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Synthesis and Characterization of Polyvinyl Alcohol/Na$^+$-MMt Nanocomposite: Effect of Charge Content and CO_2 Adsorption Properties

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ABSTRACT

The present work focuses on the synthesis and application of nanocomposites Montmorillonite-Poly-vinyl Acetate Acrylate (MMT-PVA) in CO_2 adsorption field. Firstly the montmorillonite was modified by simple cation exchange with Na$^+$, the obtained material was used as charge for polyvinyl alcohol and were characterized using various techniques such as X-ray Diffraction (XRD), Fourier transform infrared spectroscopy, Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). The results show that the nanocomposites is obtained by the intercalation of the MMT, increasing the content of MMT leads to the increase of the interlayer distance, CO_2 adsorption at 0°C was carried using a volumetric method, and the recorded isotherm indicated that the CO_2 adsorption capacity of MMT-PVA can be enhanced through modification by PVA. The Na-MMT has low CO_2 adsorption capacity compared to that Nanocomposite.

Keywords: Nanocomposite, MMT-PVA, PVA, CO_2 adsorption, Clay

INTRODUCTION

Recently several studies are oriented towards the development of low cost treatment processes in terms of protecting the environment using natural materials such as clays; these layered materials are characterized by interesting properties such as significant specific surfaces, ion exchange, inflation, availability in nature and they are able to remove organic and inorganic pollutants [1-4]. These solids are widely used for the synthesis of the new useful materials for catalysis and adsorption applications [1-4]. In order to enhance their properties several methods have been proposed such as ion exchange using metals or surfactant, pillar of a metal or immobilization of polymers and others methods [5-7].

nanocomposites polymer/clay have experiencing very rapid development in recent years especially in materials science field, since the studies on this subject have increased as well with different matrices, the combination of two different matrices clay and polymer can be result a novel properties such as improved heat resistance, heat stability, chemical stability, electric and electrochemical properties, mechanical strength, adsorption and barrier properties for gas and other properties [8-12], for example, the dispersion of few percent (typically 3-5% of MMT weight) of Na$^+$-montmorillonite in a polyvinyl alcohol matrix suffices to develop a significant mechanical strength properties [13], while maintaining interesting biodegradability properties. The properties of nanocomposite are also related to the synthesis conditions in order to obtain the desired morphology such as conventional composite, intercalated or exfoliated nanocomposite [14,15].

The nanocomposites based polyvinyl alcohol has known range of applications such as biomedical field [16-18], Thermal, optical, mechanical properties, migration, antioxidant and antibacterial activities [19], tissue engineering application [20], lithium-ion electrolyte battery separator [21] adsorption of dye and heavy metals [22,23]. The obtained adsorption results show that the materials based on polyvinyl alcohol presents interesting adsorption capacities and can be reused in several cycles to treat the industrial wastewater.

The use of nanocomposite polyvinyl alcohol/MMt in the gas adsorption field is non-existent, especially in the adsorption of CO_2 no work has been published on this subject. Knowing that nanocomposites enriched with the OH groups have higher CO_2 adsorption affinity, the work of Azzouz et al. [24-27], showed that nanocomposites polyol dendrimer bolotorne H20, H30, H40 and polyglycerol dendrimers have interesting properties via CO_2 adsorption compared to the pure clays, and they also showed in their attractive works that the nanocomposite based polyalcohols have a reversible property through desorption of CO_2 at low temperatures [24-27].

In the same context and by reviewing the literature, we find that the adsorptions of CO_2 by PVA/MMt are practically non-existent, in this work we propose to synthesize the PVA/Na-MMt nanocomposites by a two-step process, exchange of the MMt with Na$^+$ then the dispersion of PVA to obtain an intercalated nanocomposite material. The obtained nanocomposites were tested as adsorbents for CO_2 as a novel application for this range of materials.

EXPERIMENTAL

Preparation of Na$^+$-MMt

Na$^+$-MMt has been prepared by ion exchange method using NaCl as source of Na$^+$ cations. The treatment process is similar to our previously published work [28-31], Firstly 20 g of MMt was crushed for 20 min then dried for 2 h at 105°C.

