Hydrogel membranes of PVAl/ clay by gamma radiation

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ABSTRACT

In the last decades several studies concerning the new methods for drug delivery system have been investigated. A new field known as "smart therapy" involves devices and drug delivery systems to detect, identify and treat the site affected by the disease, not interfering with the biological system. Cutaneous Leishmaniasis is an endemic disease that is characterized by the development of single or multiple localized lesions on exposed areas of skin and one coetaneous treatment could be a potential solution. The aim of this study was to obtain polymeric hydrogel matrices of poly(vinylalcohol)(PVAl) and chitosan with inorganic nanoparticles, which can release a drug according to the need of the treatment of injury caused by leishmania on the skin. The hydrogels matrices were obtained with PVAl/ chitosan and PVAl/ chitosan 0.5; 1.0 and 1.5% laponite RD clay, crosslinked by ionizing gamma radiation with dose of 25 kGy. The techniques used for characterization were swelling, gel fraction, Fourier transform infrared spectroscopy (FTIR) and thermogravimetry (TGA). After synthesis, the samples were immersed in distilled water and weighed in periods of time until 60 h for the swelling determination. The obtained results have indicated that the swelling of the membranes increases with clay concentration, in consequence of ionic groups present in the clay.

1. Introduction

Clays are materials for several applications due to the interesting properties. The surface modification of clays has received considerable attention from researchers because through different modifications, it is possible to prepare new materials and propose new applications (Paiva, 2008). Laponite RD is the synthetic clay with a structure similar to that of a clay natural mineral, hectorite Wyoming. It consists of layered magnesium silicate, which is hydrothermally synthesized silicates from simple, lithium and magnesium salts in the presence of agents of mineralization.

In the last two decades, the idea of using the mineral clays in layers, for applications in polymer nanocomposite resulted in the development of advanced materials with improvements on mechanical, thermal, barrier, optical and electrical properties (Nigmatulin et al., 2008; Neto and Teixeira-Neto, 2009). This is partially due to the strong interactions at the clay–polymer interface. Owing to the nature of the complex molecules of clay, a variety of chemical reactions can take place at its surface or galleries due to its high chemical reactivity, including reactions with a complex chemistry (Peng et al., 2009).

It is also known that hydrophilic, nonionic polymers such as PVA and PEO easily adsorb onto clay surfaces. The adsorption of PVA onto clay surface occurs through strong hydrogen bonding between the hydroxyl groups of PVA and the oxygen atoms of silicate layers. Laponite is a synthetic clay, which belongs to a family of phyllosilicates (trimorphic) 2:1 with an empirical formula of $Na^+0.7[(Si_8Mg_{5.5} Li_{0.3})O_{20}(OH)_4]^{-0.7}$ having diameter of 300 Å and height about 10 Å (Nair et al., 2007).

Hydrogels are three-dimensional networks formed from hydrophilic homopolymers and copolymers (preformed macromolecular chains) crosslinked to form insoluble polymeric matrices. These branched polymers generally have a glass transition temperature (Tg) above the value of the original polymer. Hydrogels are usually soft and elastic due to its thermodynamic compatibility with water. They are used in various biomedical applications including drug delivery and tissue engineering (Peppas et al., 2000). Actually, a series of polymers have been utilized in design hydrogels as: poly(ethylene glycol) (PEG), poly(vinyl alcohol) (PVA), poly(2-hydroxyethyl methacrylate) (PHEMA) and poly(N-2-vinyl-pyrrolidone) (PVP) (Peppas et al., 2009).

For instance, the vascular tissue is one of the most successful applications using the PVA as biomedical hydrogel. They are stronger than most synthetic gels with low coefficient of friction, and structural properties similar to natural cartilage (Pan and

Xiong, 2009). Artificial meniscus using polyvinyl alcohol–hydrogel was studied as an artificial cartilage and performed animal experiments for clinical application (Kobayashi et al., 2003; Oka. 2001).

Chitosan is an amine polysaccharide, derivative of chitin by deacetilation. Chitin forms the major fraction of the shells of insects, crustaceans and fungal walls. After the cellulose, it is the most important organic compound in nature. It is a natural product, of low cost, renewable and biodegradable, of greater economic and environmental importance. The chitosan is non toxic, biodegradable and potentially attractive material for bio-medical applications (Khanafari et al., 2008).

