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Evaluation of cellulose and carboxymethyl cellulose/poly(vinyl alcohol) membranes

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ABSTRACT

Cellulose was isolated from rice straw and converted to carboxymethyl cellulose (CMC). Both polymers were crosslinked with poly(vinyl alcholo) (PVA). The physical properties of the resulting membranes were characterized by FT-IR, TGA, DSC and SEM. The cellulose and CMC were first prepared from bleached rice straw pulp. The infrared spectroscopy of the resulting polymer membranes indicated a decrease in the absorbance of the OH group at 3300–3400 cm^{-1}, which is due to bond formation with either the cellulose or CMC with the PVA. The thermal stability of PVA/cellulose and PVA/CMC membranes was lower than PVA membrane. The surface of the resulting polymer membranes showed smooth surface in case of the PVA/CMC membrane and rough surface in case of the PVA/cellulose membrane. Desalination test, using 0.2% NaCl, showed that pure PVA membranes had no effect while membranes containing either cellulose or CMC as filler were able to decrease the content of the NaCl from the solution by 25% and 15%, respectively. Transport properties, including water and chloroform vapor were studied. The moisture transport was reduced by the presence of both cellulose and CMC. Moreover, the membranes containing cellulose and CMC showed significantly reduced flux compared to the pure PVA. The water sorption, solubility and soaking period at different pH solutions were also studied and showed that the presence of both cellulose and CMC influences the properties.

1. Introduction

Numerous new functional materials from cellulose are being developed for a broad range of applications, because of the increasing demand for environmentally friendly and biocompatible products (Eichhorn, Young, & Davies, 2005; Klemm, Heublein, Fink, & Bohn, 2005; Schurz, 1999). Wood species have provided 95% of all raw materials for making cellulose pulp since more than a century (Avçar & Demirer, 2008; González-García, Hospido, Moreira, Romero, & Feijoo, 2009). However, the production of cellulose pulp from non-wood fiber had risen in recent years, where non-wood raw materials are the sole effective source of cellulose fiber in some world regions. This has boosted research into the pulp making potential of non-wood raw materials such as wheat straw, paulownia, tagasaste, bagasse or abaca, among others (Harris, Riddlestone, Bell, & Hartwell, 2008; Huang, Jeffrey, & Langrish, 2008; López et al., 2004; Navaee-Ardeh, Mohammadi-Rovshandeh, & Pourjoozi, 2004; Peralta, 1996; Ren, 1998; Roliadi, Siagian, Mas'Ud, & Gintings, 2003).

Rice straw is an abundant non-wood raw material, where it is produced throughout the world as a byproduct of rice cultivation. It is a lignocellulose-containing natural composite that is a promising cellulose source. (Kim, Yang, Kim, & Park, 2004; Park et al., 2003; Sun & Gong, 2001). Different from other lignocellulosic materials, the composition of rice straw is more complex. In addition to the main constituents, including cellulose, hemicellulose and lignin, rice straw also contains a significant content of an inorganic component, i.e. silica (Rozman, Musa, & Abubakar, 2005).

One of the current applications of cellulose derived from agricultural biomass is its incorporation into polymer matrices for membranes of cellulose filled nanocomposites (Gacitua, Ballerini, & Zhang, 2005; Ibrahim, El-Zawawy, & Nassar, 2010). The addition of cellulose to composites can promote the biodegradation process of polymer matrices, and make the final materials to be economically more competitive.

Cellulose having abundant hydroxyl groups can be used to prepare membranes and hydrogels easily with fascinating structures and properties. Cellulose membranes and hydrogels can be prepared from a cellulose solution through physical crosslinking and this is because cellulose has many hydroxyl groups which can

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easily form networks via hydrogen bonds. Cellulose derivatives, including methyl cellulose (MC), hydroxypropyl cellulose (HPC), hydroxypropylmethyl cellulose (HPMC), and carboxymethyl cellulose (CMC) have been used to fabricate cellulose-based hydrogels through physical cross-linking and chemical cross-linking (Deng, He, Wu, & Yang, 2008; Guo & Chu, 2005; Weng, Zhang, Ruan, Shi, & Xu, 2004).

Blending of different polymers is an extremely attractive inexpensive and advantageous method to obtain new structural materials (Bajpai, Shukla, Bhanu, & Kankane, 2008). Poly(vinyl alcohol) (PVA) is a good candidate for the preparation of hydrogels, which can be cross-linked by using several methods, including chemical agents, freeze-thaw cycles as well as electron beam- and γ-irradiation. PVA has been extensively studied by Lange and Wyser (2003), Bourke et al. (2003), Finch (1992), Schmedlen, Masters, and West (2002), Wan, Campbell, Zhang, Hui, and Boughner (2002) and Paralikar, Simonsen, and Lombardi (2008) as hydrogel for controlled drug release, as membrane material for chemical separations, barrier membrane for different applications and as a biomaterial.

