SYNTHESIS OF MEMBRANES FROM A MIXTURE OF POLYVINYL ALCOHOL/CHITOSAN CROSSLINKED AND LOADED WITH NANOCLAY FOR CO_2 SEPARATION

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ABSTRACT

In this research, crosslinked polyvinyl Alcohol (PVA)/Chitosan blends loaded with 1, 3, and 5 %w/w of nanoclay were synthesized to investigate its potential as membranes for CO_2 separation. Elaborated membranes were characterized by using FTIR, water uptake, contact angle, porosity, and mechanical measurements. The separation capacity was evaluated through pure gases CO_2 and N_2 permeability tests. The addition of nanoclay caused a higher porosity and water absorption capacity, and better mechanical properties in the membranes. Moreover, the contact angle decreased, which signs the hydrophilic character of this material. The CO_2 permeability increased with nanoclay addition, and the maximum CO_2 permeability was reached for 1 %w/w nanoclay PVA-Chitosan membranes; the selectivity CO_2/N_2 also presented highest value with this nanoclay concentration.

Keywords: CO_2 separation, blend polymer, PVA, Chitosan, nanoclay.

1. INTRODUCTION

The CO_2 is one of the called greenhouses gases accompanied by water vapor, methane, nitrous oxide and chlorofluorocarbons compounds, their presence in the atmosphere is crucial for the greenhouse effect that allows the warming the earth. However, human activities have increased the emissions of these gases to the environmental. Greenhouse gases have a long lifetime, and part of them can remain in the atmosphere for thousands of years. As a result, its concentration in the atmosphere has risen, especially CO_2, enhancing the greenhouse effect and then the warming earth. The carbon capture and storage (CCS) technologies are an option of mitigation actions for the reduction of atmospheric greenhouse gas emissions, which consist of the separation of CO_2 from the gas streams, compression, transportation, and storage in a geological site or to enhance oil recovery [1].

Carbon dioxide separation and capture processes are carried out through different routes. According to the chemical process involved in fossil fuel combustion, there are three mechanisms applied for CO_2 gas separation and capture, such as pre-combustion, post-combustion, and oxy-combustion [2]. The second one, post-combustion, is a suitable option due to it can be implemented with existing systems. Technologies like chemical/physical absorption, biological methods, adsorption, and membrane separation are investigated to separate CO_2 from flue gas and off-gas from industry [3-5]. The absorption technologies based on the interaction of CO_2 with aqueous solutions of alkanolamines is the technology that has been most widely applied [6].

Membrane separation is an emerging technology, and it is considered a competitive alternative for conventional since it is one of the most energy-efficient, and it has a small environmental footprint besides its operational simplicity [2, 7]. Membrane separation is a thin barrier that acts as a filter to separate a gas from a mixture and generate permeate, which passes through the semipermeable membrane and the concentrate that contains the effluent rejected by the layer [8, 9]. For this purpose, the separation membrane performance is evaluated through permeability and selectivity. Those are two critical parameters; the first one is related with the flux of a specific gas through the membrane, and the selectivity is associated with the preference of the layer to allow the pass one particular gas [9].

In this paper, the blend obtained from PVA and biopolymer (chitosan) loaded with nanoclay was evaluated as membranes for CO_2 separation. For this purpose, CO_2 and N_2 permeability and selectivity were studied. Other of the properties assessed were water uptake, porosity percentage, contact angle, and mechanical properties of membranes.

2. MATERIALS AND METHODS

2.1 Materials

Poly (vinyl alcohol) PVA - 99% hydrolyzed powder (Mw 77000-79000) was obtained from J.T Baker. Sigma Aldrich supplied chitosan (75 - 85% deacetylated). Formaldehyde (37 wt% aqueous solution), sulfuric acid 98 %, and Acetic acid were purchased from Panreac.

