POLYMER NANOCOMPOSITE OF LAPONITE RD PREPARED BY GAMMA IRRADIATION

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Abstract:

Nanocomposite hydrogels based on polyvinyl alcohol (PVAl) and polyvinylpirrolidone (PVP) containing 0–5 wt % of the synthetic laponite RD clay were prepared by gamma irradiation process. The morphology of the nanocomposite hydrogel was observed by characterizations techniques using: scanning electron microscopy (SEM) and atomic force microscopy (AFM). The structural properties crosslinking was determined by measuring the crosslink gel content extraction on mesh 500 sizes and swelling kinetics at 22 °C. The results showed that crosslinks have inverse dependence on the clay level in the nanocomposite hydrogels, while swelling shows direct dependence.

Keywords: *Hydrogels, clay, nanocomposite*

1 Introduction

The current study of polymer science considers the ares of biomedical application areas of great importance to establish developments in new polymeric materials. Example of that are hydrogels for controlled release of drugs made synthetic through nanogel and microgel [1; 2]. The use of radiation processes to polymeric croslinking of those hydrogels is reported [3].
Recently, especially polymeric nanocomposites with natural clays have been focus of interest of many researchers [4]. These represent a rational alternative to conventional polymers, employing a small percentage of clay to improve mechanical properties, good transparency, thermal stability, low gas permeability [5], incluing the high capacity of clays to adsorb different substances [6]. The exfoliated clay nanocomposites are attracting more interest, owing to the increase of interactions between the polymer and clay [7].
In this work, hydrogels were formulated from polyvinyl alcohol (PVAl) and poly (N-2-vinyl-pyrrolidone) (PVP) with nanostructured clays in order to enable controlled release systems of high efficiency.

2. Experimental

2.1 Materials and Methods

Poly(vinyl alcohol) (PVAl) (Mw = 85000, degree of hydrolysis 98,4%) CelvolTM 325 provided by Dermet Agekem, Poly(N-2- vinyl-pyrrolidone) (PVP), K-90 supplied by BASF, agar provided by Oxoid and clay laponite RD coding S/1116/10 provided by Buntech were used. The membranes were processed according to IPEN protocol of hydrogel crosslinking by gamma irradiation in ^{60}Co source using 25 kGy dose.

2.2 Swelling

Hydrogels membranes previously dried were immersed in distilled water and weighed periodically until 30h. The swelling was calculated according to the equation A.

$$S\% = (Ms-Md)/Md.100\ (\%H_2O \text{ per g hydrogel}) \quad (A)$$

2.3 Gel fraction

The gel fraction was obtained by immersion of the samples in water at around 100°C, for 12h to the extraction, under stirring. The water was replaced after each 4h. After that the samples were dried in oven (100 °C) and the gel fraction was calculated by the equation B.

$$\text{Gel fraction} = Mf / Ms .100 \quad (B)$$

where: Ms is the dry mass before extraction and Mf is the mass of the dried sample after extraction.

2.4 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) was done using an EDAX PHILIPS XL 30. In this work, gold sputter-coated layer was deposited onto the samples of nonconducting materials, to proceed morphological observations.

2.5 Atomic Force Microscopy (AFM)

The use of AFM for the study of polymers is very widespread, since it allows new information about the surface of polymers, such as morphology, phase distribution composites, among others. The apparatus used was SOLVER (Scanning Probe Microscope) NT-MDT, located in Brazilian Synchrotron Light Laboratory (LNLS) Campinas-SP.

3 Results

3.1 Swelling and gel fraction

Fig. 1 shows that the water absorption rate is significantly higher at the immersion times minor than 5h, after it the rate of absorption increases only slightly. Swelling is similar for PVAl/PVP hydrogels and hydrogels with 0.5% and 1.0 % of clay. The hydrogel with 1.5% clay showed a significant decreased swelling. The influence of clay content in the hydrogels behavior is shown at table 1. In the hybrid

hydrogel the increase in clay content increases the gel proportion, which can be related to the increase of covalent interactions obtained by gamma crosslinking.

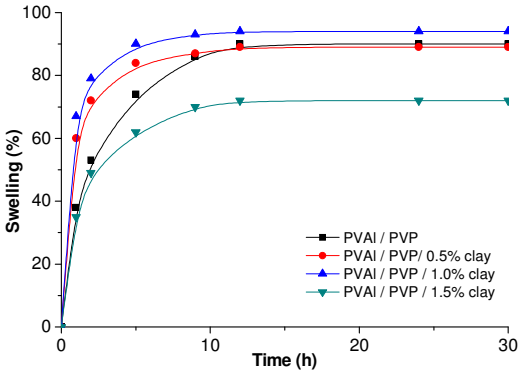

Figure 1 – Swelling of PVAl/PVP/laponite RD, hydrogels obtained by gamma irradiation.

