



11th International Congress on Metallurgy & Materials SAM/CONAMET 2011.

Effect of relative humidity on the mechanical properties of micro and nanocomposites of polyvinyl alcohol

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Abstract

The effect of relative humidity on the mechanical properties of poly(vinyl alcohol) (PVOH) micro and nanocomposites was evaluated. Two different commercial fillers (microcellulose and bentonite) were used as reinforcement. PVOH and PVOH composite films were prepared by casting technique. The incorporation of microcellulose increased the content of water absorption and the modulus, especially for the higher contents of filler. The effect of reinforcement on the mechanical properties was more pronounced at higher relative humidity. On the other hand, the incorporation of nanofiller produced a decrease in water absorption probably due to the decrease of mean free path of water molecules. The modulus of the nanocomposites improved from the matrix, but the mechanical properties are deteriorated by effect of the humidity.

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Keywords: degradable polymer, water absorption, microcomposites, nanocomposites ;

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1. Introduction

Research on the production and characterization of biodegradable films has taken great importance in last years due to increasing interest in minimizing the ecological impact caused by the use of synthetic packaging. Most of these investigations have relied on the use of biopolymers from renewable sources, such as proteins [Maria et al, 2008]. However, there are certain synthetic polymers derived from renewable sources that are degradable; such is the case of poly (vinyl alcohol) (PVOH).

PVOH is a synthetic, semi-crystalline, non-toxic and hydrophilic polymer [Kaczmarek et al, 2007], recognized as biodegradable [Carvalho et al, 2009]. It has recently received much attention in pharmaceutical, biomedical and biochemical applications, due to its attractive characteristics, such as biocompatibility, water-solubility, chemical resistance, excellent ability to form membranes and hydrogels, transparency and flexibility. However, its use is limited due to its high degree of swelling and solubility in water, which affects its mechanical and barrier properties [Sriupayo et al, 2005]. These disadvantages are relevant in the packaging industry and can be improved by the incorporation of reinforcements. Clay and cellulose are interesting as reinforcements of various polymeric materials because, in addition to environmental and economic factors, they have a natural abundance, high mechanical strength and good chemical resistance.

In this work is studied the effect of relative humidity on the mechanical and barrier properties of polyvinyl alcohol films with two kinds of reinforcements, at micrometric scale: cellulose, and other at nanometric scale: bentonite.

2. Materials and Methods

PVOH of 89000-98000 g/mol with a degree of hydrolysis higher than 98% was purchased from Sigma-Aldrich.

Microcrystalline cellulose powder from Sigma-Aldrich was used as filler to prepare the microcomposites.

Bentonite (platelets of 1 nm thick and 100 nm long), supplied by Minarmco S.A.. (Neuquén, Argentina), was used as filler to prepare the nanocomposites.

Because PVOH and reinforcements are very hydrophilic, no compatibility pretreatments were required [Döppers et al, 2004].

PVOH, *PVOH-cellulose* and *PVOH-clay* films were prepared by casting technique (adapted from Sharaf et al 1996). PVOH solution was prepared by dissolving PVOH (2 g) in distilled water (98 ml) and maintained for 24 h at room temperature to allow the swelling process. Then, the solution was heated to 90°C and stirring using a magnetic stirrer for 4 h to ensure the complete dissolution of the polymer. The solution was then poured into glass plate dishes and it was dried in an oven during 48 h at 40°C. Homogeneous films of 0.1-0.2 mm in thickness were obtained.

In the case of *microcomposites*, three different amounts of cellulose were used: 10, 20 and 30 wt. %. Cellulose microfibrils, previously placed in distilled water (proportion: 1 g cellulose/ 100 ml distilled water), were incorporated before stirring the solutions; the rest of the procedure was the same.

In the case of *nanocomposites*, 5 wt. % of bentonite was employed. In this case, different incorporation steps were studied: I) PVOH + Clay (swelling 24 h in water at room temperature in separated flasks), named NA; II) PVOH + Clay (swelling together 24 h in water at room temperature), named NB; III) PVOH (24 h in water at room temperature) + Clay (dried), named NC.