2.2 Membrane Preparation

Membranes were elaborated by using the casting method. For this purpose, a PVA solution was prepared by dissolving 3.5 g of PVA powder in 50 mL of distilled water under stirring at 80°C for 24 h. 1.5 g of chitosan powder was added to 50 mL of 1 % aqueous acid acetic solution under constant stirring at room temperature overnight. Both solutions were mixed by using magnetic stirring at room temperature for 24 h to remove the bubbles formed during the mixture (blending ratio PVA/chitosan 70:30 v/v %). The homogeneous blend

obtained was crosslinked with 0.3 ml formaldehyde and 0.05 ml of sulfuric acid as a catalyst [10] for 24 h. The PVA/chitosan blend membranes loaded with nanoclay were obtained by adding the required amount of nanoclay to the mixture and stirring for 6 h. The previous solution was poured on glass Petri dishes and heated in a vacuum oven at 45°C.

2.3 Membrane Characterization Methods

The elaborated membranes with different concentrations of nanoclay (1, 3 and 5%) were characterized by using different technique of analysis. FTIR analysis was applied to identify the effect of the crosslinking in the polymer's chemical structure and the existence of nanoclay. FTIR Spectra were recorded from 4000 to 400 cm-1 using an IRAffinity-1S Fourier Transform Infrared Spectrophotometer – Shimadzu - serie: A213749. For determination of porosity percentage was carried out by immersing membranes in distilled water for one hour. After that, superficial water was dried by absorbent paper, and membranes were weight. Membranes dried were placed in an oven at 80°C for 24 h, and its weight was measured again [11]. The equation 1 was used for the porosity calculation.

$$\% P = \left[\frac{Q_0 - Q_1}{Ah}\right] \times 1000 \qquad (1)$$

where P is the prepared membrane porosity, Q_0 and Q_1 are the weight (g) of the wet and dry membrane, respectively, A is the membrane area (cm^2), and h is the membrane thickness (mm).

Water uptake in the membranes was measured by weighing dry and wet samples of membranes before and after subsequent immersion in water at room temperature at 24 and 48 h. The excess of water on membranes was removed before each measurement. The percentage of water uptake was calculated by using the equation 2 [12].

$$Water\ uptake\ \% = \left[\frac{W_w - W_d}{W_d}\right] \times 100 \qquad (2)$$

where W_d and W_w are the weight in grams of membranes before and after immersion, respectively.

The contact angle was determined to establish the hydrophilicity of elaborated membranes, for this porous material was carried out the sessile drop method. A droplet was placed on the membrane surface, its contour was registered by photography, and the profile of the droplet with the horizontal was filled using ImageJ software [13]. The contact angle was measured in three different positions on the membrane surface. Mechanical properties of the elaborated membranes, such as tensile strength and elongation at break, were determined by using an EZ test Text Analyzer.

Membranes were tested by using CO_2, and N_2 pure gases thought a constant pressure method. This technique allows the calculation of permeability (equation 3) and selectivity of the different membranes through the obtained data [14].

$$P = \frac{L}{A(p_2 - p_1)}Q \qquad (3)$$

where P is the permeability, L is the membrane thickness, Q is the volumen of the permeate in cm^3 in a time t in seconds, A is the effective area for the gas transport in cm^2, p_2 is the absolute pressure of food (cmHg), p_1 is absolute pressure of permeate (cmHg). Also, the selectivity of CO_2/N_2 was calculated by the equation 4:

