Poly(Vinyl Alcohol) (PVAl) and Poly(N-2-Vinyl-Pyrrolidone) Hydrogels Nanostructured by Laponite Clay for Drug Delivery

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Abstract: Hydrogels for wound dressings are usually developed for contact surfaces where mechanical properties are conveniently required. In this sense nanocomposite hydrogels based on PVAl (poly(vinyl alcohol) and PVP (poly(N-2-vinil-pirrolidone)) containing 0.5-1.5 wt% of the synthetic laponite RD clay were prepared by a gamma radiation process and compared with similar membranes composed separately of PVP or PVAl. This study aimed to evaluate the effect of clay on the properties and the differences of the polymer blend instead of a unique polymer. The morphology of the hydrogels was evaluated by spectrometric techniques using XRD (X-ray diffraction), SEM (scanning electron microscopy), swelling assay, and FTIR (infrared spectroscopy). The swelling kinetics at 22 °C and the mechanical properties by a tensile test comprised the structural properties that were assessed. The results showed PVA/PVP network depends directly on the clay concentration in the nanocomposite hydrogels. The blend PVP/PVAl proved to have potentially efficient mechanical properties for drug delivery in the treatment of wounds.

Key words: Hydrogels, clay, nanocomposite, drug delivery.

1. Introduction

Clays, one of the most ubiquitous layered minerals available in nature, have a nanometric lamellar structure and are composed of thin layers spaced by alkaline or alkaline earth cations adsorbed on the surface, interacting through Van der Walls forces with one another and with organic molecules. These cations balance the isomorphic substitutions of Al^{3+} atoms by Mg^{2+} or Fe^{2+} atoms, or Mg^{2+} atoms by Li^+ in the octahedral sheets, which cause distortions in the lamellar structures, generating a negative excess of charge in the layers of the clays [1, 2] (Alexandre and Dubois 2000, Baniasadi et al., 2021).

Clay-polymer NCs (nanocomposites) present excellent physical properties, such as increased internal connectivity (higher modulus values and longer relaxation times), heat resistance and transparency, among others. These properties are much superior to those that would be expected by a simple additive rule, partially due to the strong interactions at the clay-polymer interface (Tanna et al., 2019). These interactions consequently lead to the intercalated or exfoliated composite structures and influence on their overall performance (Karimi et al. 2015).

Exfoliated clay-polymers nanocomposites, in particular, have attracted the attention of researchers in the last few years due to the combination of organic molecules and inorganic ions, offering new perspectives in terms of products for several applications (Herrera et al. 2005). The higher the compatibility between the polymer and the clay, the better is the exfoliation, therefore some surface modifications are often performed on clays in order to increase their hydrophilicity and, consequently, their compatibility with the polymer matrices (Ismail et al.,

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2019). Among various polymeric matrices, hydrogels are investigated as biomaterials with great interactions with the exfoliated clay due to their hydrophilic surface area. Polymeric hydrogels with dispersed clay are a new class of polymer composites that combine elasticity and permeability of hydrogels with high capability of absorbing different clay substances (Nair et al. 2007).

Hydrogels are three-dimensional mesh-like materials formed by polymeric crosslinking. They offer excellent biocompatibility for a variety of applications, i.e. health, environment, among others (Dai et. al. 2017; Al Assaf et al. 2016). Hydrophilic hydrogels are made of water-soluble polymers, as long as the polymer is crosslinked (Park et al. 2003). The terminally-attached polymer chains are flexible and capable of rapidly changing their conformation. This feature has been used for increasing the swelling degree and swelling rate of hydrogels (Savina et al. 2007), and to accelerate the rate of shrinking/swelling of stimuli-sensitive hydrogels in response to external changes (pH, temperature) (Yoshida et. al. 1995). Furthermore, hydrogels bearing carboxilic groups were used to develop formulations that release drugs in a neutral pH environment (Gao et al. 2010).

The aim of this work was the synthesis of PVP/PVAl (poly(N-2-vinil-pirrolidone)/poly(vinyl alcohol)) nanocomposites with clay nanoparticles as devices for feasible controlled release of high efficiency systems (Oliveira et. al. 2016). A gamma radiation process was used to crosslink and to sterilize the hydrogel nanocomposites simultaneously, creating the nano and micro-structures. The irradiation is recognized as a very viable tool, as there is no need to add neither initiators nor crosslinker agents that are potentially harmful and difficult to remove (Erizal et al. 2013).

2. Materials and Methods

2.1 Materials

PVAl, and PVP *Kollidon* 90F were procured from Basf. Agar provided by Oxoid, clay laponite RD coding S/11176/10 provided by Buntech.