Water absorption tests were carried out at controlled relative humidity, simulated from a solution of water and glycerine. Before tests, all the samples were dried under vacuum until constant weight. Samples were weighted at prefixed times and the absorption at each time was calculated as:

$$M_t(\%) = \frac{M_t - M_0}{M_0} \times 100 \quad (1)$$

Where M_t is the mass of the sample at a time t and M_0 is 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 D882-91 standard. Before tests, all specimens were preconditioned at different relative humidity. Tests were carried out at room temperature.

3. Results and Discussion

3.1. Micro and nanocomposites characterization

Microcomposites: The length and average diameter of the microfibrers were $144.3 \pm 18.6 \mu\text{m}$ and $65.5 \pm 37.0 \mu\text{m}$ respectively. The transparency of the resulting films showed a homogeneous dispersion of microcellulose in the PVOH matrix up to 20 wt. %. At higher cellulose content, macroscopic agglomerations were observed. As it can be noted in Table 1, there was a clear increase in the degree of crystallinity, X_{cr} , and the glass transition temperature, T_g , compared to the PVOH matrix. Also, good adhesion matrix / reinforcement, was confirmed by means of SEM microscopy of cryo-fractured surfaces.

Table 1. Characterization of PVOH/cellulose microcomposites.

Cellulose content (wt. %)	X_{cr} (%)	T_g (°C)	T_m (°C)
0.0	35.8	102.5	225.2
10.0	35.6	105.9	224.3
20.0	43.4	111.8	226.4
30.0	46.8	120.6	222.3

Nanocomposites: In all cases, a homogeneous dispersion of the bentonite was observed. The incorporation of clay to PVOH produced a small enhancement in the thermal stability and also in the degree of crystallinity, without changing significantly its melting temperature. Further information can be found in a previous work [Ollier et al 2010].

3.2. Water absorption

Figures 1 (a) and (b) show the effect of relative humidity in the water uptake of the matrix. The amount of absorbed water increased with increasing relative humidity of the environment, because the driving force for the process of diffusion of water within the material is greater.

Figures 2 (a) and (b) shows the water absorption of the composites PVOH / cellulose (at relative humidity of 43% RH) and PVOH / clay (90% RH) respectively during 20 days. *Table 1* presents the values of water

uptake once equilibrium is reached at long times (M_{∞}), that is, the maximum water absorption that each material can incorporate.

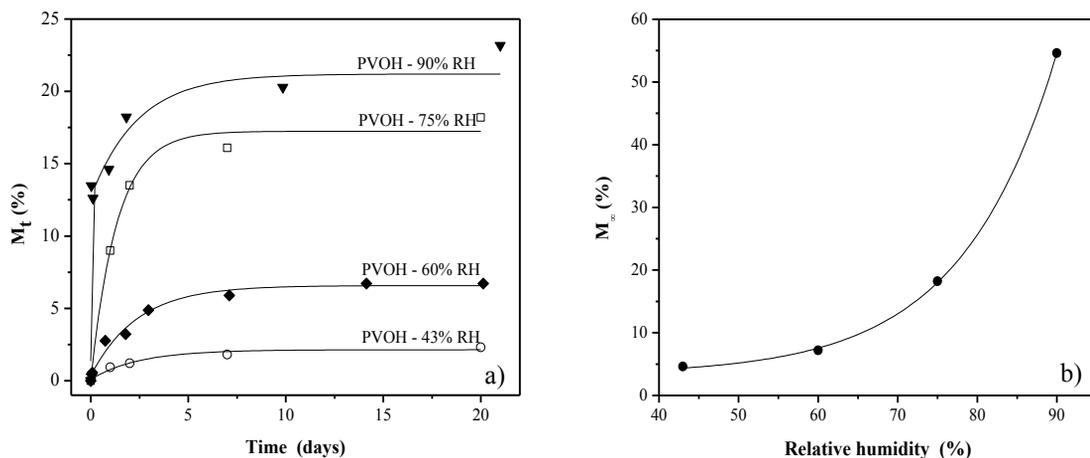


Fig. 1. Effect of relative humidity in the water uptake of PVOH matrix: (a) at short times (20 days); (b) at long times (M_{∞}).