$$S_{CO_2/N_2} = \frac{P_{CO_2}}{P_{N_2}} \qquad (4)$$

3. RESULTS

3.1 FTIR Spectrum Analysis

FTIR spectrum is depicted in Figure-1, in the crosslinking PVA/Chitosan blend spectra is showed an absorption band at 3438 cm^{-1}, which refers to –OH stretch vibration of the PVA and the N-H stretching vibrations of primary amine of chitosan [12, 15]. The band bending type scissoring at 1558 - 1560 cm-1 is related to the –NH. At 1340 cm-1 it is observed a weak band associated with C-H bending out of the plane. The band around 1650 cm-1 is assigned with stretching vibration of –N=C, which corresponds to imine group due to formaldehyde treatment. A peak at 1050 cm-1 in the spectra of membrane with nanocaly is attributed to Si-O-Si vibration [16].
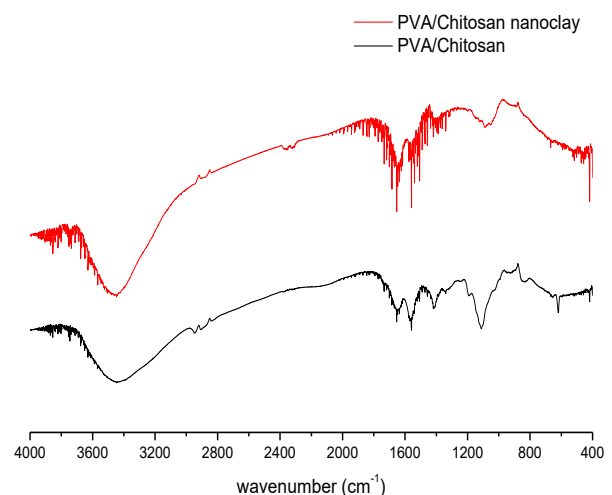

Figure-1. FTIR spectra of PVA/chitosan crosslinked and loaded both with and without nanoclay.

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3.2 Porosity Analysis

Figure-2 shows the porosity of the different elaborated membranes. The porosity of PVA/Chitosan was 184%, which increased after the addition of 1 and 3 wt% of nanoclay. However, the porosity decreased at 5 wt%. The addition of the nanoclay leads to the generation of

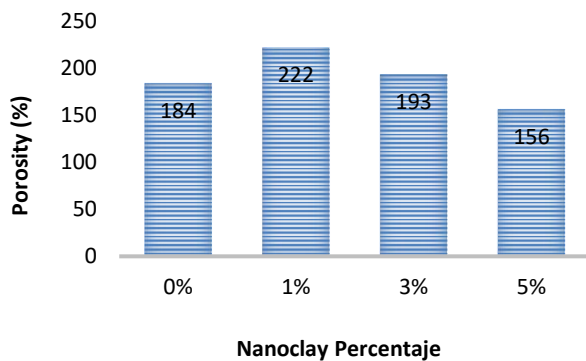defects in the polymeric material, yet its excess could generate agglomerates.

Figure-2. Porosity of PVA/Chitosan membranes, and loaded both with and without nanoclay.

3.3 Water Uptake Analysis

PVA is a synthetic polymer that has a high amount of OH groups, which form hydrogen bonds with water molecules. At the same time, chitosan can form hydrogels that also contain active NH2 and OH groups. For that reason, those polymers can absorb a high amount of water. The mixture of PVA and chitosan tends to increase the water uptake capacity of the blending PVA/chitosan membranes [17]. The treatment with the crosslinking agent in an acid medium leads to a decrease the water uptake; this happens due to the carbonyl group of the primary crosslinking reacts with the amine of the chitosan to form an imine trough covalent bond, which results in the reduction of the percentage of free N atoms. Moreover, the hydroxyl groups of the network configuration of PVA react by the formaldehyde, which is translated in a decrease of free OH groups to react with water [18]; therefore, in the blend membrane are reduced the polar groups to interact to water molecules.
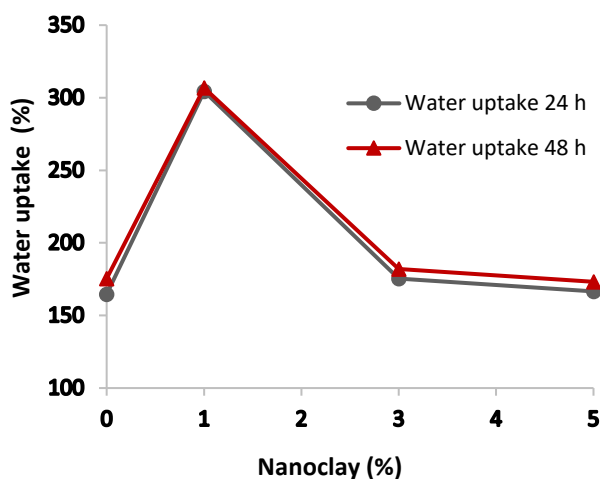

Figure-3. Water uptake of crosslinking PVA/Chitosan membranes, and loaded with different amount of nanoclay.

