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Water soluble nanocomposite films based on poly(vinyl alcohol) and chemically modified montmorillonites

Teresa M Pique¹, Claudio J Pérez², Vera A Alvarez² and Analía Vázquez¹

Abstract

Different montmorillonites were added to poly(vinyl alcohol) in order to improve their properties. The used montmorillonite's were: Cloisite Na+ (Na), Nanofil (NF), and Cloisite 30B (30B). Poly(vinyl alcohol) + montmorillonite films, obtained by casting, were characterized by means of Fourier transform infrared spectroscopy, differential scanning calorimetry, thermogravimetric analysis, X-ray diffraction pattern, transmission electron microscopy, water absorption, contact angle, and mechanical properties. Sodium and organically modified montmorillonites were used. The montmorillonite basal peak shifted to a lower angle for composites, with sodium montmorillonites, and the films were exfoliated–intercalated nanocomposites. Composites with organically modified montmorillonites presented a micro-morphology and the lowest water absorption. The best mechanical properties were obtained for the composite with sodium montmorillonites.

Keywords

Poly(vinyl alcohol), montmorillonite, organoclay, characterization, Nanocomposite

Introduction

Poly(vinyl alcohol) (PVA) is a thermoplastic water-soluble polymer with high elongation at break and, as a consequence, it has a small Young's modulus. It is known that montmorillonite (MMT) addition to polymers increases, among other properties, its stiffness.^{1–4} Due to the hydrophilic nature of MMT and PVA, completely or partially exfoliated PVA/MMT nanocomposites can be obtained.^{1–5}

Applications of PVA/MMT nanocomposites are being studied in several fields. For example, for: biomedical purposes,⁶ construction industry as an adhesive⁷ and as a concrete additive.^{8,9} Since PVA's elastic modulus, strength, thermal stability, fire retardancy, gas barrier properties, and solvent resistance enhance due to the addition of MMT, this nanocomposites is an attractive alternative for using in the packaging and automotive industries.¹⁰

MMT is an aluminum layered silicate of 100–200 nm long with an interlayer space of 1 nm where silica is the main component. The configuration of the silica sheet is tetrahedral while the octahedral sheet comprises diverse elements such as aluminum, magnesium, and iron.¹¹

PVA and MMT in water solution remain in colloidal distribution.³ Polymer in solution can enter into the interlayer of the MMT together with water. During the solution drying at ambient temperature MMT can be re-aggregated but if the polymer is trapped into the galleries it can inhibit MMT's shrinkage.¹²

Pristine PVA has hydrogen bonds that interact between themselves in order to create the molecular structure. When dissolved in water, the water acts as a plasticizer and increases the free-volume fraction of its amorphous structure. This interaction increases as a function of hydrolyzed groups.¹³

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This study was focused on the addition of different MMT to PVA to enhance its thermal and mechanical properties. Nanocomposites with natural MMT in fully hydrolyzed PVA (98–98.8%) was studied by Soundararajah et al.¹⁰ They used different quantities of clay and the best results were obtained for 4 wt% of clay. Strength increased 1.6 times and the Young's modulus increased 60% respect to the pristine PVA. However, the use of chemically modified MMT as additive of PVA has not been fully researched. In this case, three different commercially available MMTs were chosen taking into account its different chemical structures and their interaction with 88% hydrolyzed PVA. The percentage of clay was maintained constant at 4 wt%.¹⁰ Morphology, water absorption, mechanical and thermal analysis in each sample were analyzed.

Experimental

Materials and methods

PVA (Celvol 823, Celanese Chemicals) with 88% of hydrolysis degree was used. Figure 1 shows its chemical structure. PVA is an hydrolyzed poly(vinyl acetate) product, some interaction with the remained acetate groups in the polymer chain can be expected.¹²

MMTs were provided by Southern Clay Products, Inc., United States. MMTs used were: Cloisite Na+ (NA), Nanofil (NF), and Cloisite 30B (30B). They were used as received and their characteristics are summarized in

Table 1. These selected MMTs have different hydrophilic characters. Na and NF are the most hydrophilic. Cloisite 30B has two hydroxyl groups but the long tallow chains make the clay less hydrophilic than the first one.

Nanocomposites fabrication

Polymer solution (4 wt%) was prepared as follows: PVA was dissolved in water at 80°C, sonicated for 30 min and poured into an anti-adhesive mold and left in the oven at 40°C. The films were demolded 3 days later and stored at dry conditions (into a desiccator).

For incorporating MMT to the solution, it was first agitated in water at 40°C during 1 h and sonicated for 30 min. Then, the temperature was raised to 80°C and PVA was added to the solution. This solution was sonicated for 30 min. Again, 100 g of solution was poured into an anti-adhesive mold and left in the oven at 40°C. After 3 days, the films were demolded and stored at dry conditions (into a desiccator).

Characterization

Fourier transform infrared spectroscopy (FTIR) experiments were developed using a Shimadzu IRAffinity-1 spectrometer equipped with a single-reflection attenuated total reflectance accessory. A ZnSe crystal mounted in tungsten carbide was used. The analysis was carried out in the frequency range 400–4000 cm⁻¹, using 4.0 resolution and 40 scans were made for each sample.

