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PROPERTIES OF HYBRID FILMS BASED ON POLY(VINYL) ALCOHOL AND POROUS CLAY HETEROSTRUCTURES

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The goal of this paper was to study the effect of porous clay heterostructures (PCHs) concentration on the thermal and swelling properties of hybrid materials based on poly(vinyl alcohol) (PVA)-PCHs. The hybrid films (PVA-PCHs) were synthesized by solvent casting method using different PCHs concentrations. These materials were characterized by Fourier transform infrared (FTIR) spectrometry, thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA). The swelling properties were also investigated. The results showed that the PCHs concentration influences the thermal stability and the swelling properties of hybrid films.

Keywords: Poly(vinyl) alcohol, Porous Clay Heterostructures (PCH)**,** Hybrid films**,** Thermal stability, Dynamic mechanical analysis

1. Introduction

Poly(vinyl) alcohol (PVA) is a semi crystalline synthetic polymer that is included in the class of hydrophilic polymers being attractive due to the features such: film forming capacity, nontoxic, biodegradability and biocompatibility [1-3]. PVA is extensively used in biomedical applications (drug delivery systems, cardiovascular devices, surgical repairs, artificial skin, wound dressing, dialysis membranes, pharmaceuticals), food applications, flexible water-soluble packing films, separation membranes, paper coating, and adhesives, protective colloids for emulsion polymerization, packaging [4-6].

The polymers such as: polysaccharides, polyesters, starch, cellulose acetate, and poly(vinyl) alcohol (PVA) show poor thermal, mechanical, water resistance properties and high flammability [7, 8]. Various strategies were developed in

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order to solve these drawbacks. The dispersion of inorganic nanostructures into the polymers or the preparation of complex systems based on two or more polymers are the most used methods to increase of some properties.

The hybrid materials based on polymer and different inorganic compounds combine the properties of both components, thus resulting a new material with improved properties. The addition of inorganic components into polymer increase the properties (thermal stability, chemical resistance to solvent, fire retardancy, molecular barrier, corrosion protection properties) of material [4, 9-12].

Porous clay heterostructures are a new type of mesoporous materials characterized by a layered structure and a high porosity that combines micro and meso- structures. These materials exhibit remarkable textural properties (high specific surface area, ability to control the pore volume and pore size distribution), capacity to adsorb alkaline metals from aqueous solution, capacity to adsorb VOC (volatile organic compounds), high thermal stability and host capacity to encapsulate drug [13-16].

In this paper, new hybrid materials based on PVA matrix and porous clay heterostructures (PCHs) were prepared. The influence of PCHs concentration on the hybrid materials properties (thermal stability, swelling degree) was investigated. The influence of PCHs on PVA glass transition temperature was studied by Dynamic mechanical analysis (DMA).

2. Experimental

2.1. Raw materials

A natural clay, montmorillonite (Nanofil 116 (MMT-Na)) with a cationic exchange capacity (CEC) of 116 mEq/100g was supplied from Southern Clay Products. PVA 98-99% hydrolyzed, molecular weight of 31,000-50,000 g/mol, hexadecyltrimethylammonium bromide, (**HDTMA**), tetraethyl orthosilicate (**TEOS**) and dodecylamine (**DDA**) were supplied from Sigma-Aldrich and used as received. The chemical structures of the raw materials are shown in Fig. 1.