The effect of the addition of different amounts of nanoclay (Montmorillonite) is showed in Figure-3. PVA/chitosan blend membranes modified with nanoclay have higher water uptake values than unmodified ones; however, as the concentration of the nanoclay into the mixture increased, the blend membranes absorbed less water. Similar behavior was observed for [19]. Montmorillonite nanoclay are phyllosilicates. Its structure is organized in layers, which are conformed of two sheets of tetrahedrally coordinated silicon atoms and an octahedral sheet of aluminum or magnesium dihydroxide [20]. Metallic cations as Na^+ and Ca^+ are present between the adjacent layers, which increases the nanoclay hydrophilic behavior; therefore, the higher values of water retained of nanocomposites membranes could be attributed to the affinity of those cationic elements with the water. According to the graph, the water uptake percentage does not increase significantly at 48 h compared to the 24 h, which means that passed that time, the material has reached the saturation state [21].

3.4 Contact Angle Analysis

The contact angle is related to the wettability grade of a solid surface, and it is dependent on the surface energy. Once a liquid is placed on a solid, it experiences adhesion forces acting in the interface (liquid-solid surface) and cohesion forces acting within the fluid. In contrast, the adhesion forces encourage the drop spreading; the cohesion forces counteract it; the equilibrium between these forces establishes the contact angle [13, 22]. The contact angle of the crosslinked PVA/chitosan and crosslinked PVA/chitosan loaded membranes were measured by using ImageJ software with the plugin developed by Marco Brugnara [23].

Table-1. Contact angle of crosslinking PVA/Chitosan, and loaded both with and without nanoclay.

Membrane	Average Contact Angle (°)
Crosslinking PVA-Chitosan	84.7
Crosslinking PVA-Chitosan 1% nanoclay	73.32
Crosslinking PVA-Chitosan 3% nanoclay	68.72
Crosslinking PVA-Chitosan 5% nanoclay	50

The contact angle for each type of membrane elaborated is summarized in Table-1, according to this, the nanoclay incorporation in the PVA/chitosan membranes leads to the decrease of contact angle values from 84.7° for not loaded samples to 50° for the higher concentration of nanoclay. Contact angle values less than 90° are characteristic of wettability surfaces [13]. These results confirm the hydrophilic character of membranes elaborated. The contact angle decreases with the increase in the hydrophilicity of the material. The presence of nanoclay in the polymeric matrix rose this property; this

effect happens due to the hydrophilic character of the nanoclay employed (montmorillonite) [24].

3.5 Mechanical Properties Analysis

Table-2 shows the testing results of mechanical properties. The tensile strength increased with nanoclay as a filler of the PVA/chitosan blend. However, it is important to remark the high value of tensile strength of membranes without nanoclay too, which could be associated with the crosslinking treatment. The mechanical properties of polymeric nanocomposites present a significant improvement, even at low silicate content, between 3-6% [25].

Table-2. Mechanical properties of crosslinking PVA/Chitosan, and loaded both with and without nanoclay.

Membrane	Tensile strengh (Kpa)	Elongation to rupture (%)
PVA-Chitosan	173,50	49,66
PVA-Chitosan 1% nanoclay	178,79	49,28
PVA-Chitosan 3% nanoclay	180,53	81,32
PVA-Chitosan 5% nanoclay	195,11	53,54

The large surface area of nanoclay is the main responsible for strengthening since it assists interactions between the polymer and the load [26]. Moreover, whereas polymeric matrices are soft materials, nanoclay are rigid fillers, which are inherently resistant to straining, so the polymeric reinforcement with those restrict the movement of the polymeric chains adjacent to the nanoparticles [17, 20, 27]. The addition of montmorillonite nanoclay to the PVA/chitosan matrix corroborated this behavior, which is attributed to interactions between OH and NH_2 groups of chitosan molecule with hydroxyl groups of nanoclay and PVA. Besides, the elongation percentage increased with the addition of the nanomaterial, except at 1% nanoclay in the PVA/chitosan membrane, it is related to the nanoclay effect. However, there is no tendency in the behavior associated with the concentration of the load.

