Thermal properties of hydrogel-clay nano-composites

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Abstract

Hydrogels are one of the most widely employed materials in biological, medical and technological areas. However, the use of hydrogels sometimes is restricted due to their specific properties. It is well-known that polymeric nanocomposites reinforced with clays show valuable improvements in their properties. In this work, eco-friendly composite hydrogels were prepared employing polyvinylalcohol (PVA) and bentonite (abundant and low cost smectite-type clay in Argentina) as raw materials through the previously optimized freezing-thawing (F-T) crosslinking method. Different nanocomposite hydrogels were obtained by varying the corresponding reactor feed. These materials have been recently chemically, morphologically and mechanically analysed in a recent work. Specifically, in the present work, thermal degradation behaviour of PVA-bentonite hydrogels was studied. Kinetic analytical models were applied to non-isothermal thermogravimetric (TGA) measurements trying to identify the possible mechanism for PVA degradation in the presence of bentonite. Copyright © 2018 VBRI Press.

Keywords: Hydrogel, bentonite, thermal properties.

Introduction

Man-made composite materials could be considered as natural biocomposite inspired materials. As examples, horn, bone and nacre are natural inorganic/organic nanocomposites with excellent mechanical properties [1]. The addition of both natural and synthetic nano-fillers to polymeric materials leads to have modifications on solvent, heat and impact resistance, transparency, electrical conductivity, molecular barriers, flame retardancy and corrosion protection properties, mechanical strength and certain gases permeability of the composite material when compared with either the pure polymer or their conventional microcomposites, even at very low filler concentrations [2-14].

Durability, shelf lives, spectral stability, mechanical properties and life cycles of polymeric-based materials are ultimately governed by their thermal resistance due to all the above-mentioned properties will be gradually affected if the degradation process begins. As a result, controlling the material thermal resistance is a priority [15]. For this, a variety of fillers have been added to a number of polymeric matrix, including carbon, ceramics, clays, metals and metal oxides, among many other examples [8, 13].

Hydrogels are one of the most widely employed materials in biological, medical and technological areas. They consist essentially on a low-cost and hydrophilic soft polymer, which forms a three-dimensional network and has the ability to absorb a large amount of water. In particular, the cryogels of polyvinylalcohol (PVA) constitute an eco-friendly alternative due to they can be obtained by a physical crosslinking method (through freezing/thawing cycles, F-T) thus avoiding the use of potentially harmful components. PVA is a water soluble biodegradable polymer with a large extent of applications, usually considered as a good host synthetic material [2, 4, 16-18]. Several nanocomposites were prepared by employing PVA as matrix and silica [4, 15], montomorillonite (MMT) [5, 6, 19, 20], gold nanoparticles [21], $CoFe_2O_4$ magnetic nanoparticles [22], bentonite [16], magnetite nanoparticles [23], kaolinite [3], iron, cobalt and nickel sulfides [24] as fillers, among many other ones.

Clay materials constitute good raw materials since mostly of them are abundant and low-cost. Enhanced thermal stability temperatures for several PVA-clay nanocomposites have been reported [1, 4-6, 13, 18]. The physical properties improvement achieved on the final nanocomposite product is strongly dependent on the clay mineral–polymer compatibility as well as on the corresponding processing conditions [12]. Three different morphological structures are mainly achievable: intercalated nanocomposites (polymer chains are inserted into a layered silicate structure in a crystallographically regular fashion), exfoliated or delaminated nanocomposites (the individual silicate layers are separated in the polymer matrix by average distances,) or flocculated (the hydroxylated edge–edge interactions of the silicate layers produce intercalated and stacked silicate layers flocculated to some extent) clay mineral particles [25]. It is important to remark that only exfoliated clay particles being part of the nanocomposite material could offer remarkable improved properties.

In the present work, composite hydrogels prepared by employing PVA and bentonite as raw materials through the previously optimized freezing/thawing cycles (F-T) physical crosslinking method, thus avoiding the use of potentially harmful components. Particularly, bentonite is a smectite-type clay very abundant in Argentina characterized for having a moderate negative charge and good mechanical and chemical resistance [16]. Different nanocomposite hydrogels were obtained with bentonite contents from 1 to 5 wt. %. These materials have been recently chemically, morphologically and mechanically analyzed [16]. Specifically, in the present work, the thermal degradation behavior of PVA-bentonite hydrogels will be deeply studied. The thermal degradation process will be modeled in order to explain the clay effect on it.