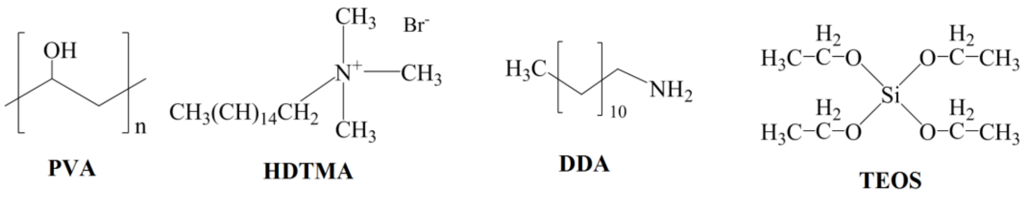


Fig.1. Chemical structure of raw materials

2.2. Synthesis of porous clay heterostructures (PCHs)

The PCHs were prepared using the same protocol work described in our previous paper [13]. Briefly, synthesis of PCHs was performed using modified montmorillonite with HDTMA (MMT-HDTMA, 5 g) hydrated with 5 mL of demineralized water, DDA co-surfactant (34g) and silica precursor (TEOS, 250 mL). In the first step, hydrated MMT-HDTMA was mixed with DDA and stirred for 10 minutes at room temperature. In the second step silica precursor (TEOS) was added and the obtained suspension was maintained at room temperature for 5 h under magnetic stirring. For this synthesis, a molar ratio between MMT-HDTMA: DDA: TEOS (1:20:120) was used. The final product was washed with ethanol and air-dried and then the PCHs precursor was calcined at 650°C, with a heating rate of 1°C/min aiming to remove the organic fractions.

2.3. Synthesis of hybrid films

The hybrid films based on PVA and PCHs were prepared by solvent casting method. This synthesis was performed in three main steps. In the first step the PVA solution was prepared by autoclaving for 1h at 120^{0}C. In the second step two different PCHs concentrations (1 and 10 wt.%) were dispersed into PVA solution by sonication (Power=130 W and Amplitude 50%) for 30 minutes and, in the final step, the hybrid films were obtained by casting each suspension into polystyrene Petri dishes and dried at room temperature for solvent evaporation.

The synthesis of hybrid films (PVA-PCHs) was done using the method schematically described in Fig. 2.

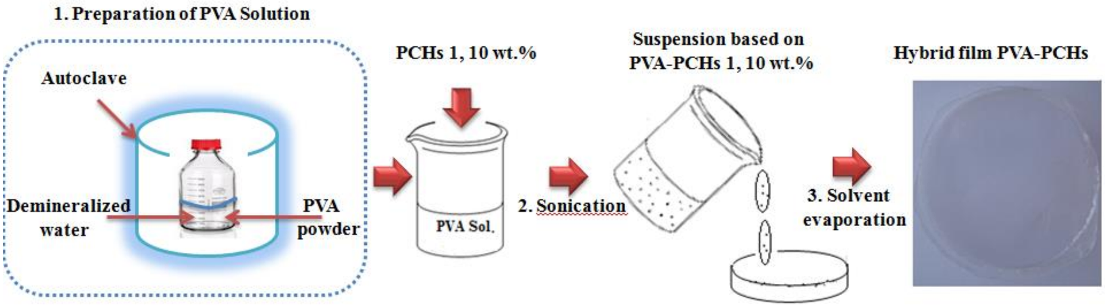


Fig.2. Synthesis steps of hybrid films

2.4. Characterization techniques

FTIR spectra were recorded on a Bruker VERTEX 70 spectrometer with ATR (attenuated total reflectance) accessory using 32 scans with a 4 cm^{-1} resolution.

Thermogravimetric analysis (TGA) measurements were done on using a Q 500 TA Instrument. The films were heated from 20 to 800°C at a heating rate of 10°C/min under a constant nitrogen atmosphere flow rate.

Dynamic mechanical analysis (DMA) tests were run on a TRITEC 2000 B instrument operated in single cantilever bending mode. The samples were tested at 1 Hz frequency using 5°C/min heating rate in the -50÷150°C temperature range.

3. Results and discussion

3.1. FTIR characterization

The FTIR was employed to study the presence of PCHs into PVA films and to point out the possible interactions between PVA and PCHs. Figure 3 shows the FTIR spectra of hybrid films PVA-PCHs (PCHs 1 wt.%, 10 wt.%), neat PVA and PCHs powder.

The FTIR spectrum of PVA film presents the following characteristic peaks: 3310 cm^{-1} (assigned to O-H stretching vibrations of the PVA), 2938 cm^{-1} (attributed to the stretching vibrations of C-H from alkyl groups) and 1084 cm^{-1} (assigned to the –C-O stretching vibrations). The -O-H bending vibration was detected at 1418 cm^{-1} and the peak at 1720 cm^{-1} was attributed to the carbonyl group (C=O) from residual acetate groups. Similar spectra of PVA films were reported in the literature [11].