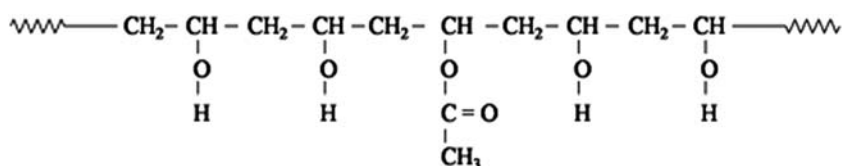


Figure 1. Chemical structure of PVA obtained by the partial hydrolysis of poly(vinyl acetate). PVA: poly(vinyl alcohol).

Table 1. Characteristics of the commercial MMT.

MMT	Organic modifier	Modifier concentration (meq/100 g clay)	CEC meq/100 g clay	d_{001} (Å)
Cloisite Na + (NA)	None	None	92	11.7
Nanofil 116 (NF)	None	None	116	12.5
Cloisite 30B (30B)	$\begin{array}{c} \text{CH}_2\text{CH}_2\text{OH} \\ \\ \text{H}_3\text{C}-\text{N}^+-\text{T} \\ \\ \text{CH}_2\text{CH}_2\text{OH} \end{array}$	90	92	18.5

MMT: montmorillonite.

T is tallow (~65% C18; ~30% C16; and ~5% C14).

For contact angle measurements, the films were placed over aluminum substrates. Static contact angle determination was made by the sessile drop method. Drops of doubly distilled water (5 μ L) were formed on the surfaces of plaques of the specimens. The contact angles (θ) were measured with a goniometer Ramé Hart model 500, using DROPimage advanced software to analyze the images. Between 5 and 10 measurements were performed for each sample.

Thermogravimetric analysis (TGA) measurements were carried out using a Shimadzu TGA-50. The films were heated from 25°C to 1000°C at a heating rate of 10°C/min under nitrogen atmosphere in order to avoid thermo-oxidative degradation.

Differential scanning calorimetry (DSC) tests were performed in a DSC Perkin Elmer 7. The films were first tested from 25°C to 250°C at a heating rate of 20°C/min in order to erase their thermal history. Then, they were cooled to 25°C and tested again up to 250°C at a heating rate of 10°C/min. The test was performed under nitrogen atmosphere (ASTM D3417-83). The glass transition temperature (T_g) was obtained from the curves. The degree of crystallinity was calculated from the following equation

$$X_{cr}(\%) = \frac{\Delta H_m}{w_{PVA} \times \Delta H_{100}} \times 100 \quad (1)$$

where ΔH_m is the experimental heat of melting, w_{PVA} the PVA weight fraction, and ΔH_{100} the heat of melting of 100% crystalline PVA and its value is 150 J/g.¹⁴

Transmission electron microscopy (TEM) was carried out for small solutions drops which were deposited on a copper mesh for TEM observations on a Philips EM 301.

X-ray diffraction patterns (XRDs) were obtained from a PW1710 diffractometer equipped with a Cu-K α generator ($\lambda = 1.5406 \text{ \AA}$) operating at 45 kV, 30 mA, and room temperature. Films and MMT powder were studied. The specimens were placed in vacuum oven at 60°C for 48 h and then placed in desiccators before used.

Water absorption tests of films were carried out at controlled relative humidity (65%), simulated from a solution of water and glycerin. For the MMTs, the test was carried out at controlled relative humidity (90%), also simulated from a glycerin solution.

Before tests, all the samples were dried under vacuum until constant weight. Samples were weighted at each time and the absorption was calculated as

$$M_t(\%) = \frac{M_t - M_0}{M_0} \times 100 \quad (2)$$

where M_t is the mass of the sample at a time t and M_0 the initial mass of the sample (dried).

Tensile tests were performed in a universal testing machine Instron 4467 at a constant crosshead speed of 2 mm/min. Samples were prepared according to the ASTM D882-02 standard. Before tests, all specimens were preconditioned at 65% relative humidity. Tests were carried out at room temperature.

Results and discussion

Fourier transform infrared spectroscopy

Representative FTIR spectra of PVA, modified PVA films with 4 wt% MMT and MMT powders are shown in Figure 2.

PVA polymer has a peak at 1635 cm^{-1} that is attributed to the stretching bond of carbonyl group (C=O). Vinyl polymers exhibit typical bands at 2800–3000 cm^{-1} due to stretching vibrations of CH and CH₂ groups. Hydroxyl groups in PVA and PVA + MMT nanocomposites exhibit a strong peak at the range 3200–3650 cm^{-1} . The absorbance at 1091 cm^{-1} in PVA + MMT nanocomposites was ascribed to the Si–O bond that has overlapped with the stretching bond attributed to C–O bond at 1000–1200 cm^{-1} . The peak around 1734 cm^{-1} , which appears in PVA spectrum, is attributed to residual acetate groups in PVA.¹⁵

Contact angle

The modified PVA films hydrophilicity was measured by studying the contact angle of double distilled water over the film surface (Figure 3). It was observed that the contact angle increased as follows

PVA + NA < PVA + NF < PVA + 30B < PVA (Table 2)

As it was observed, the bigger angle was the one formed over pristine PVA film. The addition of hydrophilic MMTs (Na and NF) produces the lowest contact angles.