3.6 Permeability - Selectivity Analysis

Figure-4 shows the CO_2 permeability, through PVA/Chitosan membranes and PVA/Chitosan membranes loaded with nanoclay. The CO_2 permeability increased with the nanoclay addition. The maximum permeability value was reached at 1% nanoclay PVA/Chitosan sample, with 3 and 5 % this value decreased as the nanoclay content increased. The CO2 gas transport through membranes is due to the solution-diffusion mechanism. The increase of defects in the interface leads to lower resistance to gas permeance [28]. However, the dispersion of nanoclay in the polymeric membrane network at superior values of 1%w could form agglomerates, which generate a tortuous path and act as barriers for gas diffusion [29], for that reason higher nanoclay content decreased the CO_2 permeability.
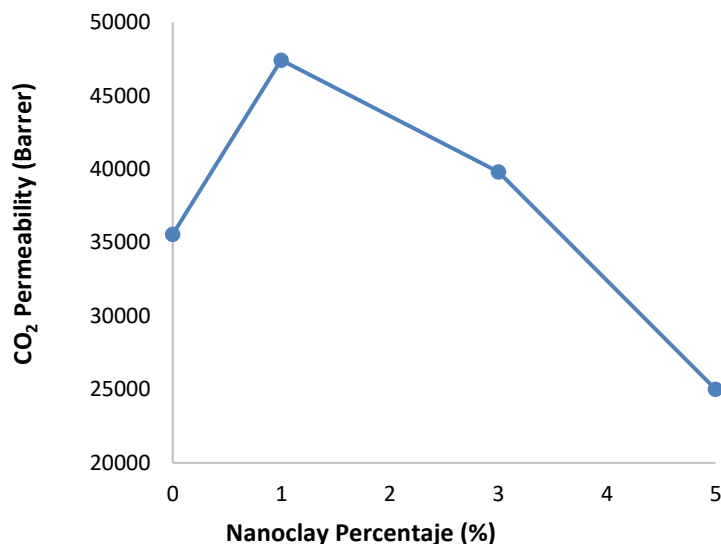

Figure-4. CO_2 Permeability of elaborated membranes.

These results are associated with the results obtained for porosity and water uptake; the higher porosity was reached for 1% nanoclay PVA/Chitosan membranes. Also, the higher water absorption capacity improves the CO_2 uptake due to the affinity of this gas with water [30]. Nitrogen permeability is showed in Figure 5; the presence of nanoclay led to a decrease in N_2 permeability, which is due to the restriction of diffusion of gas molecules through the tortuous path.
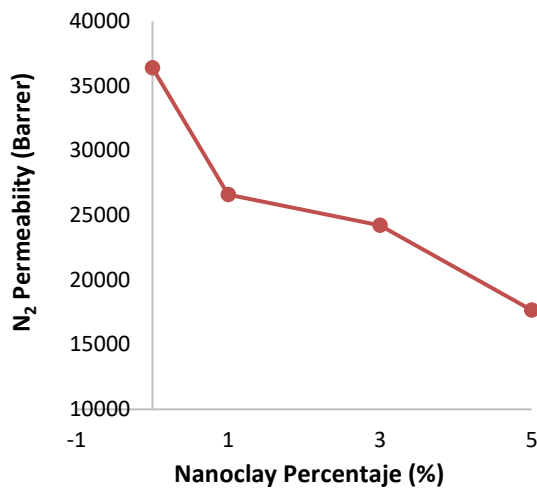
Figure-5. N_2 Permeability of elaborated membranes.