The characteristic infrared peaks of PCHs include: a broad peak at 3436 cm^{-1} assigned to O-H stretching vibrations of the water molecules adsorbed on PCHs, a peak at 1632 cm^{-1} attributed to H-O-H bending vibrations of physically adsorbed water on PCHs surface, and the peak at 1081 cm^{-1} attributed to three-dimensional silica network. The absorption peak at 3738 cm^{-1} and the small peak shoulder at 3635 cm^{-1} were assigned to the terminal silanol groups and geminal and associated terminal silanol groups, respectively [15, 16].

The presence of PCHs in the hybrid materials based on PVA-PCHs was highlighted by the following two peaks: one at 3731 cm^{-1} assigned to the terminal silanol groups vibrations and the other one at 3617 cm^{-1} attributed to the geminal and associated terminal silanol groups (Fig. 3).

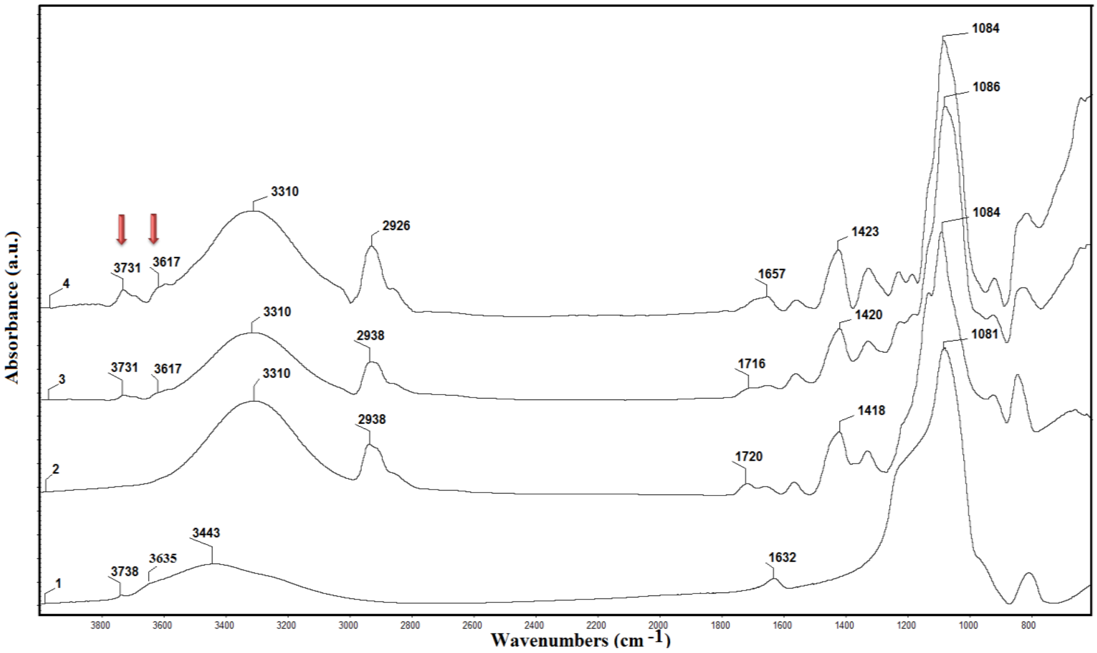


Fig.3. FTIR spectra of: 1-PCHs, 2-PVA, 3-PVA-PCHs 1 wt.%, 4- PVA-PCHs 10 wt.%

3.2. Thermogravimetrical analysis

TGA tests were performed in order to investigate the influence of PCHs on the thermal stability of hybrid films. The thermal degradation profiles of PVA, PCHs, and hybrid films are presented in Fig. 4.

In case of TG profile of PCHs, two main weight losses were recorded as follows: **(1)** weight loss of hydroxyl groups from pillars (300-500^{o}C) and **(2)** weight loss of hydroxyl groups that exists between MMT sheets [15].

The thermogravimetric (TG) profile of PVA film shows three degradation steps: **(1)** an initial weight loss that is assigned to the evaporation of absorbed water (50-170^{o}C), **(2)** the second step is attributed to the elimination of residual acetate groups from PVA (200-420^{o}C) and **(3)** the last step is assigned to the decomposition of polymer structure (420-800^{o}C) [17, 18].