Thermo gravimetric analysis

The addition of MMT to PVA influences the thermal resistance of PVA; Figure 4 shows the thermal degradation of pristine PVA and the nanocomposites. The decomposition of PVA occurred from 200°C to 500°C¹² and the nanocomposites have also the same range of decomposition temperature. However, the addition of MMT improved the thermal resistance of PVA shifting the degradation temperature to higher values.^{4,14,16,17} The weight loss due to the decomposition of PVA is nearly the same until 370°C. After this point, silicates inhibit PVA's weight loss, which reaches a maximum lag of about 45°C for PVA + Na.⁴ This lag is smaller for PVA + 30B and PVA + Na. The same behavior was found for the residual mass at 800°C.

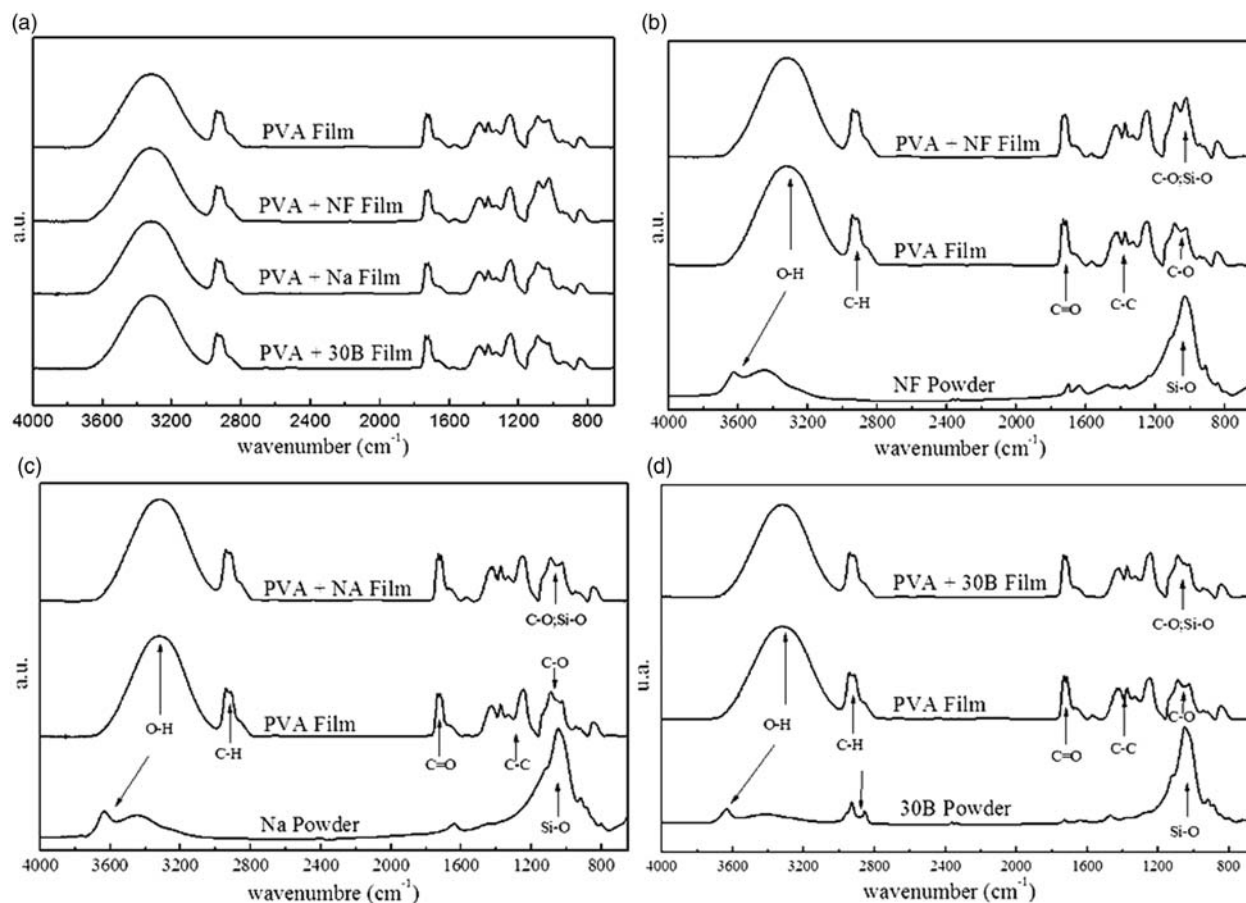


Figure 2. FTIR spectra of the PVA films in contrast with the modified PVA films and the MMT powder. FTIR: Fourier transform infrared spectroscopy; PVA: poly(vinyl alcohol); MMT: montmorillonite.

