

PREPARATION OF POLI (VINYLALCOHOL)/ORGANOCLAY NANOCOMPOSITES BY CASTING AND IN SITU POLYMERIZATION

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Abstract

In this paper was studied the preparation of nanocomposite polyvinylalcohol (PVA) /organophilic montmorillonite (MMT_{HDTMA}), 5 wt %, obtained by two methods: the first in situ polymerization and the second mixed by solution (casting). The polymerization in situ was carried out by the addition of organophilic clay in the monomer (vinyl acetate, VA), using benzoyl peroxide as initiator. Poly (vinyl acetate)/MMT_{HDTMA} was obtained and then an alcoholysis in an alkaline medium was made, to finally obtain the composite of PVA/MMT_{HDTMA} (In situ polymerization). In the method of obtaining by mixing in solution (casting) organophilic clay dissolved in water. Moreover, the PVA was obtained by hydrolysis of polyvinyl acetate in alkaline medium. PVA was added to the dispersion of clay in water and heated to 90 ° C until complete dissolution of polymer, the solutions were added in petri plates and obtained PVA/MMT_{HDTMA} (casting) films. The composites were characterized by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The thermal properties were evaluated by thermogravimetric analysis (TG) and differential scanning calorimetry (DSC).

1 Introduction

The synthesis of PVA/organophilic montmorillonite nanocomposites, obtained via in situ polymerization, was only reported by Yu et. al, 2003 [1]. Naidu et al., 2005, [2] reported the preparation of nanocomposites by in situ polymerization of PVA polymeric matrix and polyaniline as nanofiller. In 2007, Jia et al. reported obtaining nanocomposites with this method but of PVA/silica nanoparticles and in 2008 used the same method but with other types of clay as kaolinite [3, 4].

The preparation of nanocomposites by casting, in 1963, Greenland [5] reported the first production of compounds of PVA with montmorillonite (MMT) of different cationic (Na⁺, K⁺ and Ca²⁺) by the method of mixing solution using a solvent water and found that the adsorbed sodium MMT is better than any other type. In 1997, Ogata et. al [6] used the same technique for the production of PVA composite polyethylene oxide and MMT.

In this paper we study the preparation of nanocomposite PVA/MMT_{HDTMA} (5 wt%) obtained by two methods: *casting and in situ polymerization and subsequent hydrolysis*. The composites were characterized by X-ray diffraction (XRD) and infrared spectroscopy with

Fourier transforms (FTIR). The thermal properties were evaluated by thermogravimetric analysis (TG) and differential scanning calorimetry (DSC).

In the XRD results can be seen that the composites obtained by the two methods of preparation the characteristic peak of the organophilic clay is shifted towards lower angles, with the compounds led to greater d-spacing ($d = 34 \text{ \AA}$) the PVA/MMT_{HDTMA} (casting).

According to the results of DSC, the material that showed higher melting temperature was obtained by in situ polymerization.

From the results we can conclude that using the method of preparation of nanocomposites by in situ polymerization a composite much more thermally resistant is obtained and is associated with increased interaction between clay and polymer.

2 Experimental

2.1 Material

The type of clay used in this study was sodium montmorillonite (MMT) provided by MINARMCO S.A. and exchanged with hexadecyltrimethylammonium chloride (Merck) (MMT_{HDTMA}) following the modified technique of Yeh et al., 2006.

The monomer used for the in situ polymerization was vinyl acetate (VA) (M = 86.09 Veteco. Boiling point: 73°C. I: 1.394 to 1.396) which was previously stabilized with hydroquinone (Reagen-Industry C₆H₆O₂. M = 110.11 g / mol) and purified by distillation.