Experimental

Materials

Polyvinyl alcohol (PVA) was supplied by Sigma-Aldrich (Molecular weight of 89000-98000 g/mol, hydrolysis degree of 98-99%). Bentonite, supplied by Minarmco S.A. (Neuquén, Argentina), was used as received to prepare the nanocomposites.

Materials preparation

Materials were prepared according to authors previous reports [16]. First, 100 mL of 1, 3 or 5 wt. % aqueous suspension of bentonite was prepared and left overnight in order to swell the bentonite. Then, 10 g of PVA were dissolved in the suspension under constant stirring at 85°C during 4 hours. When the solution reached room temperature, the PVA-bentonite composite suspension was casted onto a series of anti-adherent containers. The samples (named *1 wt.% Bent, 3 wt.% Bent and 5 wt.% Bent*, respectively) were frozen (-18 ºC, 1h) and then placed at room temperature (25 ºC, 1h), completing 3 of this freezing-thawing cycles (F-T), and thus obtaining 4 physically cross-linked hydrogels through the F-T method. PVA hydrogel (sample named PVA) samples were obtained in a similar procedure, without the addition of the nanoclay.

Characterization techniques

All prepared materials have been recently chemically, morphologically and mechanically analyzed [16]. Briefly, Fourier transformed infrared spectroscopy (FTIR) spectra of samples were acquired with a Nicolet 6700 Thermo Scientific instrument equipped with a diamond ATR probe, over the range 400–4000 cm^{-1} from 32 coadded scans with 4 cm^{-1} resolution. X-Ray diffraction (XRD) tests were performed to characterize the clay dispersion inside the polymer matrix using an X-Pert Pro diffractometer, operating at 40 kV and 40 mA, with CuK$_\alpha$ radiation (λ = 0.154 nm). All samples were scanned in the range of 2θ = 2 to 50 º at a rate of 2 º/min. Field Emission Scanning Electron Microscopy (FESEM) was employed to analyze the pore morphology and sizes of hydrogels on a FESEM Zeiss Supra. Each sample was swollen, frozen, lyophilized, cryofractured and then coated with gold before testing. Thermogravimetric Analysis (TGA) measurements were carried out using a Shimadzu TGA-50 instrument at a set of heating rates: 5, 10, 15, 20 and 25 °C/min from room temperature to 800 °C under N$_2$ atmosphere in order to avoid the thermo-oxidative degradation. Degradation temperatures (Tp) were obtained from the maximum of the main loss-weight event in the derivative curves of TGA (DTGA).

Results and discussion

Morphological and Structural Characterization

From FTIR data the interaction between PVA matrix and bentonite can be studied. Concisely, there are shifts from 995 to 1040 cm^{-1} and from 3269 to 3287 cm^{-1} that were previously reported by our research group [16]. They could be attributed to the presence of hydrogen bonding between –OH groups of PVA and Si-O groups present in bentonite, allowing them to be considered as compatible one with the other one.

According to our previously reported XRD results [16], good dispersion of the filler inside the PVA matrix is observed for 1 and 3 wt.% bent, based on the fact that no characteristic clay diffraction peak appears at 2θ = 2-10 º.This absence is related to the possibility of having exfoliated or mixed exfoliated-intercalated silicate layers of the clay dispersed in PVA matrix [5]. In the case of nanocomposite with 5 wt.% bent sample, a minor increase in the interlamellar space in the clay could be inferred from the presence of a little peak around 4°, which is associated with the polymer entrance in clay galleries [16].

Fig. 1 shows the FESEM micrographs of neat PVA and PVA-nanocomposites. As it can be seen in **Table 1**, the introduction of clay inside the PVA hydrogel matrix produces a decrease on the pore size [16]. Regarding the microarchitecture of these materials, apparently hydrogel networks may have not interconnected pores.
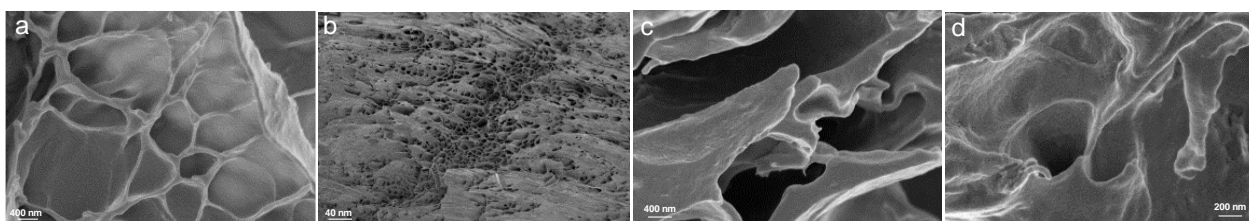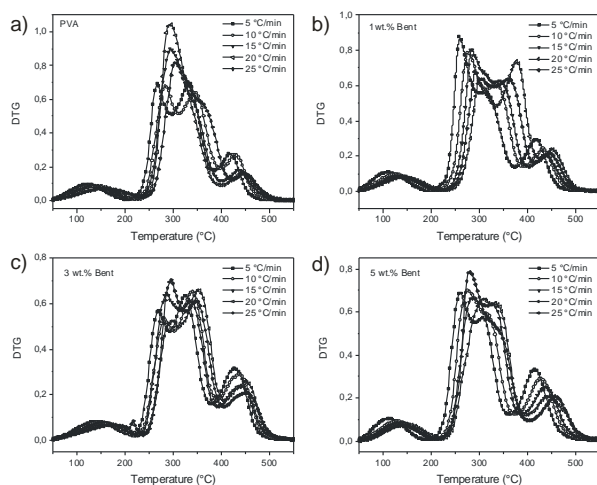

