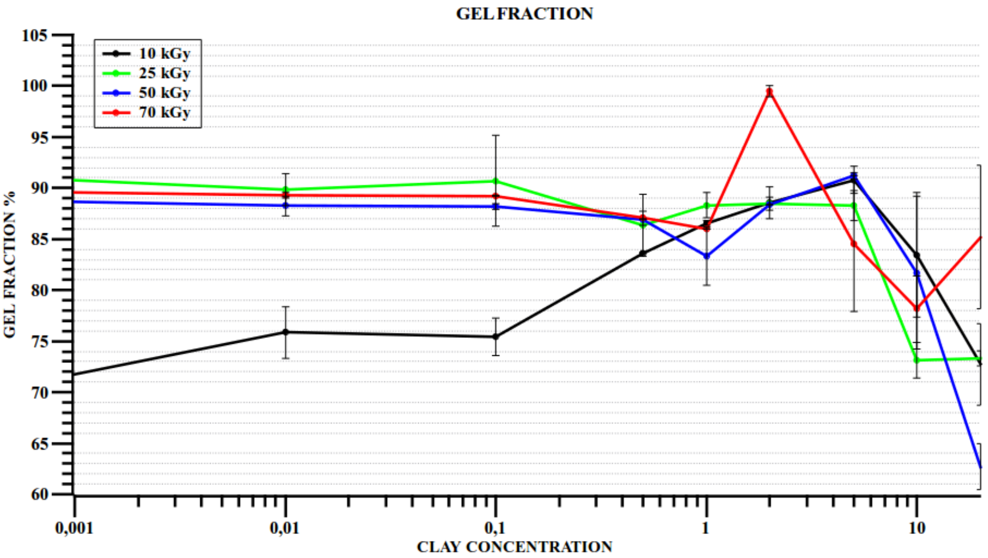

Figure 3: Gel fraction percentages in relation to clay concentrations.

3.1. Swelling

Table 1 shows the results of swelling of the hydrogel membranes at different concentration of clay (0; 0.01; 0.1; 0.5; 1; 2; 5; 10; 20 %) and irradiated in different doses (10; 25; 50; 70 kGy). Through these results it was possible to observe that for hydrogels containing high concentrations of clay the swelling was relatively higher in relation to the hydrogels without clay. It is also clear that while increasing the irradiation dose the swelling decreases however in high concentrations of clay this effect is not very effective because the high swelling remains. For hydrogels containing 20 % of clay compared to hydrogels without clay, we obtain a gain of 7,68; 7,40; 23,07; 77.64 times of increase on swelling for the respective irradiated ones at doses 10, 25, 50 e 70 kGy reflecting the capacity of the clay swells the water. In other hand hydrogels with 20% of clay showed decrease of swelling with increase of absorbed dose reflecting the crosslink under radiation.

Table 1: Numerical results of the swelling test in water.

Clay concentration/radiation dose	10kGy	S.D.	25kGy	S.D.	50kGy	S.D.	70kGy	S.D.
0	36.44	2.83	23.69	0.72	7.00	2.05	2.89	2.16
0.01	37.68	0.63	26.14	1.50	7.92	1.84	9.88	0.39
0.1	33.59	1.12	31.00	1.89	12.50	4.42	8.14	0.14
0.5	37.66	0.39	27.89	6.06	9.16	2.03	11.06	0.65
1	56.69	0.03	39.67	3.66	10.30	4.19	7.40	2.69
2	60.27	5.30	26.84	3.10	7.11	2.10	7.03	2.25
5	54.58	3.32	47.84	2.11	18.77	0.76	24.97	1.57
10	142.39	2.90	73.36	12.35	54.71	2.06	69.53	2.31
20	280.02	23.87	175.49	7.70	161.52	14.47	224.74	15.72

4. CONCLUSIONS

In the present work, it was produced different PVP hydrogels in composition with Laponite RD clay. It can be concluded from this study that the addition of laponite clay may promote the increase in the degree of swelling of PVP hydrogels owing to the capacity of the clay swells in the water. In other hand hydrogels with >5% of clay showed decrease of gel fraction because the high clay:polymer ratio. Swelling capacity reflected both capacity of clay water absorption and increase with absorbed dose reflecting the crosslink under radiation.