2.2 Preparation Method

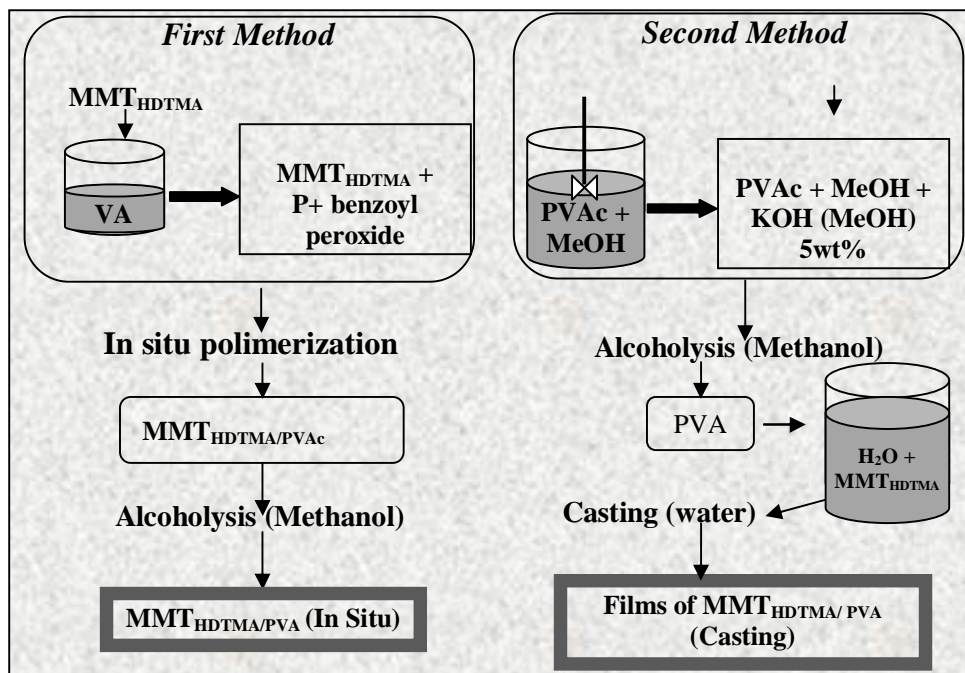
In the *first* method, Scheme 1, the organoclay (MMT_{HDTMA}) was treated with the monomer (VA) for 24 hours with stirring at room temperature to get the swelling of clay, with the burden of MMT_{HDTMA} 5% compared to vinyl acetate. Reached the time of treatment, the suspension was placed in the polymerization reactor and mixed with propyl alcohol (CH₃CH₂CH₂OH: anhydrous Q chemical groups. M = 60.10 g / mol. Boiling point: 97.4 ° C. ID 30 = 1.385. $d = 0.8040$. > 99% purity) in a ratio of 1.5 with respect to the monomer and then adding the initiator (benzoyl peroxide: C₁₄H₁₀O₄. Veteco. M = 242.23 g/mol) at a concentration 1% with respect to vinyl acetate. The reactor was closed and the process conditions were: 70°C with mechanical stirring for 5 hours in an inert atmosphere of N₂, to avoid possible inhibition of polymerization reaction due to the presence of oxygen.

Once the MMT_{HDTMA}/polyvinyl acetate (PVAc) alcoholysis was performed with methanol (CH₃OH: Merck KGaA. M = 32.04 g / mol. > Purity 99.9%. G/cm³ $d = 0.791$ to 0.793) and a 5 wt% solution of potassium hydroxide (KOH Veteco. > Purity 85 wt%. M = 56.11 g/mol) / methanol (MeOH) at a temperature of 60°C, with mechanical mixing for 1 hour.

In the *second* method, Scheme 1, PVA/ MMT_{HDTMA} membranes were performed by hydrolysis of polyvinyl acetate (PVAc), ALDRICH, in pellet, with average molecular weight $M_w = 113000$ and purity of 99 %, was mixed with absolute methanol and solution ANEDRA 5 wt% potassium hydroxide (KOH) Cicarelli.

Into a reactor was placed PVAc with methanol, stirred mechanically at a temperature of 60 ° C for one hour, until the total dissolution PVAc pellets, then the solution was added 5% KOH and stirring continued for 30 minutes approximately. A white precipitate confirming pulverulent aspect was observed obtaining poly (vinyl alcohol). Once hydrolysis finished the solution was cooled down to room temperature, filtered in a Buchner filter and washed with methanol. Finally was carried a vacuum oven at a temperature of 40 ° C for one day to complete drying of the PVA.

