O Poly(N-2-vinylpirrolidone) (PVP) Poly(vinylalcohol)(PVAl)/Laponite RD Hydrogels Nanocomposite Membranes

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Abstract., Nanocomposite hydrogels based on Poly(N-2-vinylpirrolydone)(PVP)/ Poly(vinylalcohol)(PVAl) were synthesized using laponite RD. Ionizing process from gamma radiation (25 kGy) was used as network crosslinker. Swelling behavior of nanocomposite hydrogels was analyzed in function of clay concentration. The structure of nanocomposite hydrogels was investigated by Scanning Electron Microscopy (SEM) and Thermogravimetric Analysis (TGA) techniques.

Resumo. Hidrogéis nanocompósitos de Poly(N-2-vinylpirrolydone)(PVP)/ Poly(vinylalcohol)(PVAl) foram sintetizados com laponita RD. A reticulação foi feita por processo de irradiação de fonte gama (25 kGy). O intumescimento foi analisado em função Ca concentração de argila. A estrutura do nanocompostp foi investigada por Microscopia Eletrônica de varredura (SEM) e termogravimetria (TGA).

Keywords: Hydrogel, PVP/ PVAl, Nanocomposite.

1. Introduction

Recently, clay–polymer nanocomposites (NCs) have been the focus of much attention due to their excellent physical properties, such as heat resistance, transparency, and so on. These properties are much superior to those that would be expected by a simple additive rule. This is partially due to the strong interactions at the clay–polymer interface [1].
Exfoliated clay-polymers nanocomposites have attracted attention of researchers in last years due to the combination of organic molecules and inorganic ions, offering new products perspective, with different applications [2]. Among polymeric matrices, hydrogels are investigated especially as biomaterials and the exfoliated clay shows great interactions with the polymer due to their hydrophilic superficial area. The polymeric hydrogel with dispersed clay is a new class of polymeric composites that combine elasticity and permeability of hydrogels with high capacity of absorbing different substances of clay [3].
The hydrophilic hydrogels are made of water insoluble polymeric materials, since the polymer is crosslinked [4], generating a tridimensional mesh, that shows the capacity of absorbing water in its interior keeping the balance without breaking its structures [3]. The swelling results from a balance between dispersion strength acting in hydrated chains and the cohesion strength due to its covalent crosslinks. The terminally attached polymer chains are flexible and capable of fast changing their conformation. This feature has been used for increasing the swelling degree and swelling rate of hydrogels [5] and to accelerate the rate of shrinking/swelling of stimuli-sensitive hydrogels in response to changes of external condition (pH, temperature) [6].
The aim of this work was the synthesis of hydrogels nanocomposites from PVP / PVAl with clay nanoparticles with the objective of feasible controlled liberation of high efficiency systems. Gamma rays reticulation process was used to synthesize and sterilize the hydrogel nanocomposites at once and creating the nano and microstructures.

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/11176/10 provided by Buntech were used.

The formulations prepared for crosslinking were obtained by dissolving PVAl (10% w/v) in water using a hot plate with magnetic stirrer and temperature between 80 and 85 °C for 40 minutes. PVP (10% w/v) was dissolved using the same way at 100 °C for 5 minutes. The clay was added to PVP and PVAl solution under agitation at 85 °C for five minutes. The resulting solutions were placed in Petri dishes and sent to the crosslinking process by gamma irradiation in ^{60}Co source using 25 kGy dose.

2.2 Swelling

After synthesis, dry samples were immersed in distilled water and weighed periodically until 60h. The swelling was calculated according to the equation A.

S% = (Ms-Md)/Md.100 (%H_2O per g hydrogel)   (A)

where: Ms is the mass of swelled polymer and Md is the mass of the hydrogel .

2.3 Gel fraction

The gel fraction was obtained by immersion of the samples in water at around 100°C, for 12h to proceed 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. Gel fraction = Mf / Ms x100 (B), where: Ms is the dry mass before extraction and Mf is the mass of the dried sample after extraction.

2.4 Thermal Analysis

Thermal analysis were carried out by Thermogravimetry (TG), performed in a Mettler-Toledo TGA/SDTA 851 thermobalance, under inert atmosphere of N_2 from 25 to 600 °C at heating rate of 10 °C min^{-1}. 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. The technique was used for verification of pores and clusters of nanoparticles

3. Results and Discussion

3.1 Swelling and gel fraction

The presence of clay interferes in the crosslink of the polymeric system. The addition of 0.5% of clay increased at about 110% the swelling and decreased at about 12% the gel content. The influence of laponite content in the hydrogels swelling (S%) and gel content behavior is shown in table 1. In the hybrid hydrogel the increase in clay content decreases the swelling proportion, which can be related to the increasing of covalent interactions, obtained by gamma crosslinking. The result of gel fraction indicates that increasing of clay increases considerably the crosslink and corroborates with the decreasing of S%. The nucleation effect observed in the hybrid material is more effective than superior doses of radiation in the interval 20-35 kGy usually used in hydrogel membranes. In this case we can affirm that the clay reduces the spaces between polymeric chains.