Table 1 - Gel fraction CONTENT of dried hydrogels PVAl/PVP/ laponite RD

Samples	Gel Fraction (%)
PVAl / PVP	69.0
PVAl / PVP / 0.5 % clay	57.3
PVAl / PVP / 1.0% clay	73.7
PVAl / PVP / 1.5% clay	83.9

3.2 Scanning Electron Microscopy (SEM)

The fracture surface micrography, Fig. 2 of dried PVAl/PVP hydrogel present random lacunas and pores.

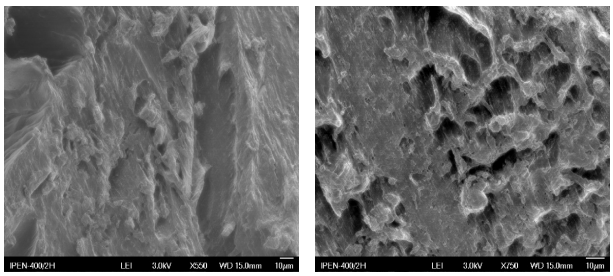

Figure 2 – SEM images of dried PVAl/PVP hydrogel, obtained by gamma irradiation

Hydrogel with 1.0% of clay present the smallest and more organized porosity. It is possible to deduce that the clay is homogeneously dispersed, without micro agglomeration, Fig. 3.

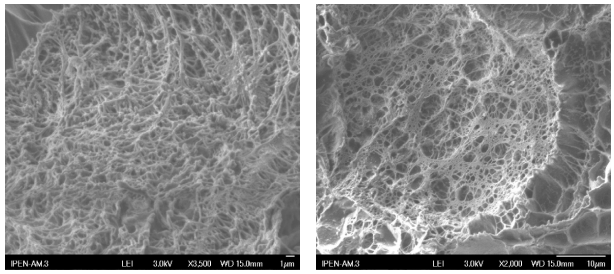

Figure 3 – SEM images of dried PVAl/PVP hydrogel with 1.0 % of clay laponite RD, obtained by gamma irradiation

3.3 Atomic Force Microscopy (AFM).

Atomic force microscopy has been used to study the properties of nanocomposites. In Figure 4 is shown the dispersion of nanoparticles on the surface of polymeric samples. The roughness was attributed to the clay content observed in the surface and the crosslinked surface.

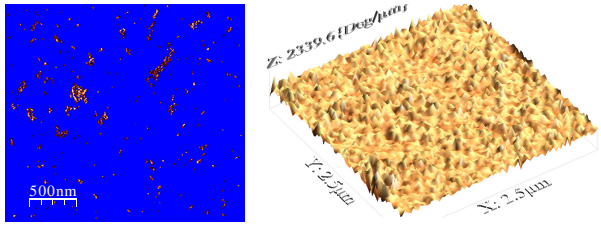

Figure 4 – AFM hydrogels PVAl/PVP/clay laponite RD, obtained by gamma irradiation, dose 25 kGy.

4. Conclusion

The results are coherent with the expectations, demonstrating that the combination of PVAl/PVP/clay increases the crosslink and reduces spaces between polymeric chains in the hybrid material of hydrogel nanocomposites.

Acknowledgements

Support by FAPESP 09/50926-1, FAPESP Process nº 2009/18627-4 CNPq Process n° 310849/2009-8, CAPES, IPEN/CNEN, and technician Eleosmar Gasparin for thermal analysis. Laboratory (LNLS) Campinas-SP by analyses AFM.

References

[1] T. Daniel, et. al., Synthesis of Poly(vinyl acetate) Nanogels by Xanthate-Mediated Radical Crosslinking Copolymerization, *Macromol. Rapid Commum*, 29, 1965-1972, 2000.

[2] P. Ulanski, et al., Nano-micro and macroscopic hydrogels synthesized by radiation technique, *Nuclear Instruments and Methods in Physics Research B*, 208, 325-330, 2003.

[3] [3] J. Jagur-Grodzinzki, Polymeric gels and hydrogels for biomedical and pharmaceutical a pplications, Review, *Polymers Advanced Technologies*, 2010.

[4] J. H. Lee, et. al., Poly(Acrylamide/Laponite) Nanocomposite Hydrogels: Swelling and Cationic Dye Adsorption Properties, *Journal of Applied Polymer Science*, Vol. 111, 1786– 1798, 2009.

[5] Y. Takeoka, et. al., Recent advances in hydrogels in terms of fast stimuli responsiveness and superior mechanical performance, *Polymer Journal*, Vol. 42, 839–851, 2010.

[6] N. H. Norma, et al., Silylation of laponite clay particles with monofunctional and trifunctional vinyl alkoxysilanes, *J. Mater. Chem.*, 15, 863–871, 863, 2005.

[7] K. A. Carrado, *Polymer-clay Nanocomposites*, Advanced Polymeric Materials-structure Property Relationships, chapter 10, 2003.