A water suspension of a 10% load of clay (MMT_{HDTMA}) was prepared in was stirred at room atmosphere PVA was then added, stirring was continued for one temperature of 90 ° C until complete dissolution of poly (vinyl alcohol), the solution obtained was casted onto Petri dishes and dried at room temperature.



Scheme 1. Method of obtain of composite by in situ polymerization (first) and casting (second) of PVA/clay.

3 Characterizations

The materials obtained were characterized by X-ray diffraction (XRD) in a Rigaku diffractometer Miniflex, ranging from $2\theta = 2^\circ - 10^\circ$, also by infrared spectroscopy (FTIR) using a FTIR Perkin Elmer, 1720x, with a frequency resolution of 2 cm^{-1} .

The thermal behaviour of the compounds was carried out using a TGA Instrument model Q500 v6.7 with a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$ and a DSC model 2920 in an N_2 inert atmosphere.

4 Results

The Figure 1 shows the characteristic pick of organoclay in $2\theta = 4.7^\circ$, of material obtained by casting a peak at a lower angle of $2\theta = 2.6^\circ$ and the material obtained by in situ polymerization did not show much change compared to organoclay pristine where $2\theta = 4.4^\circ$.

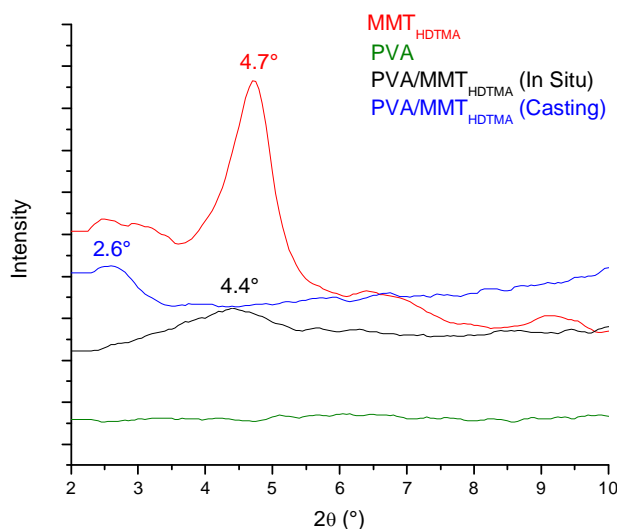


Figure 1. DRX of PVA, $\text{MMT}_{\text{HDTMA}}$ and $\text{PVA}/\text{MMT}_{\text{HDTMA}}$

(5wt %) by casting and in situ polymerization.

Based on Bragg's law was obtained d-spacing of the clay layers and the results are shown in Table 1, an increase in "d" with respect to the pristine organoclay, were observed for both samples. The highest increase in the d-spacing was presented in the material obtained by the method of casting.

Material	2θ (°)	d (nm)
MMT _{HDTMA}	4.7	1.88
PVA/MMT _{HDTMA} (casting)	2.6	3.40
PVA/MMT _{HDTMA} (In situ)	4.4	2.01

Table 1. d-spacing of: MMT_{HDTMA}, and material obtained by different methods.

Table 2 shows the characteristics vibration bands at 3382 PVA (-OH), and 2931 (-CH₂) and that corresponding to clay: 1037 (Si-O).

	MMT _{HDTMA}	PVA	PVA/MMT _{HDTMA} (Casting)	PVA/MMT _{HDTMA} (In situ)
Si-OH Stretching	3633	-	-	-
-OH Stretching	3431	3382	3269	3359
ν _{CH₂} Asymmetrical	2948	2931	2926	2926
ν _{CH₂} Symmetrical	2848	2843	2848	2848
CH ₂ Scissoring band	1472	-	1420	1439
Si-O in plane Stretching	1037	-	1089	1056

Table 2. Characteristic FTIR bands of: MMT_{HDTMA}, PVA, and material obtained by different methods (Frequencies [cm⁻¹])

Figure 3 shows the curves obtained from thermogravimetric analyses of all materials. The materials obtained for two different method present enhanced thermal stability that the polymeric matrix, but the material obtained by in situ polymerization showed higher thermal stability than that obtained by casting.