Table 1 - Percentage of swelling and gel fraction of dried hydrogels PVAl/PVP and clay laponite RD, obtained by gamma irradiation.

Samples	Swelling (%)	Gel Fraction (%)
PVAl+PVP	167	69.0
PVAl+PVP+ 0.5 % clay	277	57.3
PVAl + PVP + 1.0% clay	251	73.7
PVAl + PVP + 1.5% clay	228	83.9

3.2 Thermal Analysis

3.2.1 Thermogravimetry (TGA)

Thermal decomposition occurs in three events. The first around 100~200 °C was associated to the loss of associated water; in both polymers the second event was associated to PVAl decomposition and the third to the PVP decomposition.
There are small differences on the thermal behavior of the composites when compared to the clay free hydrogel that earn attention. The second event suffers a displacement of onset decomposition temperature, at about 5-10°C. It can be associated to the interactions between PVAl and the clay, at level of the intercalation clay–polymer increasing the thermal stability. The same can be seen observing the increasing in the in the maximum decomposition temperature, figure 2. The clay intercalation affects also the third decomposition event, because part of the polymer stabilizes in the clay channels and is not eliminated at high temperature, (figure 1 A and B).

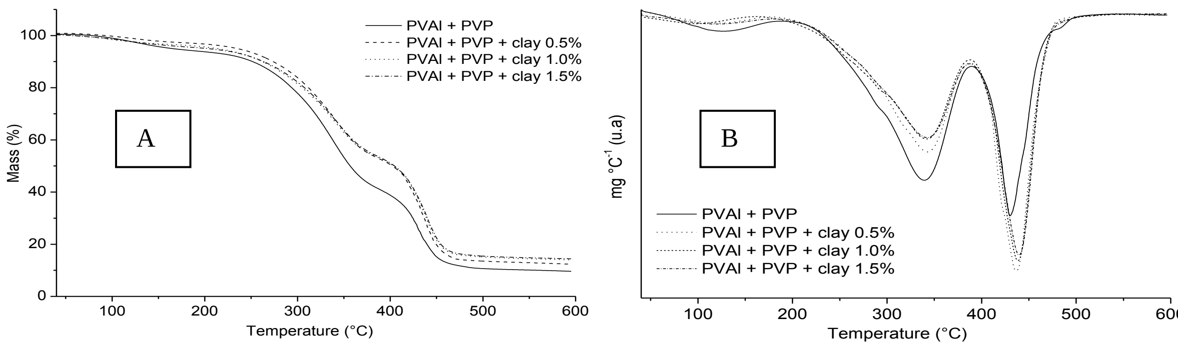

Figure 1 – (A) TG curves of dried hydrogels PVAl / PVP and clay laponite RD, obtained by gamma irradiation . (B) DTG curves of dried hydrogels PVAl / PVP and clay laponite RD, obtained by gamma irradiation

3.2.2 Scanning Electron Microscopy (SEM)

The fractured surface micrographs, (figure 2) of dried PVAl/PVP hydrogel show random lacunas and pores.

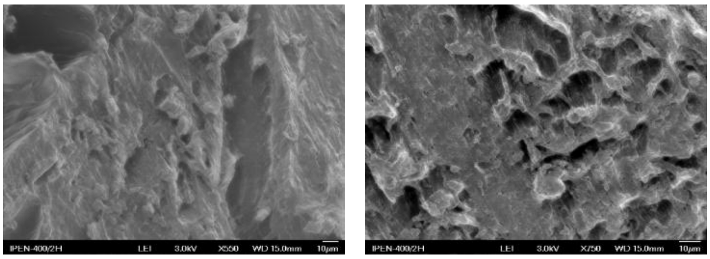

Figure 2 – SEM images of dried PVAl/PVP hydrogel, obtained by gamma irradiation

Hydrogel with 1.0% of laponite clay RD present smallest and more organized porosity. And it is possible to see that the clay is homogeneously dispersed, without agglomeration, (figure 3).

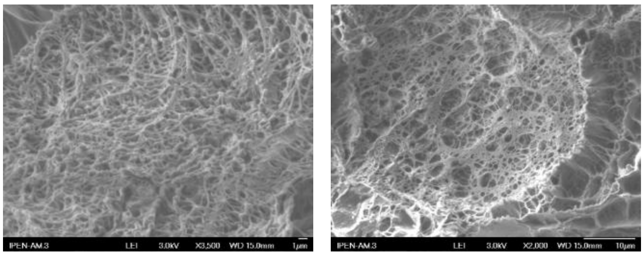

Figure 3 – SEM images of dried PVAl/PVP hydrogel with 1.0 % of clay laponite RD, obtained by gamma irradiation

4. Conclusions

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. Thus, the obtained membranes show decrease in the swelling values and relative superior thermal stability.

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