The aim of this work was the synthesis of hydrogels PVAl/ chitosan crosslinked by gamma irradiation with addition of inorganic particles such as nanostructured clay, laponite. The presence of laponite should change the kinetic characteristic of the drug released from PVAl membranes.

2. Materials and methods

Poly(vinyl alcohol) (PVAl) (Mw=85000, degree of hydrolysis 98,4%) CelvolTM 325 provided by *Dermet Agekem*, Agar provided by Oxoid and clay laponite RD coding S/11176/10 provided by Buntech.

The formulations prepared for the crosslinking radiation process 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 a period of 40 min. Chitosan (0.5 g) was dissolved in 100 mL of solution of acetic acid (0.1% v/v). Stirring up to total solution the mixture procedure was performed at room temperature. The clay, after dissolution was added to the PVAl solution and heated, at about 85 °C, for 5 min. The solutions were placed in Petri dishes and irradiated with ^{60}Co gamma radiation at 25 kGy dose.

2.1. Swelling

After synthesis, the samples were immersed in distilled water and weighed in periods of time until 60 h and the swelling was calculated according to the equation (A).

$$Swelling = (ms-md)/md \times 100 \quad (\%H_2O \text{ per g hydrogel}) \qquad (A)$$

where: ms is the mass of swelled polymer and md is the mass of the hydrogel.

2.2. Gel content

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

$$Gel \text{ fraction} = mf/ms \times 100 \qquad (B)$$

where: ms is the mass before extraction and mf is the mass of the dried sample after extraction.

2.3. Thermogravimetry (TGA)

The TGA technique was accomplished in a Mettler-Toledo TGA/SDTA 851 thermobalance, using inert atmosphere of N$_2$ from 25 to 600 °C at heating rate of 10 °C min^{-1}.

2.4. Infrared analysis

FTIR analysis was done using a Thermo Nicolet FTIR-6700 Smart Diamond ATR-Attenuation Total Reflectance, in the interval 4000–400 cm^{-1}.

3. Results and discussion

The results presented in Fig. 1 show the higher swelling value for the hydrogel obtained from PVAl/ chitosan and 1.5% clay when compared to the PVAl/ chitosan and PVAl/ chitosan with 0.5% and 1.0% clay. This swelling difference is related to the ionic character present in the clay.

The behavior of the polymer with respect to the mobility of the molecular chains is related to the functional groups present in these polymer chains. Adding particles with positive or negative charges the tendency is to increase the swelling due to the greater affinity with the aqueous solution.

In Table 1, it is observed that the hydrogel PVAl/ chitosan with 1.5% clay has the lowest gel fraction compared to PVAl/ chitosan and PVAl/ chitosan with 0.5 or 1.0% of clay. This result agrees with what was observed by the swelling. The tendency is to modify the distance between the polymer chains reducing the density of crosslinking.

Thermogravimetry (TGA) showed initial higher thermal stability to the membranes of hydrogels PVAl, according to the increase in the percentage of clay added. Fig. 2 shows three events, the first event occurs between 25 and 150 °C and is associated to the dehydration of water from the nanocomposite PVAl/ chitosan both hygroscopics (Nair et al., 2007) and later then
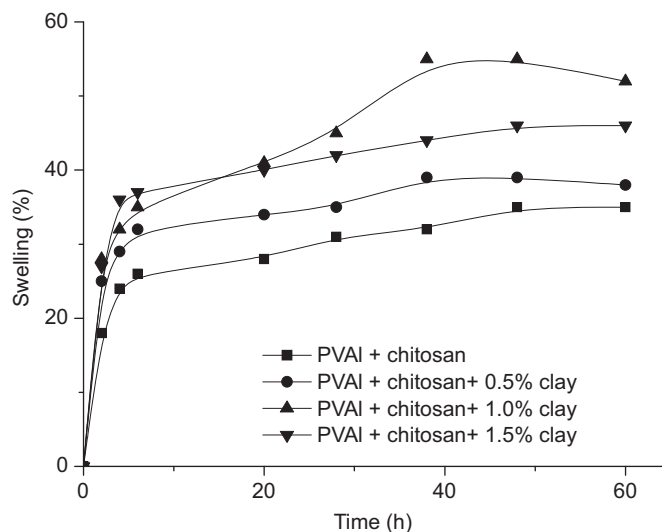

Fig. 1. Swelling behavior of hydrogels PVAl/ chitosan and clay laponite RD, obtained by gamma irradiation, 25 kGy.