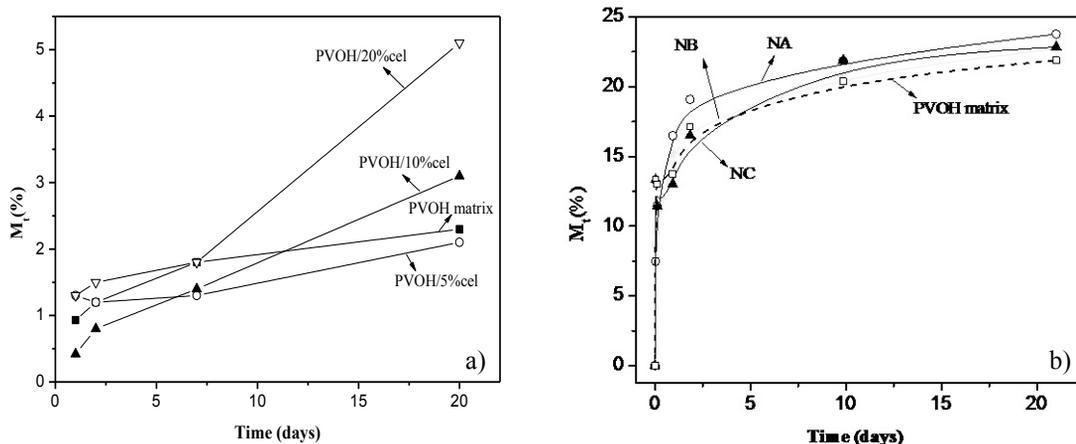


Fig. 2. Water absorption vs. time (during 20 days) in PVOH samples with: a) cellulose (43% RH); b) bentonite (90% RH).

Table 2. Water absorption (%) at equilibrium (M_{∞}).

Cellulose Content (wt. %)	M_{∞} (43% RH) (%)	Specimen	M_{∞} (90% RH) (%)
0	4.6 ± 0.5	Matrix	54.6 ± 2.0
5	3.5 ± 0.4	NA	33.5 ± 1.8
10	3.8 ± 0.2	NB	38.9 ± 1.1
20	5.6 ± 5.0	NC	43.3 ± 0.5

Table 2 shows that for 5% wt. cellulose, the microcomposite absorbs less water than the matrix; however for the highest cellulose content the water absorption increased. This result may be related to the interactions between cellulose and PVOH through the hydroxyl groups. At low cellulose content, interactions with the functional groups of PVOH are established; the number of available -OH groups is low so water absorption decreases. This occurs until a certain percentage of cellulose. At higher contents of microfibrils (20 wt. %), the dispersion is not homogeneous and agglomerates are formed. In consequence, the effective number of interactions decreases and more hydroxyl groups are available to promote absorption of water.

On the other hand, the addition of bentonite produced the opposite effect once equilibrium is reached (long times), i.e., the nanocomposites absorb less moisture compared to the PVOH matrix. This is because the dispersed nanometric scale reinforcement significantly increases the tortuosity of the path for the permeation of water molecules [Lu et al, 2007]. Therefore, the degree of dispersion of the reinforcement is the predominant effect in this work.

3.3. Mechanical properties

Mechanical properties (Young's modulus (E) and resistance (σ) of PVOH / cellulose and PVOH / clay composites under different environments of relative humidity (RH) were studied. All properties are relative to the respective value for the matrix.

In the case of microcomposites, the films were tested under three different conditions:

- Films previously dried in an oven.
- Films preconditioned at 43 and 75% RH for 1 week.
- Films preconditioned at 43% RH until constant weight.

Figure 3 shows that Young's modulus increases with the cellulose content. At the same time, the effect of reinforcement is significantly higher with increasing relative humidity.

It can be seen the remarkable effect of the incorporation of microcellulose, especially at high contents. This could be attributed to the formation of a crosslinked structure above the percolation threshold, as a result of hydrogen bonding interactions between PVOH chains and microfibrils, resulting in a strong interfacial adhesion [Samir et al, 2005]. This is consistent with the results obtained in a previous work [Ollier et al, 2010], in which SEM microscopy images confirmed a proper interfacial adhesion.

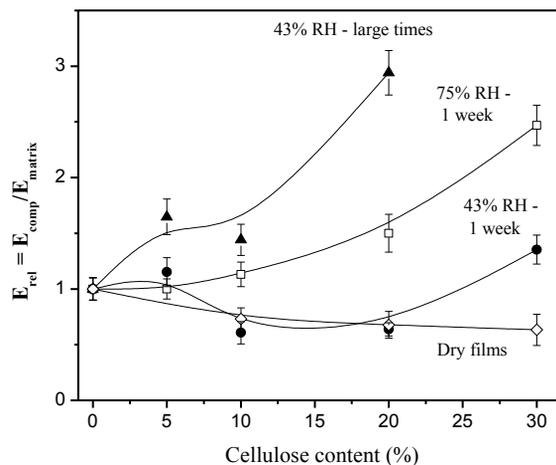


Fig. 3. Effect of cellulose content and relative humidity on the modulus of the specimens.