In the present study, cellulose was isolated by alkaline pulping of rice straw. Carboxymethyl cellulose (CMC) was prepared from the resulting cellulose. Membranes from PVA/cellulose and PVA/CMC were prepared via copolymerization reaction and water sorption at different pHs solutions, desalination, water vapor transmission rate and chemical vapor transmission rate were investigated. In addition, the membranes were studied by means of FT-IR spectroscopy, thermogravimetry, differential scanning calorimetry and scanning electron microscopy.

2. Materials and methods

2.1. Materials

Poly(vinyl alcohol) (PVA), degree of polymerization (DP) of 1700–1800 was provided from Qualikems and BDH, England, Ceric ammonium sulfate (CAS) (WakoPure Chemical Co. Ltd.), as an initiator, was used as received. Monochloroacetic acid and *N*,*N*-dimethyl acetamide (DMAc) were obtained from Aldrich Chemical Company Inc. (Milwaukee WI, USA).

2.2. Preparation of cellulose

Unbleached cellulose, approximately 45 g (consists of: holocellulose, 84.4%; determined by the chlorite method (Wise & Karl, 1962) and lignin, 7.56%; estimated according to TAPPI T222 om-98) was isolated from 100 g of rice straw by an alkaline pulping process, in which the rice straw was cut into small pieces and 10 times its weight of 1.0% (w/w) sodium hydroxide solution was added. Pulping was allowed for 2 h at 160 °C in a rotary autoclave, after which the pulp was thoroughly washed with water till neutrality. Bleached rice straw pulp (α-cellulose, 62.42% and lignin, 4.32%; estimated according to TAPPI T203 om-71 and TAPPI T222 om-98, respectively) was obtained from rice straw pulp by extracting the lignin and most of the hemicelluloses using a two stage bleaching method applying sodium hypochlorite. Briefly, the unbleached cellulose fibers were treated in two stages with sodium hypochlorite solution equivalent to 60% of the chlorine requirement, calculated from the permanganate number, for 2 h at 40 °C. The liquor to fiber ratio was 10:1 and the pH was maintained at 9 during the hypochlorite process. At the end, the bleached cellulosic fibers were washed till neutrality, and left to dry in air.

2.3. Preparation of carboxymethyl cellulose (CMC)

CMC of DS 0.76 was prepared from the resulting cellulose, where the dried cellulose resulting from rice straw was sieved first with a 0.32 mm screen, and the fine cellulose powder was weighed and dipped in a 2000 mL beaker with 20% sodium hydroxide solution. The aqueous suspension was heated and stirred at 80 °C for 4.5 h, and then the aqueous suspension filtered and washed with 95% ethanol solution. The filter residue was transferred into a beaker with 15% sodium hydroxide solution in water bath, and then interfused by monochloroacetic acid, and being stirred and heated at 70 °C for 1 h. After that, the polymer was filtered off, washed with 75% aqueous ethanol solution, and dried.

2.4. Preparation of PVA/cellulose and PVA/CMC membranes

PVA/cellulose and PVA/CMC membranes were prepared by the following procedure:

Cellulose was first dissolved in DMAc/LiCl, in which for a typical preparation, 0.5 g of dried cellulose and 20 mL DMAc were kept at 130 °C for 2 h under stirring. After the slurry had been allowed to cool to 100 °C, 1.5 g of anhydrous LiCl were added. The cellulose was completely dissolved by cooling down to room temperature under stirring. To this solution, 3.0 mL of 0.08% CAS, as initiator, was added and the mixture was immediately stirred at 60 °C for ½ h under nitrogen.

At the same time, 4 g of poly(vinyl alcohol) was dissolved in 30 mL of distilled water at 60 °C with a constant stirring. After cooling, the dissolved cellulose was mixed with the PVA solution by stirring and the reaction maintained for 3 h at 85 °C under N_2. The copolymerization reaction was continued up to 24 h with stirring at 25 °C. The formed gel was then poured into a Petri-dish for film casting.

For the CMC, an appropriate amount, 0.5 g of CMC, was suspended in 30 mL aqueous solution in a 100 mL three-neck flask, equipped with a mechanical stirrer, a reflux condenser and a nitrogen line. After being purged with nitrogen for 30 min to remove the oxygen dissolved from the system, certain amount of CAS was introduced in the mixture to initiate CMC to generate radicals and the reaction was maintained for 30 min. A solution of 4.0 g PVA was then added and the water bath was kept at 85 °C for 2 h to complete polymerization. The resulting product was poured into a Petri-dish, washed with water several times till neutrality and the membranes were formed by air drying for 48 h. The obtained membranes were then heat treated in an oven at 40 °C for 8 h.