Table 1
Gel fraction of hydrogels PVAl/ chitosan and clay laponite RD, obtained by gamma irradiation dose 25 kGy.

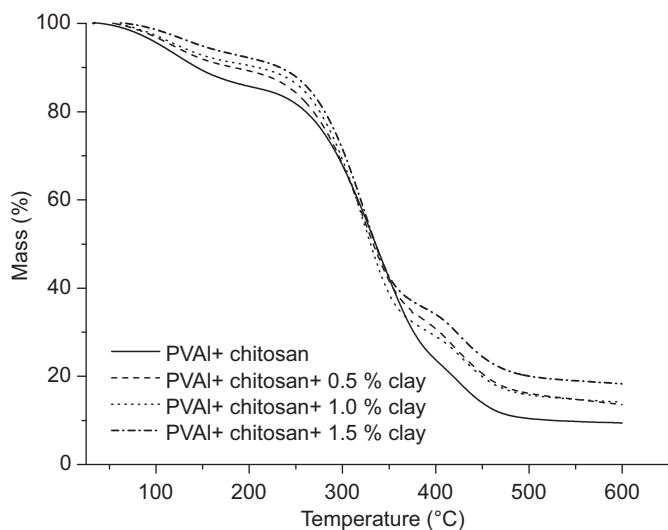| Membranes	Gel fraction (%)
PVAl+0.5% chitosan	19.0
PVAl+0.5% chitosan+0.5% clay	18.0
PVAl+0.5% chitosan+1.0% clay	16.0
PVAl+0.5% chitosan+1.5% clay	17.0

Fig. 2. TGA curves of dried hydrogels PVAl/ chitosan and clay laponite RD, obtained by gamma irradiation, 25 kGy.
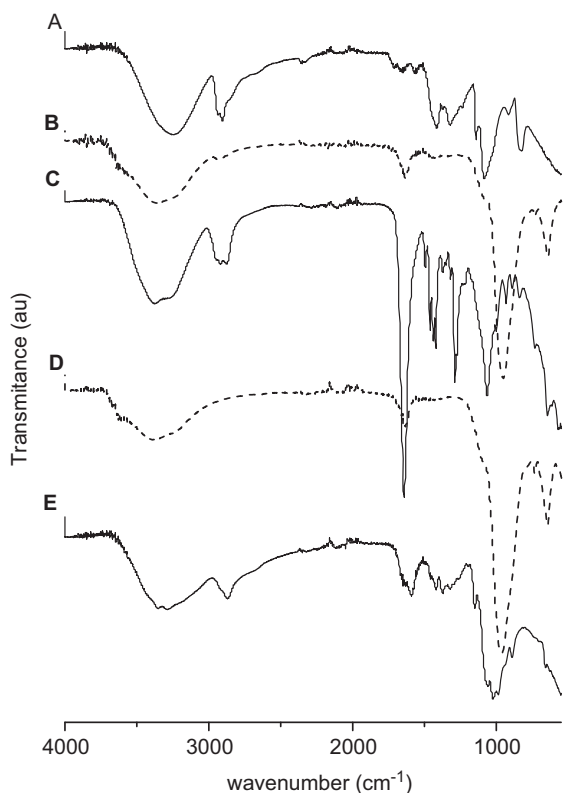