2.2 Methods

The formulations were prepared by dissolving separately PVAl (10% *w/v*), PVP (10% *w/v*), and clay in water. The solutions were added to a beaker and heated at about 85 °C, for 5 min. The formulation was placed in Petri dishes and processed for radiation in ^{60}Co gamma radiation at 25 kGy dose.

2.2.1 XRD (X-Ray Diffraction)

The XRD analysis of nanocomposites materials is aimed to evaluate the physical interaction between polymers and inorganic (clays). This analytical procedure can detect intercalation and exfoliation of clay in the polymer nanocomposite, according to the interlamellar distance that changes in consequence of polymer insertion. Fig. 1 illustrates different dispersion states of the clay compared to polymer characterized by XRD signal attributed to the plane (001) of the clay silicate.

An X-ray diffractometer, PANalytical brand, model X'Pert PRO detector X'Celerator was used for the analyses. The parameters used were: source of X-rays from Cu, energy 45 kV × 40 mA, angular range from 1.17° to 40°, 0.03° step, time/step 100 ms. The basal interplanar spacing "*d*" of the clay structures was determined by Bragg Law, according to the equation:

$$2dsen\theta = n\lambda \qquad (1)$$

where: n = an integer; λ = wavelength of the incident radiation; d = the distance or spacing set to "hkl" levels (Miller index) of the crystal structure; θ = angle of incidence of X-rays (measuring between the incident beam and the crystal plane).

2.2.2 SEM-EC (Scanning Electron Microscopy with Field Emission)

The technique was used for verification of polymeric structures, obtaining high resolution structures of pores in the macro and micro level by using low voltage in the range of 5 keV. The device used was the JSM-6701F.
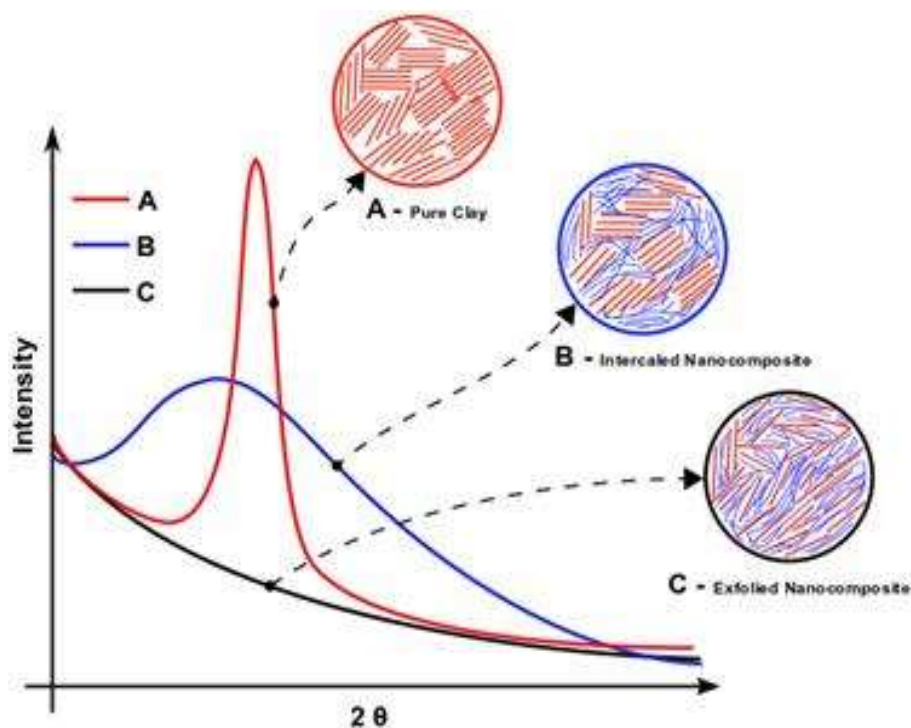
Fig. 1 Different representations of the clay dispersion compared to the polymer by XRD analysis (A) pure clay (B) the intercalated clay and the polymer (C) exfoliated clay relative to the polymer.

2.2.3 Swelling

After the synthesis, the samples were immersed in distilled water and weighed periodically until 48 h, and the swelling was calculated according to the equation B.

$$\text{Swelling} = \frac{Ms - Md}{Md} \times 100 \ \ (\%H_2O/g \ \text{hydrogel}) \ (B)$$

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

2.2.4 Infrared Analysis

The infrared spectra of the samples were used to provide information about the nature of PVP/PVA/Clay interactions. FTIR analysis was done using a Thermo Nicolet FTIR-6700 Smart Diamond ATR-Attenuation Total Reflectance, in the interval 4,000-400 cm^{-1}.