The obtained powder is treated in 500 ml of NaCl solution (1 M), the mixture was stirred using a magnetic stirrer until saturation was achieved after 3 h at room temperature; the mineral was then washed with distilled water to make it Cl$^-$ free and then dried at 105°C.

Preparation of polyvinyl alcohol/Na-MMt

The nanocomposites MMT-PVA were synthesized by a solution-intercalation method: this pathway consists to the preparation of a MMT/water suspension followed by addition of dissolved PVA; the synthesis protocol is similar to the literature [32]. Firstly, we have prepared a solution of Na-MMT (25% wt) using distilled water, the suspension was stirred and then sonicated about 2 h, the second step consists on the carefully addition of polyvinyl alcohol to the first solution then sonicated for 1 h, the mixtures were then heated at 90°C to dissolve the PVA and returned to the sonicator for a further 24 h. Finally the obtained materials were cast in a closed oven at 60°C for 1 day then stored at room temperature until analysis. Various compositions with different sodium montmorillonite content were prepared (1, 3, 5, 7, 10 and 15 wt%) with constant polymer content.

Characterization

XRD was carried out at room temperature on a Bruker D8 Advance X-Ray diffractometer (40 kV, 30 mA) using CuKα radiation (k=0.154 nm) at the rate of 2 min^{-1} in the 2 h range of 2.0-80°C. Fourier Transform Infrared Spectroscopy (FTIR) analysis of obtained materials was carried out using the PerkinElmer Spectrum Two FT-IR with UATR sampling accessory. The Thermogravimetry (TG) technique was also used, by means of Thermogravimetric Analysis (TGA) 51 Shimadzu equipment, operating at a heating rate of 10°C min^{-1}, from room temperature up to 900 C under an air atmosphere with a flow rate of 50 ml min^{-1}. The sample mass was 5.0 ± 0.5 mg. The TG curves were analyzed with the aid of the TASYS software from Shimadzu. The glass transition temperature Tg of the synthesized nanocomposite was determined from the corresponding transitions in the DSC thermogram using a Setaram 92 DSC instrument.

The isotherms of CO$_2$ adsorption were realized by ASAP 2020 V4.01 (Micromeritics) apparatus at 0°C. Sample cell was loaded with approximately 100 mg of the nanocomposite sorbent. In order to remove any adsorbed impurities the nanocomposites have been outgassed under vacuum at 170°C. The adsorption was performed using highly pure CO$_2$ (99.999%) at lower pressures (5-760 mmHg).

RESULTS AND DISCUSSION

The X-ray diffraction characterization was used to determine the structural properties of nanocomposite obtained at different percentages of MMT in the PVA matrix (Figure 1). The DRX spectrum of exchanged Na$^+$-MMT shows that the basal peak d_{001}=11.87 Å (d_{001}, calculated by Bragg's law, $d_{001}=\lambda/2 \sin\theta$) is displaced at a lower diffraction angle compared to the unmodified clay [30,31], confirming the intercalation of the Na$^+$ cations in the MMT clay. This displacement of basal spacing is also attributed to the hydrated galleries due to the existence of water molecules in the interlayer space [33].

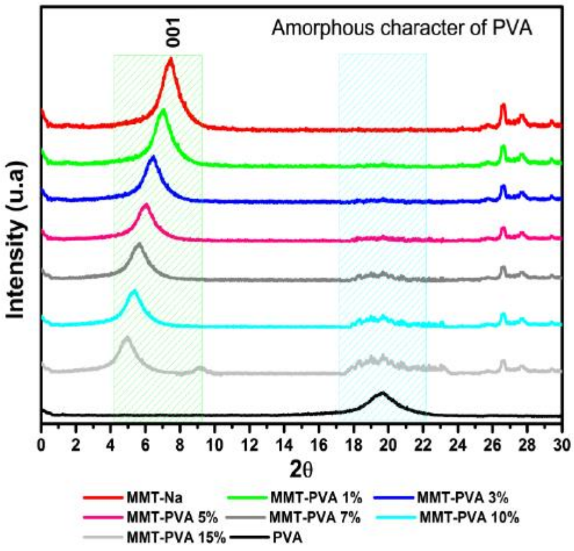

Figure 1: XRD patterns of nanocomposite MMT-PVA

The XRD pattern of nanocomposites MMT-PVA shows the displacement of the basal peak 001 compared to Na-MMT. The interlayer space of nanocomposites MMT-PVA obtained at different weight 1, 3, 5, 7, 10 and 15% are 12.54, 13.73, 14.58, 15.78, 16.64 and 17.77 Å respectively. This change in the interlayer space confirms that the clay layers are successfully intercalated by polymer chains.