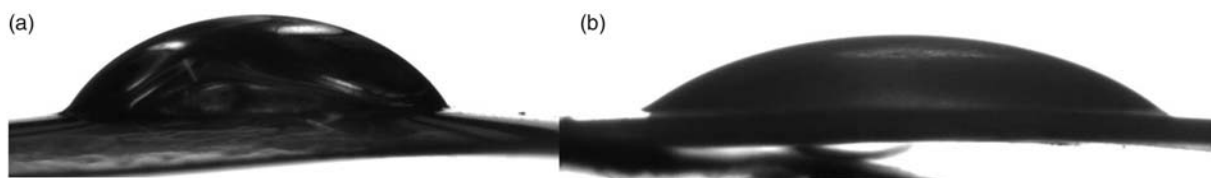


Figure 3. Contact angle of doubly distilled water over a (a) PVA film and (b) PVA + NF film. PVA: poly(vinyl alcohol).

Table 2. Contact angle of double distilled water over the film surface.

Sample	Contact angle, θ
PVA	$57 \pm 1^\circ$
PVA + 30B	$46 \pm 2^\circ$
PVA + NF	$42 \pm 1^\circ$
PVA + Na	$34 \pm 2^\circ$

PVA: poly(vinyl alcohol).

In Figure 4, the derivative of the residual mass in function of temperature can be observed. The area under the second peak is smaller for PVA + Na and PVA + NF. This should be because there is much char when organically modifiers are added to the MMTs.¹⁸

All the samples showed about 4 wt% of bonded water (Figure 5), but the temperature of water desorption is higher for the PVA + Na due to the increment of interaction between polymer chain and MMT surface.¹⁷

Differential scanning calorimetry

The films were first tested at 20°C/min in order to determine the thermal properties after the fabrication and also to erase their thermal history. Then, they were cooled at 10°C/min and tested again at 10°C/min. Figure 6 shows the thermograms obtained for PVA and the composite with MMT at their first melting, crystallization and second melting. In Table 3, the values for the glass transition temperature (T_g),

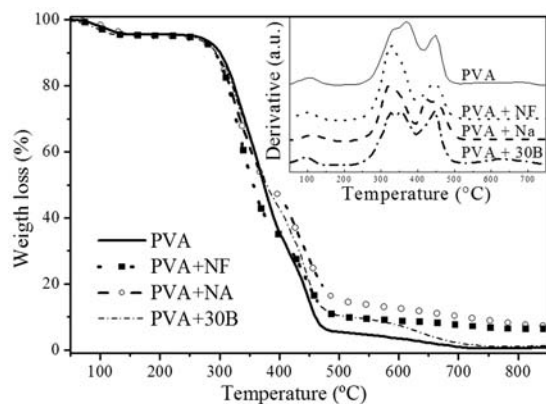


Figure 4. Thermal degradation analysis of PVA and their composites with MMTs and its derivatives.

MMTs: montmorillonites; PVA: poly(vinyl alcohol).

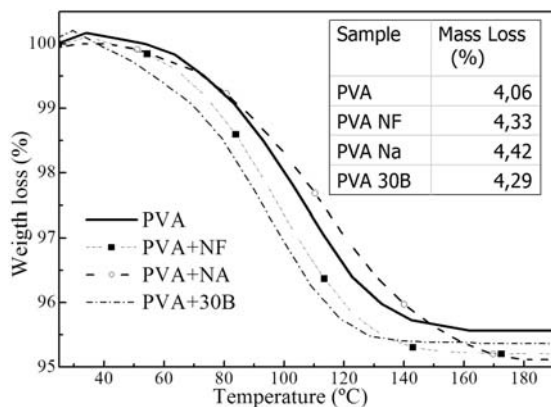


Figure 5. Mass loss due to the evaporation of water.

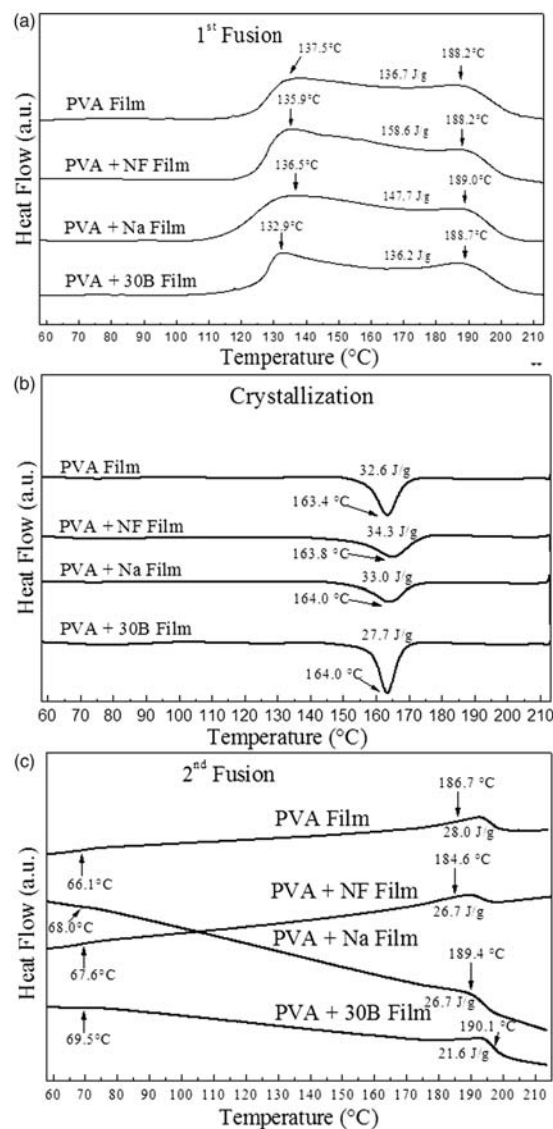


Figure 6. DSC thermograms of the polymer and nanocomposite samples: (a) first melting at 20°C/min; (b) crystallization at 10°C/min; and (c) second melting at 10°C/min.