2.2.5 Tensile Test

A texture device was utilized to carry out the tensile tests following the standard procedure (ASTM D 638-02a-2003)*,* with a mild adaptation on the samples dimensions, as our samples were 60 × 24 × 3 mm in

size. The sample was fixed in one claw (model A/TGT) and submitted to draw at a speed of 0.8 mm/s based on an initial distance (lo) of 60 mm, up to break.

3. Results and Discussion

3.1 XRD

XRD analyses from the NSC (nanosheet clay) powder were performed, and the results were compared to the nanocomposite materials (polymer-clay). It was thus possible to observe the structural interactions between the NSC and polymer. The nanocomposite materials (polymer-clay) can show two types of physical interaction, e.g. exfoliation and intercalation. On the clay diffractogram, it was observed one peak of diffraction at 6.3 degrees corresponding to the inter-basal spacing of 14.03 Å. This distance can be calculated following the Bragg Law equation, and in our case it presented 7.01 Å in its nature state. The PVAl/clay nanocomposite systems diffractogram is shown in (Fig. 2a), evidencing the prevalence of clay exfoliation by the disappearance of d_{001} signal for both

concentrations of 0.5% and 1.5%. When the PVP/clay system was analyzed (Fig. 2b) and the diffraction patterns of the nanocomposites are compared to clay, we can observe that there is a shift of the peak to lower angles for PVP/0.5% clay and 1.5% clay to $2\theta = 2.2°$ and $2\theta = 5.5°$, representing the interlayer distances of 39.6 Å and 17.6 Å, respectively, characteristic of an interleaving effect.

These evidences of effective exfoliation corroborate to the assumption that our PVA1/clay nanocomposites are promising materials for a plethora of applications. It is known that nanocomposites with significantly exfoliated clay embedded in the matrix offer several advantages over their bulk counterparts, i.e. enhanced mechanical properties, higher thermal stability and barrier properties, probably due to the interactions among clay nanolayers and the polymer matrix (Zhu et al., 2019). Systems presenting interleaving effects have improved properties, especially regarding fracture toughness, as demonstrated by Shivakumar & Panduranga (2015), therefore the combination of PVP and clay might have several potential applications.

Laponite has properties of cation exchange, intercalation and swelling which make it interesting. The hydrated cations in the interlayer surface can be replaced by others of interest by the method of ion exchange, such as the sodium ion in the structural form: $Na^{+0.7}[(Si_8Mg_{5.5}Li_{0.3})O_{20}(OH)_4]^{-0.7}$. Furthermore, neutral organic molecules such as polymers can be interdispersed between the lamellae of these clays (Silva et. al.). It is noted that systems with PVAl exfoliation occur, while the PVP system has collation, it is assumed that occurred organic polymer of molecular interaction between the clay lamellae.

3.2 SEM-FE (Scanning Electron Microscopy with Field Emission)

Regarding PVAl/clay system, the micrographs of fracture surfaces show images of nanocomposites in which the morphology of PVAl/clay 1.0% has porous format, some regions with larger and disorganized macropores, while the PVAl/1.5% clay presents homogeneous regions with some points of clay agglomeration on the surface, as shown in Figs. 3a and 3b. In the case of the PVP/clay system there is a fracture morphology of the surface of PVP/1.0% clay sample with various forms of random pores, whereas the sample PVP/1.5% clay has macropores and surface regions with clay agglomeration foci, as shown in Figs. 3c and 3d. Additionally, the micrograph of the fractured surface of PVAl hydrogel membrane/freeze dried PVP, shows macropores and random pores. Sample PVAl/PVP/1% clay shows the macro and micro pores while the sample PVAl/PVP/1.5% clay
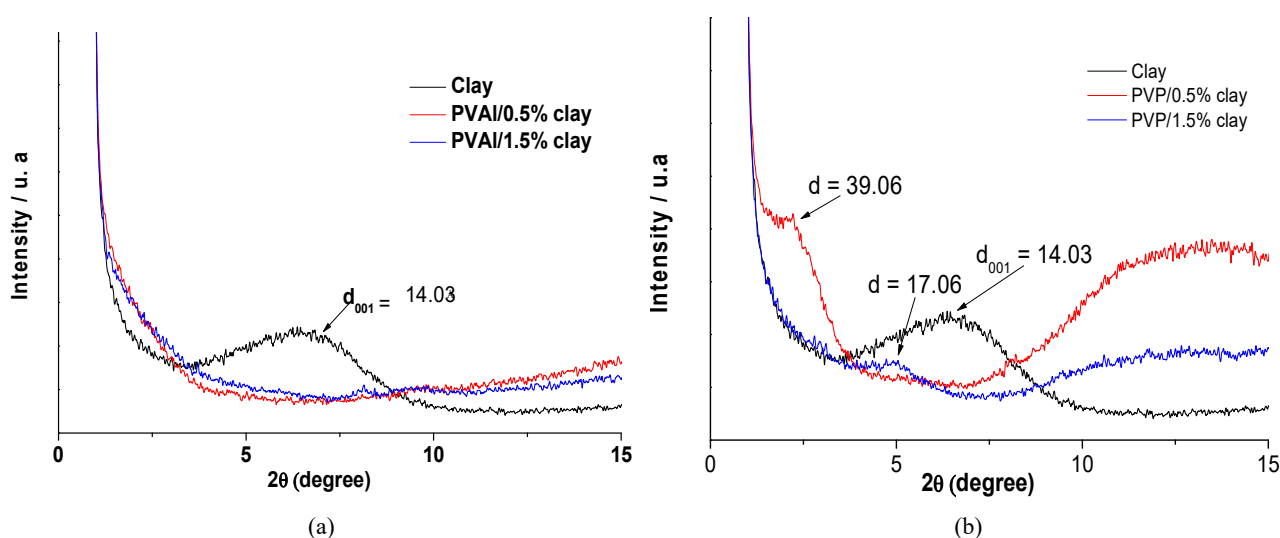