The results of TGA tests also highlight an increase of thermal stability for the samples which contain PCHs compared with neat PVA film. The sample with the lower concentration of PCHs (PVA-PCHs 1 wt.%) shows an increase of $T_{onset\ 15\%}$ with 5^{o}C and the sample with 10 wt.% PCHs (PVA-PCHs 10%) shows an increase of $T_{onset\ 15\%}$ with 12^{o}C compared to neat PVA film. The improvement of thermal stability of hybrid films was attributed to the barrier effect that was induced by the presence of PCHs. This behavior was also reported in case of polymer- layered silicates based nanocomposites [17, 20]. Similar results were obtained for various hybrid materials based on PVA and different nanostructured agents [9, 10, 19].

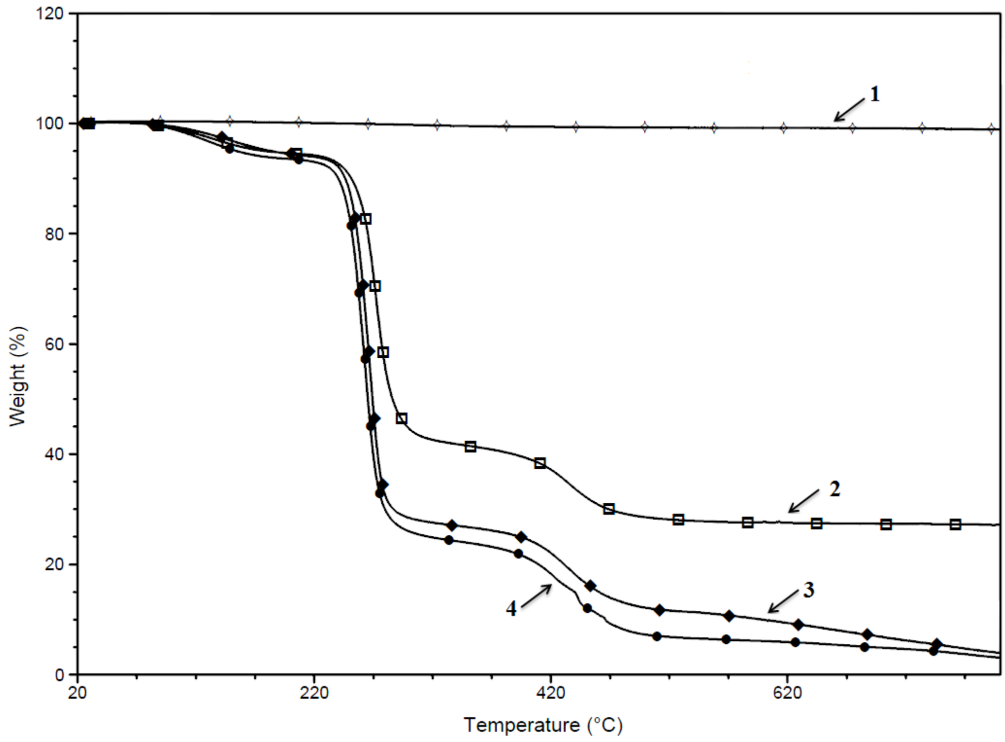


Fig.4. TGA curves of: 1-PCHs, 2- PVA, 3- PVA-PCHs 1 wt.%, 4- PVA-PCHs 10 wt.%

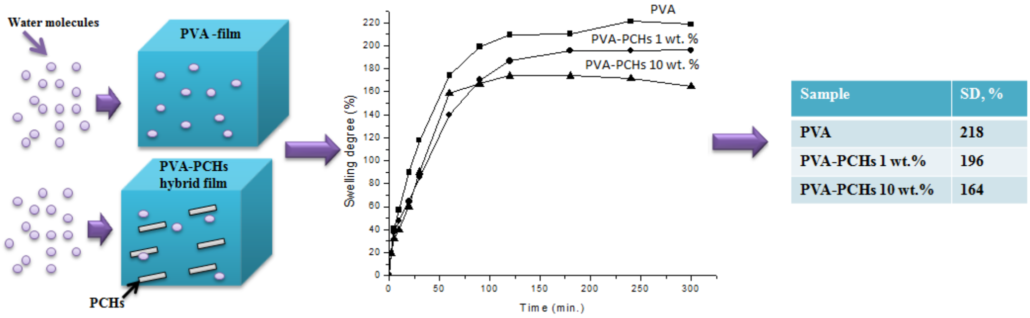
3.3. Swelling degree

The swelling of hybrid materials based on PVA-PCHs has been determined according to a modified method reported [11] for PVA-montmorillonite hybrid films. The swelling evaluation involved the following experimental protocol: the samples were initially weighted before being immersed in a tube that contains 10 mL of demineralized water and after being removed the excess of water, they were weighed at different swelling times. The swelling degree was calculated according to the following equation [12]:

$$\mathbf{SD = (m_t - m_0)/m_0 * 100} \tag{1}$$

where: m_t is the weight of the swollen sample at different times (t) and m_0 is the weight of the dry sample. The films were weighted until their weight has reached an equilibrium.

The barrier effect of PCHs was also confirmed by swelling tests. From the swelling results, it can be observed that the presence of PCHs causes a decrease of the swelling degree, this being assigned to the barrier effect of PCHs (Fig. 5). Thus, the sample with the higher concentration of PCHs (PVA-PCHs 10 wt.%) exhibits a swelling degree of 165% in comparison to neat PVA film that provides 218% swelling degree. The barrier effect of PCHs prevents the diffusion of water molecules into the PVA films [19, 21].



Sample	SD, %
PVA	218
PVA-PCHs 1 wt.%	196
PVA-PCHs 10 wt.%	164

Fig.5. Schematic diagram of water diffusion in PVA film and hybrid materials based on PVA and PCHs. In the middle, the swelling degree curve of: 1-PVA film, 2-PVA-PCHs 1 wt.%, 3- PVA-PCHs 10 wt.%

3.4. Dynamic mechanical analysis (DMA)

The dynamic mechanical analysis (DMA), which is most useful for studying the viscoelastic behavior of polymers, was used to investigate the influence of PCHs concentration on the glass transition temperature (T_g). T_g values were determined from tan δ against temperature curves, where the tan δ is the phase angle that is given by [22]:

$$\tan \delta = G''/G', \tag{2}$$

where G' is the stotage modulus and G" is the loss modulus.

DMA results confirmed that the dispersion of PCHs in PVA does not affect the T_g value of polymer (Fig. 6.). Even at high PCHs concentration (10 wt.%) the T_g value remains constant and therefore it can be concluded that the PCHs does not induce a plasticizing effect like other clays (e.g. MMT) [22]. The hybrid films based on PVA-PCHs show similar values of T_g even at high PCHs concentration (10 wt.%).

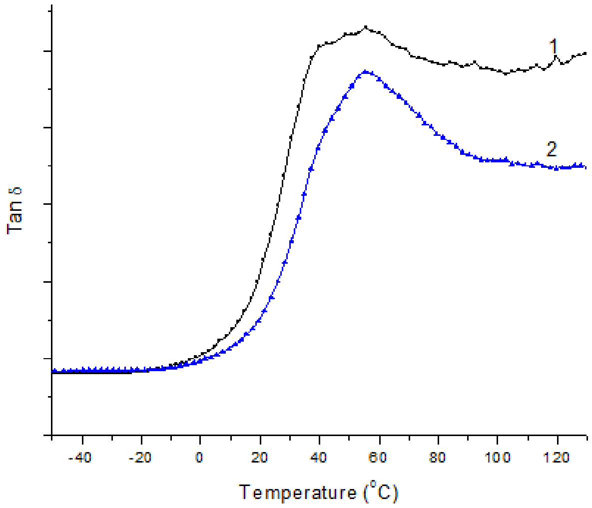


Fig.6. The dependence of Tan δ against temperature for: 1-PVA film, 2 PVA-PCH 10 wt.%

4. Conclusions

New hybrid films based on PVA-PCHs were successfully prepared by solvent casting method. FTIR analysis confirms the presence of PCHs in PVA films. TGA results indicated that the presence of PCHs improves the thermal stability of hybrid films. The improvement of thermal stability of hybrid films (PVA-PCHs 10 wt.%) was attributed to the barrier effect that was induced by the presence of PCHs.

The barrier effect of PCHs was also confirmed by swelling tests. The presence of PCHs induced a decrease of the swelling degree due to the barrier effect. The dynamic mechanical analysis (DMA) confirmed that the dispersion of PCHs in PVA does not affect the T_g value of polymer.

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