In the case of the PVOH / bentonite nanocomposites, the mechanical properties were determined in two different conditions:

- Films previously dried in an oven.
- Films preconditioned at 60% RH until constant weight.

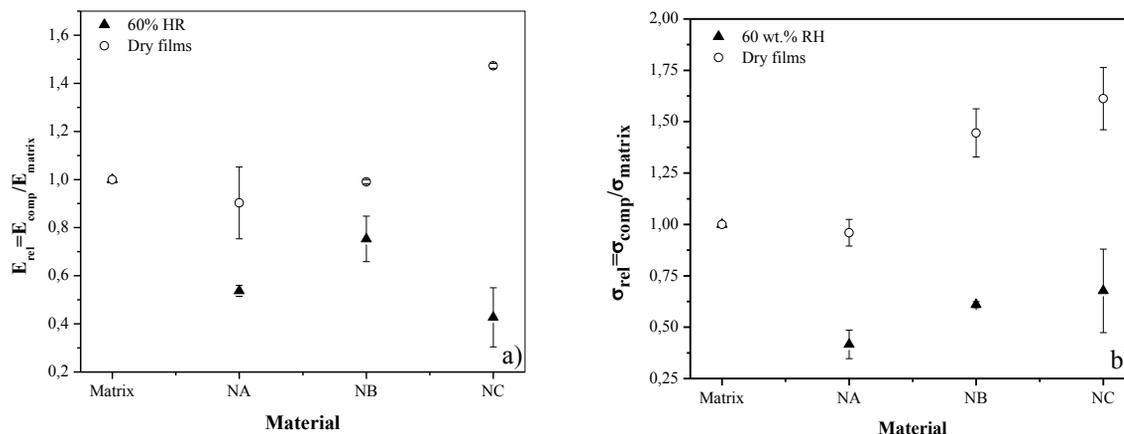


Fig. 4. Effect of incorporation of bentonite and humidity on: (a) the modulus of PVOH; (b) the fracture stress of PVOH.

Figure 4 shows that, in dry films, the modulus of the nanocomposites was improved compared to the matrix, probably due to the method of preparation. The same behavior is seen in the resistance of materials. The best results were obtained for the compound NC. This can be attributed to better distribution of clay in the matrix.

In the case of wet films, the opposite effect is observed for the modulus. Despite improved barrier properties, retention of mechanical properties due to the humidity gets worse and this may be because water molecules interact with the clay, weakening the interface.

4. Conclusions

In this work, PVOH nanocomposites with 5 wt. % bentonite were obtained. Different previous conditions of swelling were evaluated. In all cases a good dispersion of clay throughout the matrix was achieved.

PVOH microcomposite films with cellulose (5 to 30 wt. %) were also obtained. Uniform dispersion was achieved up to 20 wt. % microcellulose content.

The effect of the addition of bentonite and microcellulose to PVOH on the barrier properties of materials was studied. On the one hand, the incorporation of microcellulose produced an increase in moisture absorption, while the addition of bentonite produced a decrease of up to 35% in this parameter. Therefore, the preparation of composites with a high degree of dispersion of the reinforcement in the matrix is a key factor to improve the barrier properties of the material.

In addition, the mechanical properties of dry materials and the effect of water absorption was analyzed. Young's modulus of microcomposites showed a marked increase as a function of cellulose content, which coincides with the results obtained in a previous work. It was also noted that the module is substantially greater with increasing humidity of the environment. In the case of nanocomposites, the modulus of dry films improved with respect to the matrix. The best results were obtained for NC composite, which was prepared by previously swelling PVOH and bentonite in the same container. However, water absorption produced a

negative effect, deteriorating the mechanical properties of materials. This could be due to a weakening of PVOH / bentonite interface.

Acknowledgements

The authors acknowledged to the National Research Council of Argentina (CONICET), National University of Mar del Plata (UNMdP) and National Agency of Scientific and Technologic Promotion (ANPCyT) for the financial support.

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