(a)

(b)

Fig. 2   (a) XRD curves of PVAl membranes of hydrogel/clay and (b) XRD curves membranes hydrogels PVP/clay.
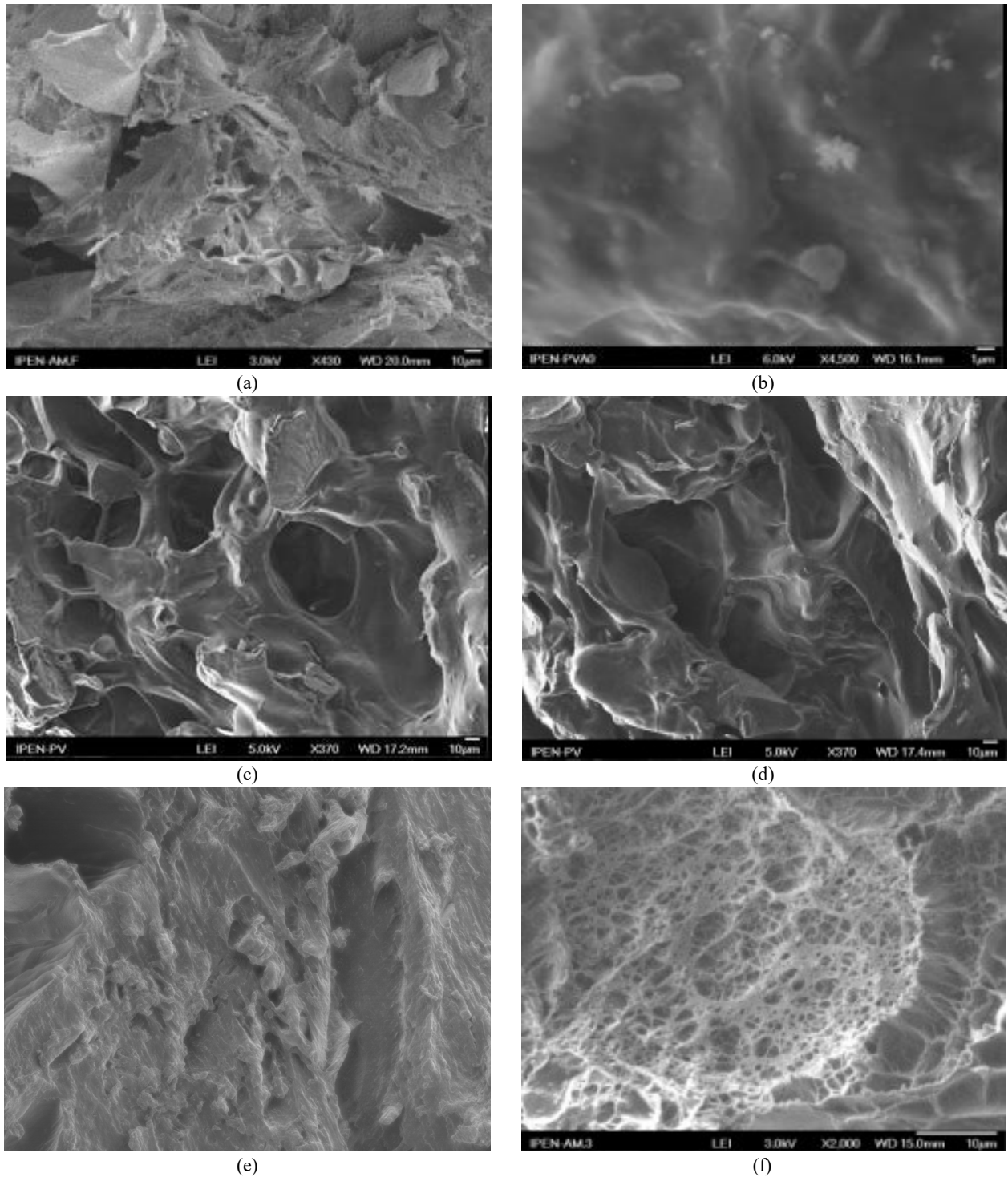
(a)