This change also related to the MMT content, the larger space is obtained by the nanocomposite containing the higher content of MMT (15% wt), we also note that a new peak was observed for this sample (MMT-PVA (15%)) due to the change of crystal structure of the clay particles [34]. all obtained nanocomposites MMT-PVA have different intensities at 2θ=19.54°C which is due to the amorphous nature of the PVA.

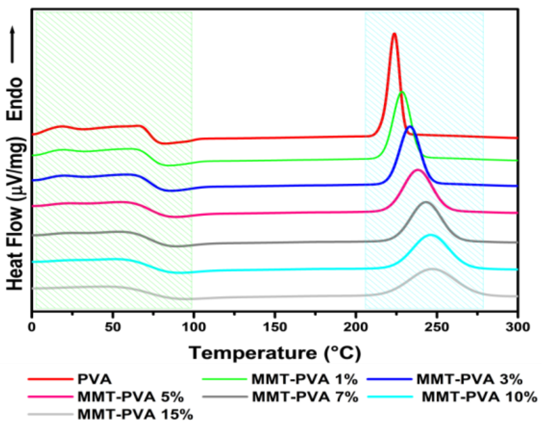

Figure 2: DSC thermogram for nanocomposites MMT-PVA

Figure 2 present the DSC results of nanocomposite MMT-PVA obtained between 0 and 300°C. The glass transition and melting transition of Bulk PVA are respectively at 70 and 225°C. As shown in this figure the Tg and Tm signals of the neatly intercalated nanocomposite weaken gradually and move to the higher value of temperature. Although the physical origins of this behaviour are still under debate [35,36] this change of thermal behaviour is due to the polymers intercalated in clays. This explains the change of the glace temperature and fusion temperature of PVA and nanocomposite MMT-PVA.

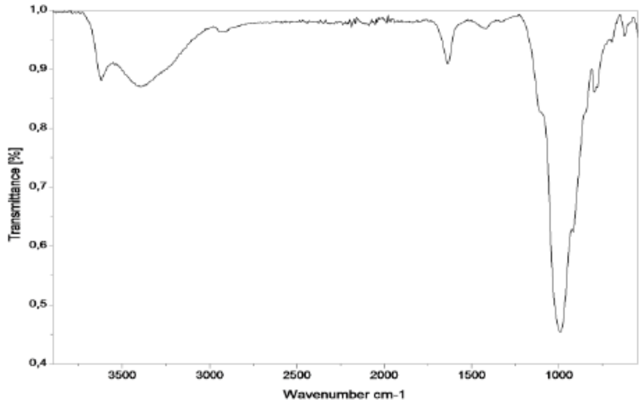

Figure 3: FTIR spectra of nanocomposite MMT-PVA (15%)

Infrared spectroscopy was used for more information on the adsorption bands of the MMT-PVA nanocomposite. Figure 3 shows the FTIR spectra of nanocomposite MMT-PVA (15%), the bands appearing at 1419, 1012 and 787 cm^{-1} are assigned to the modes vibrations of CH_2, C-C and C-O respectively for PVA polymer. A wide band at 3393 cm^{-1} corresponds to the valence vibration of the OH bond. An adsorption band located at 3620 cm^{-1} is attributed to the AlOH which overlaps with the vibrational bands of physisorbed water molecules. A intense band appeared at 1112 cm^{-1} assigned to the out-plane vibration of Si-O bond.