2.5. Water sorption, solubility and desalination

The membranes were weighed (W_1) and immersed in distilled water at room temperature. The membranes were periodically removed, wiped with a tissue to remove any surface water and weighed (W_2). The experiment was repeated twice and the average weight was determined. Next, the membranes were dried in a vacuum oven at 40 °C until a constant weight was obtained (W_3). For each soaking cycle, the % water sorption and % solubility were calculated as follows (Paralikar et al., 2008; Sivakumar et al., 2000):

$$\%\,\text{water sorption} = \frac{W_2 - W_3}{W_3} \times 100 \quad (1)$$

$$\%\,\text{solubility} = \frac{W_1 - W_3}{W_1} \times 100 \quad (2)$$

The % water sorption and % solubility were also calculated at different pH solutions, namely 3.5, 5.5, 10, and 12.5, as well as in saline solution of 0.2% NaCl solution. The chlorine content was determined by titration with $AgNO_3$ according to Mohr's method (Kraemer &

Stamm, 1942; Sheen & Kahler, 1938; Skoog, West, & Holler, 1996). Desalinaty was then calculated according to the following equation:

$$\%\,\text{Desalinaty of water} = \left(\frac{C_2}{C_1}\right) \times 100 \quad (3)$$

where C_2 is the concentration of the saline solution after using the polymer membranes and C_1 is the original concentration of the saline solution.

2.6. Water vapor transmission rate (WVTR)

The WVTR were determined in a method described by Paralikar et al. (2008), where the prepared membranes were glued onto glass jars half filled with water. The initial weights of the assemblies were noted. Three replicates of each sample were placed in a controlled environmental chamber at 30 °C. The weight change was noted as a function of time until a constant flux was obtained for three consecutive days. The water vapor transmission rate was calculated from the steady state weight loss as:

$$J = \frac{M}{At} \quad (4)$$

where, J is the mass flux (g/m^2 h), M is the cumulative weight loss of water (g), A is the area of the membrane available for mass transfer (m^2) and t is the time (h).

2.7. Chemical vapor transmission rate (CVTR)

The CVTR was conducted according to ASTM standard F 1407-99a (1999). Chloroform was used as the permeant in this experiment. In this method, a weight membrane was clamped over the permeation cup, inverted and placed in a chemical fume hood. Time and weight of the assembly were noted at regular time intervals. At the end of the experiment, a graph of cumulative solute transferred through the membrane, Q, was plotted against time, where a linear correlation was observed representing constant flux. This linear portion was modeled using a least squares regression. The regression line was extended to the x-axis intercept to obtain the time lag. The slope of regression line gave the value of flux (g/m^2 h) through the membrane (Paralikar et al., 2008).

2.8. Fourier transforms infrared spectroscopy (FT-IR spectroscopy)

FT-IR spectra were recorded in reflection mode by means of JASCO FT/IR 6100 Instrument in the range of 4000–500 cm^{-1}.

2.9. Thermal analysis

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the membranes were carried out on SDT Q600 with samples from 15 to 20 mg in the temperature range from 30 °C to 700 °C at a heating rate of 10 °C/min in nitrogen atmosphere. For DSC, the membranes were analyzed with a heating rate of 1 °C/min under nitrogen.

2.10. Scanning electron microscopy

Scanning electron microscopy (SEM) of the PVA/cellulose and PVA/CMC membranes was performed using a JEOL JXA-840A electron microprobe analyzer (JOEL USA Inc., Peabody, MA) at 30 kV. The sample was frozen under liquid nitrogen and the fracture was coated with gold before being measured.