Figure-6 shows that the membranes without nanoclay have a very low selectivity, which means that it allows the pass of both gases. The highest selectivity value was obtained for membranes with 1wt% nanoclay.
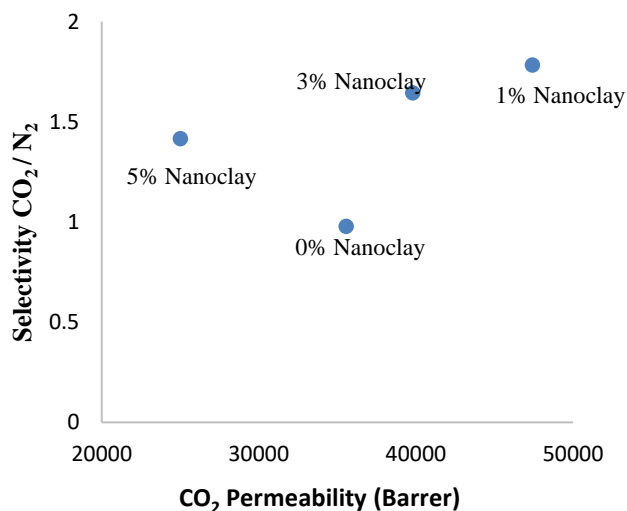

Figure-6. Selectivity CO_2/N_2 of elaborated membranes.

CONCLUSIONS

In this work, crosslinked membranes based on PVA/Chitosan and PVA/Chitosan loaded with nanoclay were obtained. The mechanical measurements revealed that the blended PVA-Chitosan membranes have good tensile strength, and the addition of nanoclay reinforced these polymeric membranes. Porosity, water uptake, and contact angle were also affected by nanoclays. CO_2 permeability was dependent on nanoclay content, it increased with 1wt% and decreased for higher concentrations, this behavior is attributed to dispersion of the nanomaterial in the polymeric network, in the same way, the selectivity determination demonstrated that the best response is obtained for 1wt% nanoclay PVA/Chitosan sample.

REFERENCES

[1] Pachauri R. K., Meyer L. A. 2014. IPCC: Climate Change 2014: Synthesis Report. Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. IPCC, Geneva, Switzerland, 151 pp.

[2] Labreche Y. 2016. Functionalized polymeric membranes for CO2 capture. Journal of Membrane Science and Research. 2: 59-65.

[3] Makertihartha I., Dharmawijaya P. T., Zunita M., Wenten I. G. 2016. Post combustion CO2 capture using zeolite membrane. Engineering International Conference. Published by AIP Publishing.

[4] Yang H., Xu Z., Fan M., Gupta R., Slimane R. B., Bland A., Wright I. 2008. Progress in carbon dioxide separation and capture: A Review. Journal of Environmental Sciences. 20: 14-27.

[5] 2009. IEA Greenhouse Gas R&D Programme (IEA GHG). Evaluation of post-combustion CO2 capture solvent concepts, 2009/14, November 2009.

[6] Ivanov Y., Pyatnichko O., Zhuk H., Onopa L., Soltanibereshne M. 2017. Extraction of carbon dioxide from gas mixtures with amines absorbing process. Energy Procedia. 128: 240-247.

[7] Selyanchyn R., Fujikawa S. 2017. Membrane thinning for efficient CO2 capture. Science and Technology of Advanced Materials. 18(1): 816-827.

[8] Tong Z., Winston W. S. 2017. Facilitated transport membranes for CO2 separation and capture. Separation Science and Technology. 52(2): 156-167.

[9] Scholes C., Kentish S., Stevens G. 2008. Carbon Dioxide Separation through Polymeric Membrane Systems for Flue Gas Applications. Recent Patents on Chemical Engineering. 1: 52-66.

[10] Rao K., Subha M., Sairam M., Mallikarjuna N., Aminabhavi T. 2007. Blend Membranes of Chitosan and Poly (vinyl alcohol) in Pervaporation Dehydration of Isopropanol and Tetrahydrofuran. Journal of Applied Polymer Science. 103; 1918-1926.

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[11] Saedi S., Madaeni S., Hassanzadeh K., Shamsabadi AA. Laki S. 2013. The effect of polyurethane on the structure and performance of PES membrane for separation of carbon dioxide from methane. Journal of Industrial and Engineering Chemistry.

[12] Acevedo M., Tapia A., Realpe A. 2017. Synthesis and Physical-Chemical Characterization of DEA-Crosslinked Poly (Vinyl Alcohol) Membranes. International Journal of ChemTech Research. 10(3): 118-127.