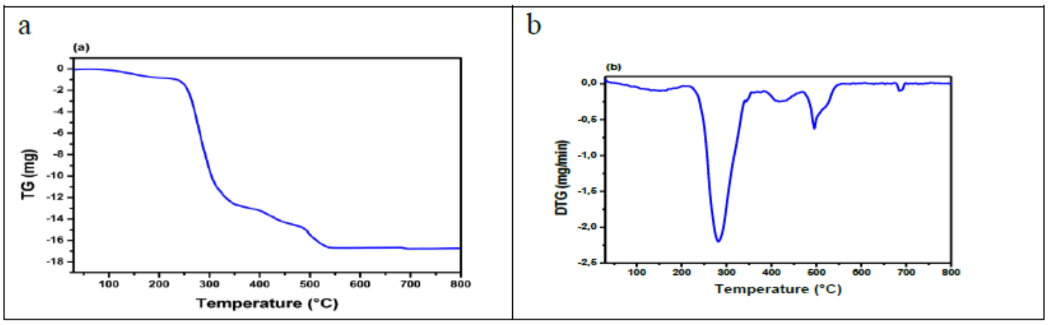

Figure 4: TGA/DTG analysis curves for MMT-PVA

The thermal stability of nanocomposite MMT-PVA (15%) was measured by TGA and was used to indicate its range of thermal stability. As shown in Figure 4 (a and b), The TGA curve of nanocomposite MMT-PVA (15%) is very similar to the literature and exhibits three mass loss stages, The first loss of mass is approximately 30-200°C, which is attributed to the mass loss of water physisorbed, this data is in agreement with the DRX and FTIR analysis, the second and the third mass loss takes place between 220-390°C and 400-531°C respectively due to the degradation of PVA, the same behaviour was observed by Strawhecker and Manias [32].

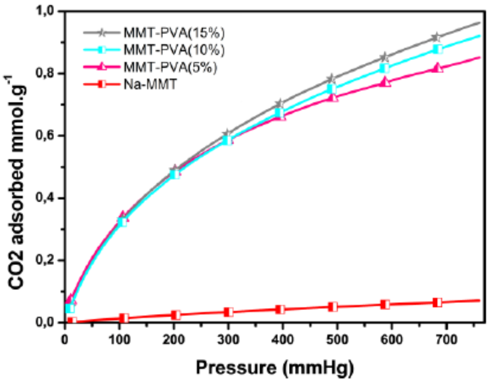

Figure 5: Sorption isotherms of CO_2 on the nanocomposite MMT-PVA at 0°C.

Figure 5 shows the adsorption isotherms of CO_2 by Na-MMT and MMT-PVA (5, 10 and 15%). It is clearly appears that the modified clay by cation exchange (Na^+) has a small amount of CO_2 adsorption estimated about 0.07 mmol·g^{-1}, if we compare these results with layered materials (e.g. Kanemite, Smectite) [11], this material exhibit the same behavior via the adsorption of CO_2, this can be explained by their low surface basicity, the application of nanocomposites (5, 10 and 15%) in the adsorption of CO_2 shows that the adsorption of CO_2 has been enhenced compared to Na-MMT, the adsorption of CO_2 increases in the following order: 0.85, 0.92 and 0.96 mmol.g-^{1} for MMT-PVA (5%), MMT-PVA (10%) and MMT-PVA (15%), this change is strongly related to the structural and chemical nature of the nanocomposite used, the presence of OH group in the structure are considered as active sites for capturing the CO_2 molecules [24-27,37]. The CO_2 molecules can be linked with the OH groups by weak bonds and the presence of the water molecules physisorbed in the nanocomposite structure also can contribute to the adsorption of CO_2. The interlayer distance can also be considered as a key factor for CO_2 adsorption, the material that has a large distance can capture more CO_2 molecules due to easily diffusion in the structure of nanocomposite.

CONCLUSION

Nanocomposites MMT-PVA were synthesized by a solution-intercalation method using exchanged montmorillonite with the Na^+ cations, The XRD analysis clearly shows intercalation of the clay after treatment with solution containing PVA and the interfoliar distance increases significantly with increasing MMT content. Characterization by thermal analysis clearly shows that the nanocomposite MMT-PVA (15%) has a high thermal stability. The application of the obtained materials in the adsorption of CO_2 at 0°C shows that the exchanged clay has a low adsorption capacity, while the nanocomposites MMT-PVA (5, 10 and 15%) showed satisfactory results compared to Na-MMT.

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