Fig. 3. Infrared curves of hydrogels PVAl/ chitosan and clay laponite RD, dried films obtained by irradiation gamma. (A) PVAl pristine, (B) PVAl+chitosan, (C) PVAl+chitosan+0.5% clay, (D) Clay pristine end and (E) Chitosan pristine.
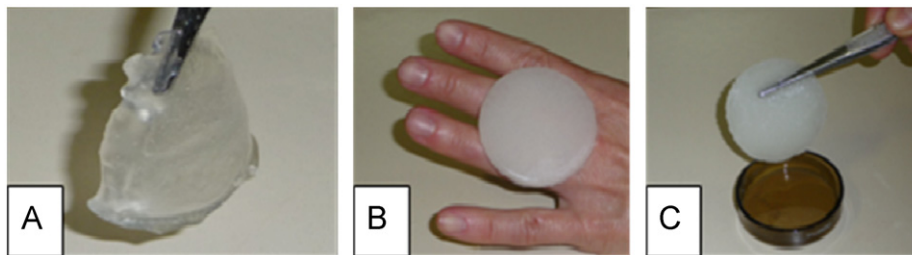
followed by the release of water from the spheres of hydration of exchangeable sodium cations of the clay (Palkova, 2009). The second event, decomposition between 200 and 380 °C, is related to the loss of PVAl dehydroxilation (Thomas et al., 2001); in this interval starts the decomposition of polymeric chains. The third event which starts at 380 °C is associated to the polymer decomposition and also to the water loss through the dehydroxilation of structural layers of clay; the loss of structural water is facilitated by the presence of polymers. The PVAl that penetrated is intercalating or exfoliating the clay according to Nair et al. (2007).

PVA has a strong tendency to form hydrogen bonding within itself as well as with other species containing highly electronegative groups. Laponite has electronegative oxygen and hydroxyl groups, which can assist the adsorption of PVA onto laponite surface. The adsorption of PVAl onto surface of laponite is presumed to occur through hydrogen bonding. Apart from hydrogen bonding, van der Waals forces between polymer segments and clay surface would also play an important role in the overall adsorption process. It is observed that the membranes containing clay showed a slower degradation above 380 °C due to the presence of clay Fig. 2.

The IR spectra for all samples, including pristine samples used as a point of reference in identifying the peaks of the nanocomposites PVAl/ chitosan and PVAl/ chitosan and clay, showed broad bands in the region from 3000 to 3500 cm^{-1} (Fig. 3) related to stretching of OH present in all samples. In the nanocomposite, Fig. 4(B) is observed peaks in the region 3000–3500 cm^{-1} assigned to the hydroxyls of PVAl/ chitosan. The observed signal at 1593 cm^{-1} in 3E is assigned to the NH_2 stretching of chitosan, in which sample 3B is shifted to 1623 cm^{-1}, when irradiated with PVAl as a result of the formation of hydrogen bonding between the hydroxyl PVAl and the NH_2 group of chitosan. Furthermore the nanocomposite 3C, added of 0.5% clay increases the relative intensity of the stretching absorption peaks in the bands 3000–3500 cm^{-1} including clay.

Characteristic bands at 1035 and 656 cm^{-1} correspond to the stretching of Si–O–Si (Fig. 3(C) and (E)). The membrane, 3C, shows slight shift to 938 cm^{-1} of the Si–O–Si stretching when compared to clay. This shift can be attributed to interaction between the polymer PVAl/ chitosan and the clay through Si–OH groups (Nair et al., 2007).

As described by Nair et al. (2007) in the PVAl/ poly (N-isopropylacrylamide)/ clay hydrogels, the presence of laponite can accelerate the degradation of the membrane when the copolymer is obtained by chemical crosslinking. In the present case it is observed that the membranes of PVAl/ chitosan with laponite clay have an increase in the decomposition temperature showing strong interaction between chitosan and laponite.

These membranes of PVAl/ chitosan and clay hydrogels are shown in Fig. 4. They have become more firm and opaque compared to the membranes obtained with PVAl/ chitosan without clay.

4. Conclusions

The hydrogels of PVAl/ chitosan with clay present considerable increase in swelling. At the same dose of irradiation, different concentration of clay reduces the concentration of gel content in

Fig. 4. Photos of the hydrogels (A) PVAl/ chitosan, (B) PVAl/ chitosan with 1.0% of clay and (C) PVAl/ chitosan with 1.5% of clay.

the membrane. Unlike membranes obtained by chemical cross-linking, the membranes containing laponite processed by gamma irradiation increases in the thermal stability with slower degradation of the organic components.

FTIR results indicated the displacement of absorption peaks. These shifts can be attributed to interaction between the polymer PVAl/ chitosan and clay through Si–OH groups. This hydrogel can be exploited for drug delivery in biological systems.

Acknowledgments

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