[13] Lamour G., Hamraoui A., Buvailo A., Xing Y., Keuleyan S., Prakash V., Eftekhari-Bafrooei A., Borguet E. 2010. Contact Angle Measurements Using a Simplified Experimental Setup. Journal of Chemical Education. 87: 1403-1407.

[14] Saedi S., Madaeni S., Seidi F., Shamsabadi A., Laki S. 2013. Synthesis and application of a novel Amino-Starch derivative as a new polymeric additive for fixed facilitated transport of carbon dioxide through an asymmetric polyethersulfone (PES) membrane. International Journal of Greenhouse Gas Control. 19: 126-137.

[15] Ma B., Li X., Qin A., He C. 2013. A comparative study on the chitosan membranes prepared from glycine hydrochloride and acetic acid. Carbohydrate Polymers. 91: 477-482.

[16] Părpăriţă E., Cheaburu C., Patachia S., Vasile C. 2014. Polyvinyl alcohol/chitosan/montmorillonite nanocomposites preparation by freeze/thaw cycles and characterization. ACTA CHEMICAL IASI. 22(2): 75-96.

[17] Mahdavi H., Mirzadeh H., Zohuriaan-Merh M., Talebnezhad F. 2013. Poly (vinyl alcohol)/chitosan/clay nano-composite films. Journal of American Science. 9(8): 203- 214.

[18] Yang J., Su W., Leu T., Yang M. 2004. Evaluation of chitosan/PVA blended hydrogel membranes. Journal of Membrane Science. 236: 39-51.

[19] Sainul K., Kannan R., Bahavan P., Rajashabala S. 2017. Role of structural modifications of montmorillonite, electrical properties effect, physical behavior of nanocomposite proton conducting membranes for direct methanol fuel cell applications. Materials Science. 35(4): 707-716.

[20] Nazir M., Mohamad M., Mohapatra L., Gilani M., Raza M., Majeed K. 2016. Characteristic Properties of Nanoclays and Characterization of Nanoparticulates and Nanocomposites. Nanoclay Reinforced Polymer Composites, Engineering Materials. 35-55.

[21] Unnikrishnan L., Mohanty S., Nayak S., Singh N. 2012. Synthesis and Characterization of Polysulfone/Clay Nanocomposite Membranes for Fuel Cell Application. Journal of Applies Polymer Science. 124: 309-318.

[22] Ahmad N, Loo C., Ahmad A., Ramli W. 2015. Membranes with Great Hydrophobicity: A Review on Preparation and Characterization. Separation and Purification Reviews. 44: 109-134.

[23] Williams D., Kuhn A., Amann M., Hausinger M., Konarik M., Nesselrode E. 2010. Computerized Measurement of Contact Angles. Galvanotechnik. 10.

[24] Hwang H., Kim D., Hong Y., Nam S. 2011. Effect of nanoclay on properties of porous PVdF membranes. Trans. Nonferrous Met. Soc. China. 21: 141-147.

[25] Patel H., Somani R., Bajaj H., Jasra R. 2006. Nanoclays for polymer nanocomposites, paints, inks, greases and cosmetics formulations, drug delivery vehicle and waste water treatment. Bull. Mater. Sci. 29(2): 133-145.

[26] Arora A., Padua G. 2010. Review: Nanocomposites in Food Packaging. Journal of Food Science. 75(1): 43-49.

[27] Pavlidou S., Papaspyrides C. 2008. A review on polymer-layered silicate nanocomposites. Progress in Polymer Science. 33: 1119-1198.

[28] Carrera M., Erdmann E., Destéfanis H. 2013. Barrier Properties and Structural Study of Nanocomposite of HDPE/Montmorillonite Modified with Polyvinylalcohol. Journal of Chemistry.

[29] Pei Ching O., Back Lung M. 2014. Effects of Montmorillonite (MMT) Inorganic Fillers on Polyvinylidene (PVDF) Mixed Matrix Membrane. Applied Mechanics and Materials. 625: 696-700.

[30] Zou J., Winston W. 2006. CO2-selective polymeric membranes containing amines in crosslinked poly (vinyl alcohol). Journal of Membrane Science. 310-321.