(b)

(c)

(d)

(e)

(f)

**Fig. 3   SEM micrographs of freeze-dried hydrogel membrane (a) PVAl/1.0% clay and (b) PVAl/1.5% clay, (c) PVP/1.0%
clay and (d) PVP/1.5% clay and membrane (e) PVAl/PVP and (f) PVAl/PVP/1.0% clay.**

presents few pores and compact surface with agglomerated clay particles in various regions (Figs. 3e and 3f). The number of pores and micropores in the samples is characteristic from lyophilized hydrogels, as after removing the water by freeze-drying there is the organization and shaping of these pores according to the percentage of clay formed during the rearrangement of the molecules in crosslinking.

Regarding the morphology of lyophilized hydrogels, after removing water by freeze-drying there was the organization and formation of pores. The fractured blend of PVP/PVA showed a smooth surface (Fig. 3e), whereas in the nanocomposites, nanoclay promotes monodispersed distribution with more homogeneous and lower sized pores (Fig. 3f). It is known that the presence of inorganic materials embedded in a polymer matrix plays a crucial role in the formation and morphology of porous structures after freeze-drying, and it seems that the higher the amount of inorganic compounds, the smaller the pores tend to be, as demonstrated by Ciołek et al. (2017) regarding the addition of bioglass in polymer matrices. The authors also point that with smaller pores, the mechanical properties, such as rigidity and mechanic resistance, are increased, which may be useful for applications where these properties are required. Our results regarding the pore morphology and inorganic composition are in accordance with the literature data.

3.3 Swelling

The swelling behavior can be seen on the swelling curves presented in Fig. 4 and can be justified according to the polymer-clay interactions in the aqueous system. Water competes with the polymer for the adsorption sites on the surface of the solid clay,

particularly when there are hydrogen bonds. As a bifunctional molecule, water can act as an ionic donor or receiver and their presence on the surface can promote or inhibit adsorption of the polymer. Water molecules on the clay surface are associated with the exchangeable cations due to the fact that basal oxygen in silicates 2:1 (siloxane surface) is weak electron donors, therefore, interactions by hydrogen bonding between water and the surface are not too strong (Theng et. al. 1979). In general, the equilibrium in hydrogel swelling depends on the reorganization of the molecules after crosslinking and the polymer-clay interaction, according to the clay concentration.

The hydrogel membranes PVAl/PVP and PVAl/PVP/0.5% clay showed similar swelling curves, although with a more rapid swelling occurring for the sample with clay, while PVAl/PVP/1.0% clay samples showed higher swelling. Note that the smallest amounts of clay favor the swelling, as PVAl/PVP/1.5% clay matrix presented the lowest swelling performance. This reduction might be due to covalent bonds formed by free radicals during crosslinking by gamma radiation. It can also be observed that the time of swelling equilibrium of the matrices takes place in approximately 10 h.

We observed different swelling behaviors between the two PVAl/clay and PVP clay systems. It is likely
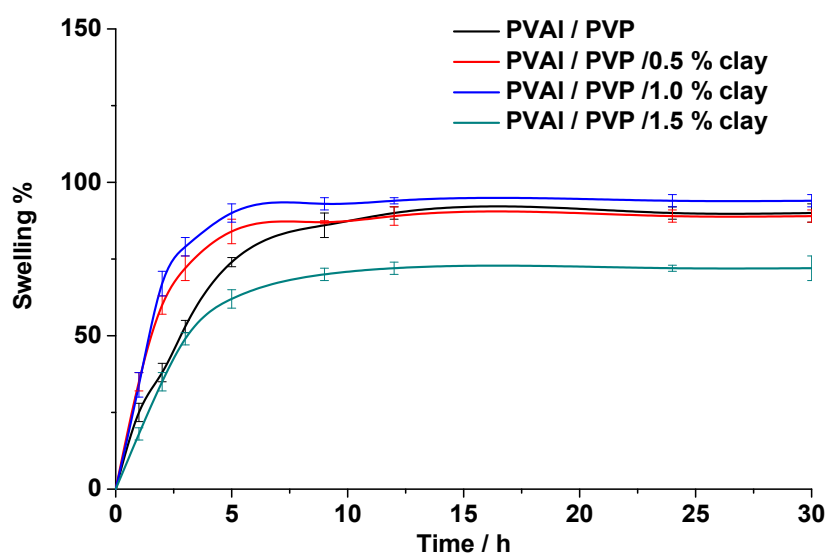