DSC: differential scanning calorimetry.

Table 3. Thermal calorimetric results for the different samples: PVA and composites.

	T_{m1}' (°C)	T_{m1}'' (°C)	ΔH_{m1} (J/g)	T_c (°C)	ΔH_c (J/g)	T_g (°C)	T_{m2} (°C)	ΔH_{m2} (J/g)	X_{cr} (%)
PVA	137.5	188.2	136.7	163.4	32.6	66.1	186.7	28.0	19
PVA + NF	135.9	188.2	158.6	163.8	34.3	68.0	189.4	28.1	20
PVA + Na	136.5	189.0	147.7	164.0	33.0	67.6	184.6	26.7	19
PVA + 30B	132.9	188.7	136.2	164.0	27.7	69.5	190.1	21.6	15

PVA: poly(vinyl alcohol).

crystallization temperature (T_c), and melting temperatures of the first fusion ($T_{m1'}$, $T_{m1''}$) and for the second melting (T_{m2}) are given as well. It also details the enthalpy (ΔH) values of each studied sample and the crystallinity degree (X_{cr}). These values are the result of the scanning of two different samples.

The first melting shows the effect of the film formation due to water evaporation. Two endothermic peaks can be found. The first endothermic peak, $T_{m1'}$, with its maxima around 132.9–137.5°C, observed for pristine PVA as well as PVA + MMT is attributed to the removal of free water, as well as hydrogen bonded water. The absence of this peak in the thermograms recorded during the cooling cycle confirms this relaxation phenomenon associated with the removal of water molecules.¹⁹ As $T_{m1'}$ and $T_{m1''}$ are the same for the four samples it can be assumed that the formed crystals are the same for all samples.²⁰

When cooling the samples, after the first melting, the degree of crystallization (X_{cr}) was measured. The highest degree of crystallization was obtained for PVA + NF and PVA + NA, whereas the lowest was for PVA + 30B. The same occurred with the crystallization's enthalpy values (ΔH_c). These results showed that the MMTs NF and Na acted like nucleating agents.

After the crystallization cycle, only one melting peak was found. The enthalpy (ΔH_{m2}) decreased as the glass temperature (T_g) increased. The lowest ΔH_{m2} and highest T_g was found for PVA followed by PVA + 30B while the highest ΔH_{m2} and lowest T_g was found for PVA + NF.^{4,20} Furthermore, the composite samples have higher T_g than pristine PVA. This can be attributed to the confinement of the polymer chains in the presence of the clay that prevents its segmental motions.¹⁵ These results are consistent with the crystallization degree and TEM results.

X-ray diffraction pattern

One clay granule with a width of 1 μm has 850 layers of MMT inside. The thickness of each layer is only approximately 1 nm.¹ This means that, when MMT's layers are separated, the specific surface area increases, therefore, MMT becomes more reactive.

When a composite is made with a polymer matrix and MMT as filler, the morphology of this composite is determined by the dispersion of the MMT inside the polymeric matrix. When the MMT's layers are not separated enough to enhance the polymer to be introduced in between its layers, the material is called micro-composite and it has phase separation. MMT's layers can be separated enough so one or more polymer chains can be intercalated into its layers, then the final morphology is called intercalated nanocomposite. When the polymer is in between the layers, their