Fig. 1. FESEM micrographs for (a) PVA and nanocomposites with (b) 1 wt.% Bent, (c) 3wt.% Bent, (d) 5 wt.% Bent.

Table 1. Pore size determined from FESEM micrographs.

Sample	Porous size (µm)
PVA	8.5 ± 4.0
1 wt.% Bent	3.2 ± 1.4
3 wt.% Bent	4.0 ± 2.2
5 wt.% Bent	4.7 ± 2.3

Fig. 2. DTG curves obtained at different heating rates for: (a) PVA and nanocomposites with (b) 1 wt.% bent, (c) 3wt.% bent, (d) 5 wt.% bent.

Thermal stability of PVA–bentonite systems has been investigated through the thermogravimetric analyses and the determination of certain characteristic temperatures was performed. **Fig. 2** shows TGA and DTG curves of PVA hydrogel matrix and nanocomposites obtained at different heating rates, whereas **Fig. 3** compares the TGA and DTG curves of PVA hydrogel matrix and nanocomposites obtained at a fixed heating rate of 10ºC/min.
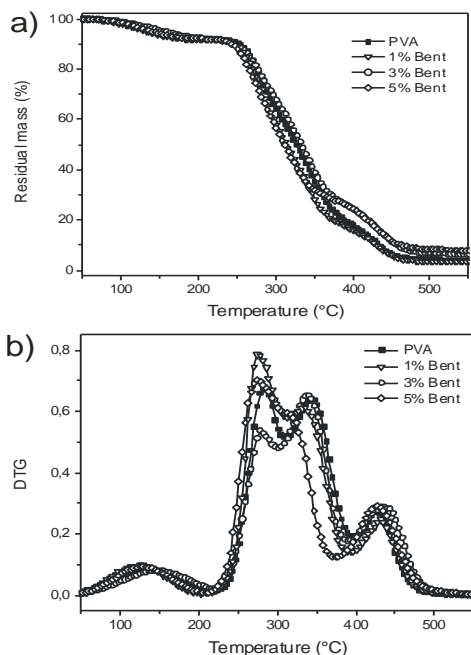
Fig. 3. (a) TGA and (b) DTG curves of PVA matrix and nanocomposites obtained at 10 ºC/min.

The obtained curves show that the thermograms of PVA matrix and nanocomposites are characterized by three distinct events. The first peak, correlated to water evaporation, occurs between ambient temperature and 183 to 200°C. A second peak at approximately 260°C is ascribed to the first step degradation of PVA-clay nanocomposite (a side peak accompanies the main peak) in which elimination reactions occur; while the third peak at around 440 °C is attributed to the second step decomposition in which chain-scission reactions take place [15]. Although some researchers reported remarkable improvements on nanocomposites thermal stability by incorporating clays as nanofillers [3, 6, 9], some other ones observed no significant changes [18].

The heating rate (β) has a significant effect on the degradation behavior of the materials. It has been reported that the increase of thermal degradation temperatures with heating rate is caused by the heat hysteresis, which means that the internal part of the materials are not able to follow the program temperature when the temperature increases rapidly.

It can be noticed that when bentonite is incorporated, there is a significant change in the shape of the first degradation peak and its shoulder in DTG curves.

Bentonite may have two opposite functions in the thermal stability of nanocomposites: a barrier effect, which should improve the thermal stability or a catalytic effect on the degradation of the polymer matrix, which should decrease their thermal resistance. The clay acts as a heat barrier improving the overall thermal stability of the system. The presence of the filler restricts the polymer chain mobility and assists the char formation, during the thermal decomposition [16, 22, 25]. Besides, the silicate layers could hold accumulated heat that can act as a heat source to accelerate the decomposition process.