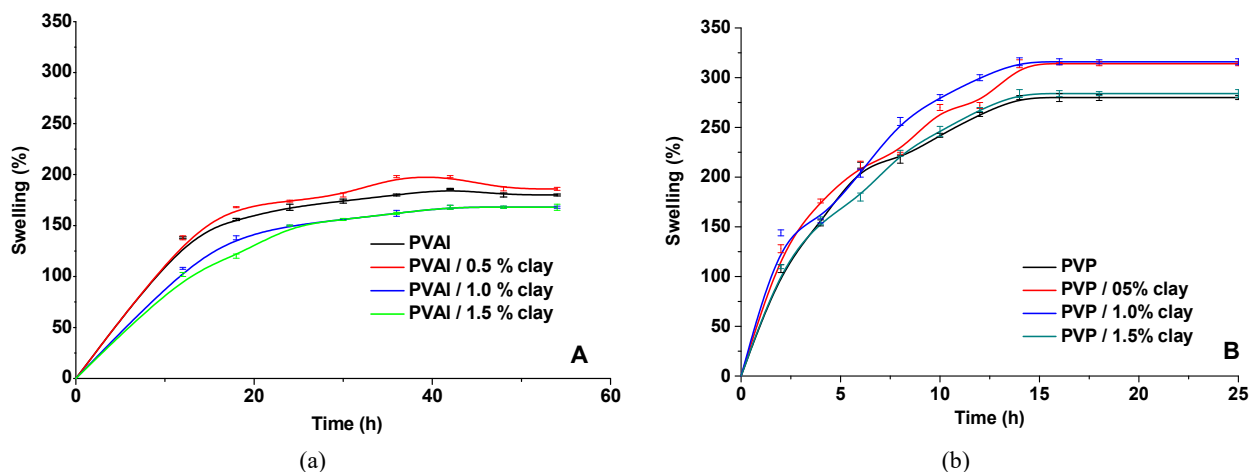**Fig. 4   Curves swelling PVAl/PVP/clay hydrogels.**

Fig. 5   (a) swelling hydrogels curves PVAl/clay and (B) swelling curves of PVP/clay hydrogels.

for the system PVAl/clay (Fig. 5a) that the beginning of swelling equilibrium occurs after 45 h at 200% for the matrix with 0.5% clay, and at 170% for matrices of 1.0% and 1.5% clay. As for the system PVP/clay (Fig. 5b), it reaches the equilibrium at only 15 h and 320% of swelling to 0.5% to 1.0% clay and matrices PVP and PVP/1.5% clay, 280% swelling.

It is worth mentioning that for PVAl/clay system, a higher percentage of clay leads to a reduction in swelling, while for the PVP/clay system it was observed that the increase of clay concentration to 1.5% had no effect on swelling, similarly to PVP behavior. This swelling behavior is associated with several factors that influence the recombination of radicals formed by radiation, i.e. clay interactions with the polymer, the functional groups along the polymer chain and ionization clay and PEG, which was used as a plasticizer for increasing the mobility and flexibility of the membranes (Rodrigues et. al. 1984; Tadmor et. al. 1979). Another explanation is the compaction of the polymer-clay composite frame due to the presence of disperse layers of clay throughout the matrix, as the swelling capacity of clay itself is usually much lower than the polymer's. Zhumagaliyeva and co-workers, for instance, observed a decrease in the swelling capacity of composite clay-polymer hydrogels, which is proportional to the amount of bentonite clay added to the mixture (Zhumagaliyeva et al., 2017).