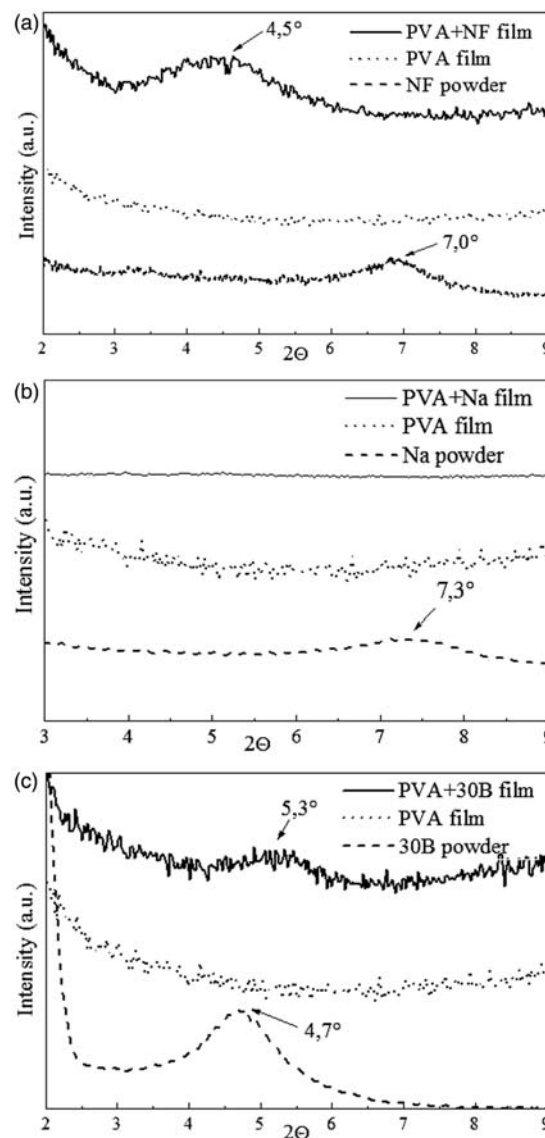


Figure 7. XRD spectrogram of: (a) PVA + NF composite, PVA film, and NF powder; (b) PVA + Na composite, PVA film, and Na powder; and (c) PVA + 30B composite, PVA film, and 30B powder.

XRD: X-ray diffraction pattern; PVA: poly(vinyl alcohol).

separation is the largest, then, the nanocomposite is called exfoliated or delaminated. This intercalated or exfoliated nanocomposite could be obtained by an effective dispersion of the inorganic nanolayers of MMT in the organic PVA matrix in a water solution.¹⁶

X-ray diffraction of the PVA films with MMT infers that the MMT were exfoliated–intercalated. The basal diffractions peaks corresponding to each MMT were observed: for 30B at $2\theta = 4.7^\circ$, for NF at $2\theta = 7.0^\circ$, and for Na at $2\theta = 7.3^\circ$. This last peak did not appear in the film (Figure 7(b)). For these result, we conclude that Na is exfoliated in the PVA matrix. The

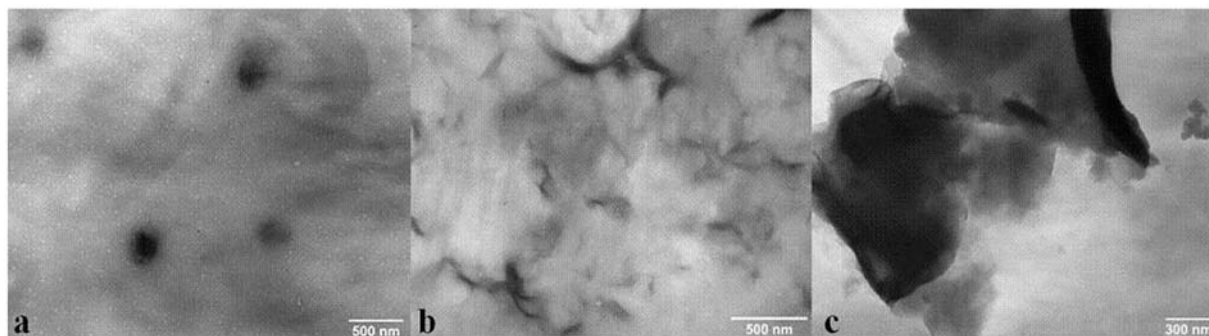


Figure 8. TEM images of PVA + MMT composite: (a) PVA+NF, (b) PVA+Na, and (c) PVA+30B. TEM: transmission electron microscopy; MMT: montmorillonite; PVA: poly(vinyl alcohol).

diffraction peak for NF powder moved from 7° to 4.5° . A shift in the diffraction peak toward lower angles with respect to the MMT alone is produced since the polymer chains intercalate between the MMT layers produce an increment in the basal spacing. Being the cation exchange capacity bigger for NF MMT than Na MMT it was expected a better dispersion for NF MMT. This happened because when a polymer with polar functional groups were introduced into the clay gallery the adhesive role of a polar polymer between hydrophilic clay layers, the so-called glue effect, tends to strongly exclude the complete dissociation of the layered structure of clay, resulting in only an ordered intercalated state. Nevertheless, it is expected an increase in the mechanical properties.²¹

The basal peak of 30B was slightly bigger for the PVA + 30B film, this means that the MMT is not exfoliated either intercalated in the film.²²

Transmission electron microscopy

The TEM images are shown in Figure 8. From the TEM images, it can be confirmed that Na and NF MMT disperse in the PVA matrix as nanoparticles as it was inferred from the XRD spectrograms. The difference is that PVA + Na formed an exfoliated/intercalated nanocomposite while PVA + NF formed an intercalated one. Na had a great degree of dispersion in the matrix, while NF formed well distributed, but not well dispersed, nanoparticle in the PVA matrix. The aggregation of 30B particles in a PVA matrix is evident from TEM micrographs. It was observed that MMT accumulated on the edges of the drop forming microagglomerates.

Water absorption under controlled humidity

Water absorption, such as other properties of the nanocomposites, depends on the interactions between the polymer-polymer chains and polymer-MMT.^{12,16}

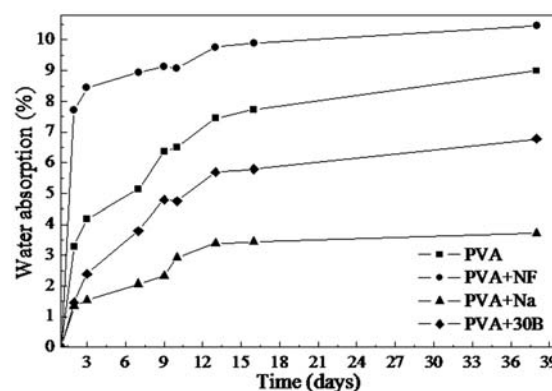


Figure 9. Water absorption vs time for PVA and their composites with MMT.