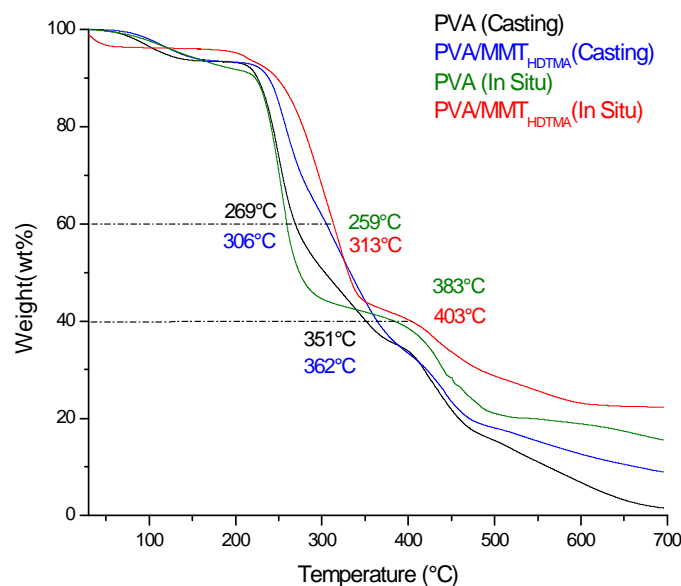


Figure 3. TGA of: PVA and PVA/MMT_{HDTMA} 5 wt % by casting and in situ polymerization.

In Figure 4 can be observed that PVA obtained by casting exhibits an endotherm peak at 218°C while the PVA obtained by “in situ” polymerization at 195°C corresponding to the crystalline melting point (T_m) of PVA. The materials of PVA/MMT_{HDTMA} (casting and “in situ”) are found to have a high T_m compared to the bulk PVA, as shown in Figure 4. This is tentatively attributed to the incorporation of clay layers which act as a thermal barrier.

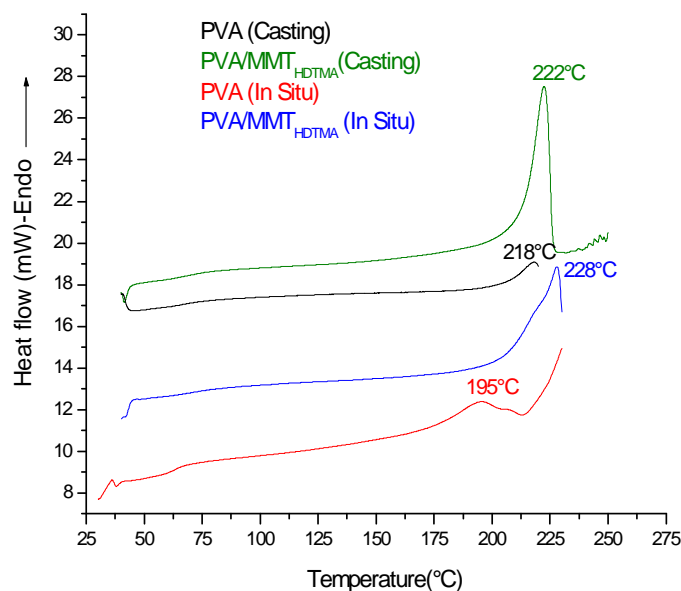


Figure 4. DSC of: PVA and PVA/MMT_{HDTMA} 5 wt % by casting and in situ polymerization.

Conclusions

In the XRD results can be seen that the composites obtained by the two methods of preparation present the intercalated structure however the material obtained by casting presents greater d-spacing.

In terms of the thermal properties are enhanced with the incorporation of clay into the polymer matrix but the material obtained by in situ polymerization showed higher thermal stability.

From the results we can conclude that using the method of preparation of nanocomposites by “in situ” polymerization a composite much more thermally resistant is obtained and this behavior is associated with interaction increasing between clay and polymer.

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