3.4 FTIR (Infrared Spectroscopy)

FTIR was used to better understand the interactions between the nanoparticle clay and PVAl polymer, and the spectra are shown in (Fig. 6a). PVAl presents well-defined bands in the range of 3,440 cm^{-1} concerning the stretch OH group, and bands in the range of 3,000-2,800 cm^{-1}, the peaks at 2,870 cm^{-1} and 2,900 cm^{-1} correspond to the symmetric bending of -CH_2-, more specifically to symmetrical and antisymmetric stretching of -CH_2-, respectively. The regions between 550 cm^{-1} and 750 cm^{-1} are corresponding signing vibration outside the OH group in the background while the peak at 837 cm^{-1} is related to the same kind of vibration, but from the CH. The peak at 1,083 cm^{-1} indicates the coupling of OH and the band at 1,070 cm^{-1} corresponds to the vibration of CH. The displacement of the band in 1,083 cm^{-1} to the region of 1,070 cm^{-1} was attributed to interaction of PVA and the clay with the contribution of the silanol group (Nair et. al. 2007). It is observed in the system PVP/clay NC a peak displacement in the region 1,270 cm^{-1} to 1,288 cm^{-1}, which was attributed to interaction of the polymer with the clay the contribution of silanol groups,   shown in Fig. 6b (Oliveira et. al 2014). It is important to notice that the addition of clay did not change   the chemical structure of the polymers, as the characteristic bands from PVA and PVP are still found in the blends, although the amplitude of some
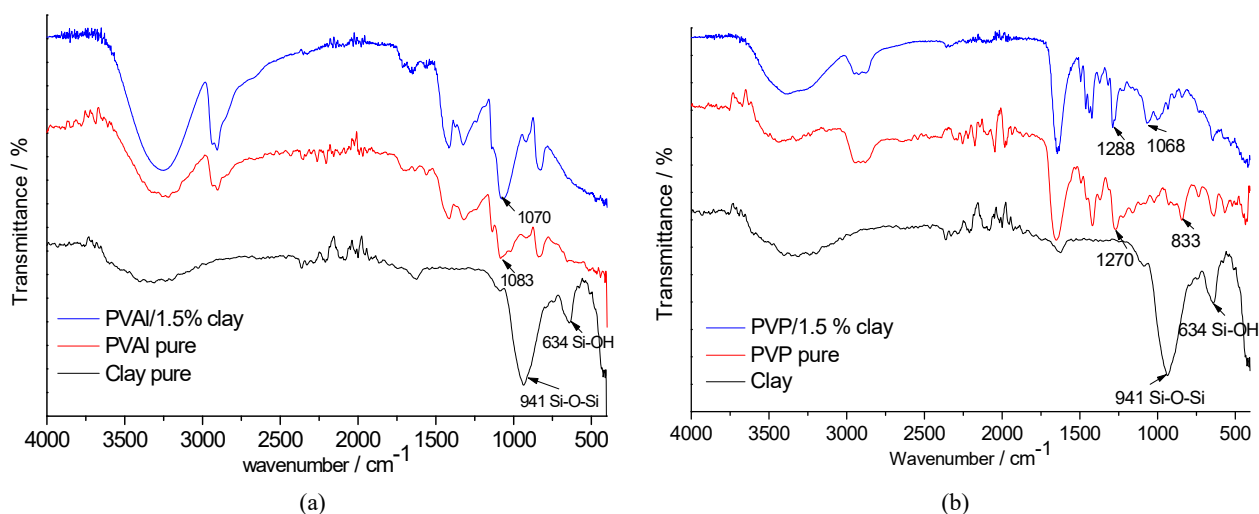
Fig. 6 **(a) Curves of vibrational spectroscopy in the infrared region of the dry hydrogel membranes in the form of films PVAl/clay and (b) films PVP/clay.**

regions changed, leading to the assumption that the clay-polymer interactions might influence the behavior of these compounds in terms of chemical bonds and functional groups (Baniasadi et al., 2021).

3.5 Tensile Test

The stress versus strain test results (Fig. 7) revealed that the addition of clay into the polymer formulations tends to increase Young's modulus, consequently decreasing the elongation before break, however, each polymer presented different results according to the clay concentration. The PVP formulations presented mostly a high break tensile strength and the lowest strain rates among all the samples. The addition of 1.5% clay increased significantly the break tensile strength and decreased the elongation compared to pure PVP.

On the other hand, PVAl formulations presented the highest strain performances while having the lowest break tensile strengths. The addition of 0.5% clay did not influence significantly the break tensile strength, though it decreased the stretching capacity of the formulation. The break tensile strength increased only when 1.5% of clay was mixed to the polymer, and the strain before break was further decreased in this case.

By mixing PVP with PVAl, we observed that both strain and break tensile strength properties reached intermediate values compared to the polymers alone,

which leads us to the assumption that the properties were mixed properly, and these polymers are compatible to make this mixture. The addition of 0.5% clay to this blend did not alter significantly the break tensile strength, but decreased the stretching capacity to a great extent. Interestingly though, the augment of clay concentration to 1.5% restored the stretching capacity of the blend, while maintaining the same average break tensile strength.