MMT: montmorillonite; PVA: poly(vinyl alcohol).

Usually, the unmodified MMT have higher water absorption due to their hydrophilic character. However, if there is a strong interaction between the hydroxyls of the polymer with the surface of MMTs, the water absorption decreases. In this case, PVA is partially hydrolyzed and the acetate groups also play an important role in the interaction between chains. The acetate produces an interaction between the metal cation on the surface of MMT, as it was shown by Sapalidis et al.¹²

Figure 9 shows the results obtained of the water absorption for all the studied PVA based materials. For a MMT with high CEC, the hydrophilic effect is higher and as consequence, water absorption is greater for PVA + NF than others materials. This is presented in Table 4 as NF, the MMT with the higher CEC had the highest M_∞ , while 30B, the MMT with the lowest CEC had the lowest M_∞ . The behavior of PVA + Na is explained on the base of his good compatibility of the MMT with the PVA. This interaction prevents the water absorption.²³

PVA + 30B absorb less water due to the long carbon chains and the results showed a lower equilibrium value than the pristine PVA.

For all nanocomposites, the weight continuously increased with immersion time until a plateau. The equilibrium water uptake, M_{∞} , was taken as the maximum value of these curves. The obtained values are presented in Table 4.

Mechanical properties

It is known that the mechanical properties of polymer/MMT nanocomposites depend on several parameters, such as: (a) interphase adhesion between polymer and the nanoclay, (b) mechanical properties of each component: the polymer and MMT, (c) the dispersion of the MMT inside the matrix, (d) the volume fraction and the orientation of the nanoclay, and (e) the distribution of the MMT inside the PVA matrix.¹¹ As a consequence, different MMTs will produce different reinforcement effect on the mechanical properties of a neat polymeric matrix. The elastic modulus (E), as well as the strength (σ), and the deformation at break (ε) were determined and the results are presented in Table 5.

Unmodified MMT interacts with the polymer chain and creates a better interphase. As a consequence, PVA + Na and PVA + NF have better mechanical properties (a higher modulus, elongation at break, and strength) than the pristine PVA.⁴ MMT Na increased about 37% the elastic modulus and a 32%

of the tensile strength with respect to plain PVA matrix whereas the elongation at break is twice than the one for pristine PVA. MMT NF increased 18% the elastic modulus, 37% of tensile strength, and has twice the elongation at break respect to pristine PVA.

On the other hand, as it was expected, the composites of PVA with organically modified MMT, 30B, has a slightly smaller modulus and tensile strength and slightly higher elongation than pristine PVA, this results are related with the presence of the cation in the polymer galleries.²⁴

Conclusions

Different nanocomposite films were obtained based on Na, NF, and 30B MMTs with PVA. The films were fabricated by casting by water evaporation. The MMTs had different chemical surface, Na and NF MMTs had sodium cations and 30B was modified with alkylammonium.

The nanocomposite films were characterized by means of FTIR and they did not show any difference in the chemical structure in comparison with pristine PVA.

DSC thermograms showed the fusion peak after water evaporation. These films showed two endothermic peaks. The first one, at 130°C is attributed to the evaporation of free and bonded water. When the thermal history was deleted, the thermogram showed only one melting peak at a higher temperature, around 189°C, reaching the highest temperature for PVA + 30B and the lowest for PVA + Na, in agreement with the minimum and maximum crystallinity.

TGA showed that the Na nanocomposite lost water slower than the other specimens, in agreement with their higher compatibility with PVA. On the contrary, 30B nanocomposites lost the highest amount of water.

The morphology of the nanocomposites were determined by XRD and TEM showing that the Na MMT was exfoliated/intercalated in PVA, NF MMT was intercalated in PVA and 30B formed a microcomposites in PVA due their lack of compatibility.

Water absorption results showed that the NF nanocomposites had the highest water absorption due to their high CEC and its higher hydrophilicity.

The contact angle measurement showed a bigger angle for pristine PVA, then PVA + 30B. The smallest one for PVA + Na.

The best mechanical properties were found for NF and Na. PVA + NF nanocomposites showed the highest tensile strength.

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Table 4. Equilibrium water uptake values by all materials.

Material	M_{∞} (%)
NF	18.9 ± 0.5
NA	13.0 ± 0.2
30B	4.4 ± 0.1
PVA	9.0 ± 0.2
PVA + NF	10.4 ± 0.5
PVA + NA	3.7 ± 0.1
PVA + 30B	6.8 ± 0.2

PVA: poly(vinyl alcohol).

Table 5. Mechanical properties of the PVA and their composite with MMT.