Modeling of the degradation process

The kinetic analysis of the degradation mechanism for polymeric materials gives information of the energy barriers of the process [15].

One of the simplest models of the degradation process can be presented by a nth order kinetic equation:

$$\frac{d\alpha}{dt} = A.(1-\alpha)^n.\exp\left(\frac{-E_a}{R.T}\right) \tag{1}$$

were α is the average advancement of the degradation reaction, proportional to the material weight loss and varied between 0 and 1. Introducing the heating rate, β in Equation 1:

$$\frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta}.\exp\left(\frac{-E_a}{R.T}\right)dT \tag{2}$$

This is the fundamental expression of the analytical methods used to calculate the kinetic parameters from TGA data. Several methods are commonly used to estimate the apparent activation energy. The method

proposed by Kissinger [14, 26] is based on the following equation:

$$\frac{d(\ln(\beta/T_m^2))}{d(1/T_m)} = \left(\frac{-E_a}{R}\right)$$

(3)

For the analysis, the whole degradation process was divided in two parts, each one associated to one of the degradation peaks. These peaks were split by a Lorentzian multi-peak curve. The results of the model fitting (from Kissinger method) of the first degradation peak temperature with maximum weight loss rate (T_{p1}) are shown in **Fig. 4** and the activation energy values associated with this process are summarized in **Table 2**. The plotted data evidence a good fit to the linear lines and the correlation coefficients are high. This implies that Kissinger method is suitable to describe the thermal degradation of PVA and PVA-Bent nanocomposites.

It is possible to observe that whereas for low clay content (1 wt.%) the apparent activation energy is reduced, the increase on the bentonite content produces an improvement on the thermal stability of the PVA hydrogel matrix. The effect at low bentonite content could be explained in terms of an easier elimination of the water and acetate groups from the PVA in the second step being facilitated by the incorporated clay [2]. However, at higher clay contents there are other factors, previously mentioned, that increase the thermal stability with respect to the neat PVA matrix. It seems that there is a clay content that acts as inflection point in the thermal properties. We are working on finding this concentration and a deeper explanation of this behavior.
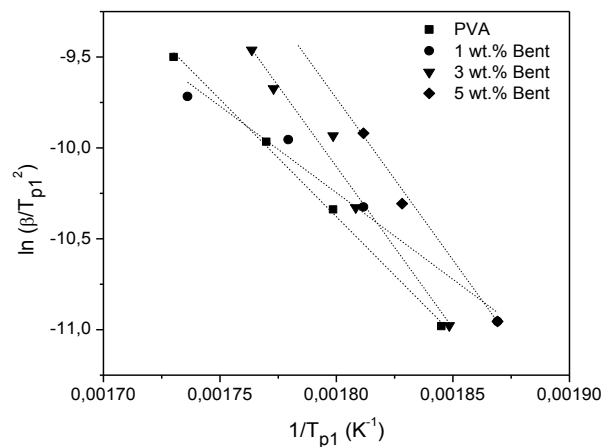

Fig. 4. Linear fitting of the first thermal degradation step with Kissinger's method.

Table 2. Activation energy of the first thermal degradation step of PVA and nanocomposites obtained from Kissinger's method.

Sample	Ea (kJ)	R²
Neat PVA	12.91	0.997
1 wt.% Bent	9.53	0.968
3 wt.% Bent	17.77	0.973
5 wt.% Bent	17.58	0.982

Conclusion

It was possible to prepare and characterize PVA hydrogels with different bentonite contents through a simple and low-cost methodology. The morphology characterization showed that the selected clay (bentonite without modifications) and the PVA matrix have interactions (as it was observed in FTIR spectra), having good dispersion (evidenced in XRD spectra) for all studied clay contents (it will be further confirmed by Transmission Electron Microscopy, TEM). Then, an initial characterization of the involved process in the PVA matrix and the nanocomposites thermal degradation showed three main degradation steps, the same for both, matrix and nanocomposites. From this, an approximation to the process modeling was done by applying the Kissinger model: it was observed that whereas for low clay content (1 wt.%) the apparent activation energy is reduced, further increase on the bentonite content produces an improvement on the thermal stability of the PVA hydrogel matrix. Application of other models in order to analyze the effect of incorporate different clay contents on the thermal degradation of PVA nanocomposite hydrogels is being carried out.

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