Baniasadi and co-authors observed that the addition of clay to polyamide formulations tends to increase Young modulus, increasing the tensile strength and decreasing the elongation at break (Baniasadi et al., 2021). This is probably due to the hindrance of the motion of polymer chains promoted by the clay layers dispersed into the matrix (Osman et al., 2015; Sharma et al., 2017). However, if the exfoliation is not complete and the mixture of clay layers into the polymer matrix is not uniform, i.e. when aggregates are present in the material, the opposite can occur, as the unexfoliated clay might act as a stress concentrator and lead to a decrease in fracture strain (Wang et al., 2016), as observed with PVP with 1.5% clay (in which we found evidences of incomplete exfoliation). On the other hand, the clay improved the elasticity of the PVP hydrogel, at about 20% and at 12% the blend of PVP/PVAl 1.5%. Furthermore, clay agglomerate
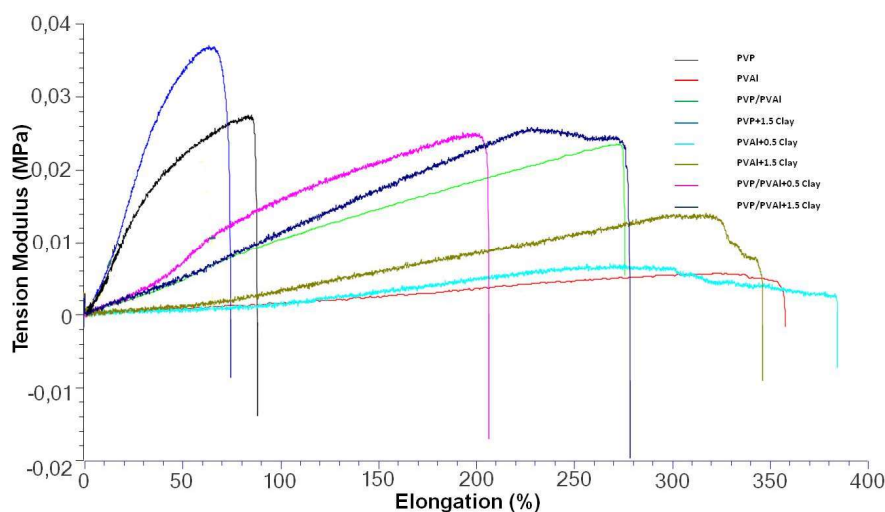
Fig. 7   Average curves of Stress X Strain.

Table 1   Young's modulus and elongation of PVP and PVP/PVA samples.

Sample	Young's modulus ($\times 10^{-3}$ MPa)	Elongation (%)
PVP	126	89
PVP + 0.5 Clay	-	-
PVP + 1.5 Clay	149	75
PVP/PVAl	109	279
PVP/PVAl + 0.5 Clay	117	208
PVP/PVAl + 1.5%	126	280
PVAl + 1.5 Clay	3	346
PVAl + 0.5 Clay	1	357
PVAl	1	385

sites can act as crack propagators due to the reduction of tensile strength (Zhang et al., 2017), therefore it could be one of the factors that led to the results found for PVP and PVP/PVAl formulations in the presence of clay, since some clay agglomerates were indeed observed in these samples.

4. Conclusion

The analyses of XRD showed intercalation and exfoliation of the polymer in the clay lamellae. These observations demonstrate the existence of a structural interaction within the polymeric/composite matrix of PVP, PVA and clay, corroborating with the swelling results where water absorptions showed a significant increase when Laponite clay was added to the hydrogels. This fact can suggest that the high water-absorption property of PVP and PVAl was increased when clay was added, and this feature is extremely relevant to wound treatment as it provides a humid environment to the injury. It was observed in micrographs of the three systems that the percentage of clay present in the sample modifies the surface and pore sizes, modifying the swelling behavior of the hydrogels. These results also confirm that the polymer/clay can interact in nano structure scale, as confirmed by FTIR CO peak corroborating to PVAl CN peak. With the tensile test results, it was observed that when the polymers (PVP and PVAl) were mixed like a blend, the mechanical properties were joined accordingly, specifically the stretching of PVAl and tensile of PVP that were combined in the PVP/PVAl blend. The elastic modulus proved one increase at about 15% when the clay is introduced in the blend at concentration of 1.5%, really important considering

the stretching of a curative to topic use. Through this study it was evidenced that it is possible to obtain a dressing after an easy processing and with good properties for topical treatments of injuries using PVP/PVAl and Laponite clay. These systems potentially offer an alternative treatment for drug delivery in the treatment of wounds with elasticity advantage.

Acknowledgments

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