Simple	E (MPa)	σ (MPa)	ε (%)
PVA	105.0 ± 9	31.3 ± 3.0	1.15 ± 0.14
PVA + Na	143.4 ± 12.9	41.2 ± 4.2	2.30 ± 0.20
PVA + NF	123.5 ± 11.5	43.0 ± 4.0	2.10 ± 0.22
PVA + 30B	103.0 ± 10.3	25.8 ± 2.6	1.40 ± 0.05

MMT: montmorillonite; PVA: poly(vinyl alcohol).

Conflict of interest

None declared.

References

- Alexandre M and Dubois P. Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials. *Mater Sci* 2000; 28: 1–63.
- Ludueña L, Balsamo V and Vázquez A. Evaluation of methods for stiffness predictions of polymer based nanocomposites: theoretical background and example of application (PCL-clay nanocomposites). In: Vinicius Cabral RS (ed.) *Nanomaterials: properties, preparation and processes*. Chapter 9. New York: Nova Publishers, 2009, pp.341–365.
- Ogata N, Kawakage S and Ogihara T. Poly (vinyl alcohol)-clay and poly (ethylene oxide)-clay blends prepared using water as solvent. *J Polym Sci* 1997; 66: 573–581.
- Strawhecker KE and Manias E. Structure and properties of poly(vinyl alcohol)/Na⁺-montmorillonite nanocomposites. *Chem Mater* 2000; 12: 2943–2949.
- Chang JH, Jang TG, Ihn KJ, et al. Poly(vinyl alcohol) nanocomposites with different clays: pristine clays and organoclays. *J Appl Polym Sci* 2003; 90(12): 3208–3214.
- Kokabi M, Sirousazar M and Hassan ZM. PVA-clay nanocomposite hydrogels for wound dressing. *Eur Polym J* 2007; 43(3): 773–781.
- Kaboorani A and Riedl B. Effects of adding nano-clay on performance of polyvinyl acetate (PVA) as a wood adhesive. *Composites Part A* 2011; 42(8): 1031–1039.
- Knapen E and Van Gemert D. Cement hydration and microstructure formation in the presence of water-soluble polymers. *Cem Concr Res* 2009; 39(1): 6–13.
- Pique TM, Balzamo HM and Vázquez A. Evaluation of the hydration of portland cement modified with polyvinyl alcohol and nano clay. *Key Eng Mater* 2011; 466: 47–56.
- Soundararajah QY, Karunaratne BSB and Rajapakse RMG. Mechanical properties of poly(vinyl alcohol) montmorillonite nanocomposites. *J Compos Mater* 2009; 44(3): 303–311.
- Tjong SC. Structural and mechanical properties of polymer nanocomposites. *Mater Sci Eng R* 2006; 53: 73–197.
- Sapalidis AA, Katsaros FK and Kanellopoulos NK. PVA/montmorillonite nanocomposites: development and properties. In: Cuppoletti J (ed.) *Nanocomposites and polymers with analytical methods*. Rijeka: InTech Publisher, 2011, pp.29–50.
- Hernández MC, Suárez N, Martínez LA, et al. Effects of nanoscale dispersion in the dielectric properties of poly (vinyl alcohol)-bentonite nanocomposites. *Phys Rev E* 2008; 77(5): 1–10.
- Mark JE. *Physical properties of polymer handbook*. New York: Springer Science+Business Media, 1996.
- Yu YH, Lin CY, Yeh JM, et al. Preparation and properties of poly(vinyl alcohol)-clay nanocomposite materials. *Polymer* 2003; 44(12): 3553–3560.
- Döppers LM, Breen C and Sammon C. Diffusion of water and acetone into poly(vinyl alcohol)-clay nanocomposites using ATR-FTIR. *Vib Spectrosc* 2004; 35(1–2): 27–32.
- Corobea MC, Donescu D, Petcu C, et al. Polyvinyl alcohol – Na montmorillonite nanocomposites films obtained by solution intercalation. *J Optoelectron Adv Mater* 2007; 9(11): 3358–3360.
- Singhal A, Kaur M, Dubey KA, et al. Polyvinyl alcohol-In₂O₃ nanocomposite films: synthesis, characterization and gas sensing properties. *RSC Adv* 2012; 2: 7180–7189.
- Chang J-H, Jang T-G, Ihn KJ, et al. Poly(vinyl alcohol) nanocomposites with different clays: pristine clays and organoclays. *J Appl Polym Sci* 2003; 90: 3208–3214.
- Strawhecker KE and Manias E. AFM of poly(vinyl alcohol) crystals next to an inorganic surface. *Macromolecules* 2000; 34: 8475–8482.
- Lee S-S, Hur MH, Yang H, et al. Effect of interfacial attraction on intercalation in polymer/clay nanocomposites. *J Appl Polym Sci* 2006; 101(5): 2749–2753.
- Manfredi LB, De Santis H and Vázquez A. Influence of the addition of montmorillonite to the matrix of unidirectional. *Composites Part A* 2008; 39: 1726–1731.
- Gaume J, Taviot-Gueho C, Cros S, et al. Optimization of PVA clay nanocomposite for ultra-barrier multilayer encapsulation of organic solar cells. *Sol Energy Mater Sol Cells* 2012; 99: 240–249.
- Pavlidou S and Papaspyrides CD. A review on polymer-layered silicate nanocomposites. *Prog Polym Sci* 2008; 33(12): 1119–1198.