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REFERENCES

1. GULREZ, S. K. H.; AL-ASSAF, S.; PHILLIPS, G. O., *Progress in molecular and enviromental bioengineering - from analysis and modeling to technology application: Hydrogels: Methods of preparation, characterisation and application.* 1 ed. Croacia: InTech, pp.117-150, 2011.
2. AHMED E. M., "Hydrogel: Preparation, characterization, and applications: A review", *Journal of Advanced Research* , **Volume 6**, pp. 105 - 121, 2015.
3. ROSIAK J.M., ULAŃSKI P., "Synthesis of hydrogel by irradiation of polymers in aqueous solution", *Radiation Physics and Chemistry,* **Volume 55**, pp. 139- 151, 1999.
4. PEPPAS N. A., BURES P., LEOBANDUNG W., ICHIKAWA H., "Hydrogels in pharmaceutical formulations", *European Journal of Pharmaceutics and Biopharmaceitics,* **Volume 50**, pp. 27- 46, 2000.
5. FISCHER F., BAUER S. "Ein Tausendsassa in der Chemie Polyvinylpyrrolidon", *Chemcal Unserer Zeit,* **Volume 43**, pp. 376 - 383, 2009.
6. WOJNÁROVITS, L. *Handbook of Nuclear Chemistry,* Kluwer Academic Publishers, cap. 1, 2003.
7. ROSIAK J.M., ULAŃSKI P., PAJEWSKI L. A., YOSHII F., MAKUUCHI K., "Radiation formation or hydrogels for biomedical purposes. Some remarks and comments", *Radiation Physics and Chemistry,* **Volume 46**, pp. 161- 168, 1995.
8. KADLUBOWSKI S., "Radiation-induced synthesis of nanogels based on poly(N-vinyl-2-pyrroliidone)-A review", *Radiation Physics and Chemistry,* **Volume 102**, pp. 29-39, 2014.
9. OLIVEIRA, M.J.A., ESTEFÂNIA, O.S. ; LÚCIA, M.A.B. ; REGINA, M. ; AMATO, V.S. ; LUGÃO, A. B. ; PARRA, D. F. "Influence of chitosan/clay in drug delivery of glucantime from PVP membranes". *Radiation Physics and Chemistry,* **Volume 94**, pp. 194-198, 2014.
10. OLIVEIRA, M.J.A.; PARRA, D.F.; AMATO, V. S.; LUGAO, A. B. "Hydrogel membranes of PVAl/ clay by gamma radiation". *Radiation Physics and Chemistry,* **Volume 84**, pp. 111-114-114, 2013.
11. CHUI, C.W., LIN, J.J., "Self-assembly behavior of polymer-assisted clays", *Progress in Polymer Science,* **Volume 37**, pp. *406– 444, 2012.*
12. HARAGUCHI K., TAKEHISA T., "Nanocomposite Hydrogels: A Unique Organic–Inorganic Network Structure with Extraordinary Mechanical,

Optical, and Swelling/Deswelling Properties”, *Advanced Materials,* **Volume 14**, pp. *1120-1124, 2002.*

13. KROON M., VOS W. L., WEGDAM G. H., “Structure and formation of a gel of colloidal disks”, *Physical review e,* **Volume** 57, pp. 1962-1970, 1997.
14. WU W., DONG Z., HE J., YU J., ZHANG J., “Transparent cellulose/Laponite nanocomposite films”, *Journal Material Sciences,* **Volume** 51, pp. 4125 - 4133, 2016.
15. LIU X., BHATIA S. R., “Laponite® and Laponite®-PEO hydrogels with enhanced elasticity in phosphate-buffered saline”, *Polymers Advanced Technologies,* **Volume 26**, pp. 874 - 879, 2015.
16. JONES V., GREY J. E., HARDING K. G., Wound dressings, *ABC of wound healing,* **Volume 332,** pp. 777-780, 2006.
17. SHIKINAKA K., AIZAWA K., MURAKAMI Y., OSADA Y., TOKITA M., WATANABE J., SHIGEHARA K., “Structural and mechanical properties of Laponite–PEG hybrid films”, *Journal of Colloid and Interface Science,* **Volume 369**, pp. *470-476, 2012.*
18. AJJI Z., OTHMAN I., ROSIAK J.M., Production of hydrogel wound dressings using gamma radiation, *Nuclear Instruments and Methods in Physics Research,* **Volume B 229**, pp. 375–380, 2005.