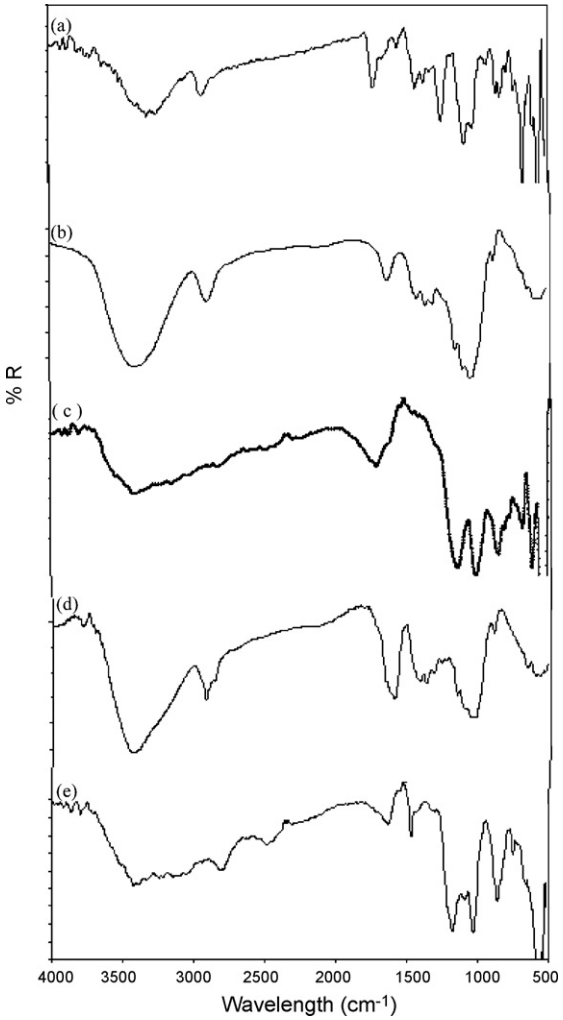

Fig. 1. FT-IR spectra of (a) PVA, (b) cellulose, (c) PVA/cellulose, (d) CMC and (e) PVA/CMC membranes.

3. Results and discussion

3.1. FT-IR and SEM

The FT-IR spectra of CMC with degree of substitution (DS) 0.76, cellulose obtained from rice straw, PVA, PVA/cellulose and PVA/CMC are illustrated in Fig. 1. The peak in the area of 3460 cm^{-1} is due to hydrogen-bonded O—H stretching vibration of CMC. The peak at 2929 cm^{-1} is due to the C—H stretching vibration in cellulose and hemicellulose, while the bands in the 1615 cm^{-1} region for cellulose may be attributed to C=O stretching vibration (Kolboe & Ellefsen, 1962). The bands from 1446 to 1346 cm^{-1} are associated with CH in the plane deformation of CH groups. The band in the region 1054 cm^{-1} involve the C=O stretching vibrations of aliphatic primary and secondary alcohols in cellulose, hemicellulose, lignin, and extractives (Khan, Idriss Ali, & Basu, 1993; Kolboe & Ellefsen, 1962; Sahoo, Swain, & Debsarkar, 2002). The peak at 902 cm^{-1} is due to β-glucosidic linkage (Ray & Sarkar, 2001; Samal, Acharya, Mohanty, & Ray, 2001), while peaks at 677 and 618 cm^{-1} are due to out-of-plane bending vibration of intermolecular H-bonded O—H group and out-of-plane O—H bending (Rana, Basak, Mitra, Lawther, & Banerjee, 1997; Ray & Sarkar, 2001; Samal et al., 2001). For PVA/CMC, Fig. 1 showed absorption bands at 3450, 2515, 1656, and 1045 cm^{-1}, characteristic of CMC, and additional bands at 3004, 1193–870 cm^{-1} (C—H stretch and out-of-plane), and

Table 1
Total % water sorption, desalinaty and solubility for PVA and blended PVA membranes.

Membrane sample	Water sorption (%)	Desalinaty (%)	Solubility (%)				
			Water	pH 3.8	pH 5.6	pH 10	pH 12.5
PVA	97.0	0	68.0	94.0	90.0	89.0	88.0
PVA/cellulose	82.8	25.0	23.6	40.0	50.0	30.7	31.0
PVA/CMC	61.6	15.0	7.0	13.0	41.0	11.0	33.0

1490–1340 cm^{-1} (CH stretch) that belong to the spectrum of PVA. The presence of these bands is attributed to the dispersion of the CMC fiber in the polymer matrix.

The same observation was noticed for PVA/cellulose (Fig. 1), where a broad band around 3420 cm^{-1} in both the cases is attributed to the O—H stretching vibration of hydroxyl group of PVA. A sharp band at 1178 cm^{-1} corresponds to an acetyl C=O group present on the PVA backbone. The presence of these bands is attributed to the dispersion of the dissolved cellulose fiber in the polymer matrix.

Moreover, the intensity of the absorption band assigned to the OH group (3300–3400 cm^{-1}) is decreased in the spectra of PVA/CMC or PVA/cellulose membranes (Fig. 1).

The SEM micrographs of the PVA/cellulose and PVA/CMC fractures are shown in Fig. 2. A homogenous structure with smooth surface can be observed in case of the PVA/CMC membrane while a rough surface was found in case of the PVA/cellulose. The SEM indicated that the structure of the resulting membrane depends on the type of the filler used either cellulose or CMC.

3.2. Solubility and sorption

Table 1 showed that the addition of both 12.5% of cellulose and CMC reduces the amount of soluble parts of the membranes suggesting a decrease in the unreacted PVA molecules, which would otherwise leach out in the water. The amount of the soluble parts of the membranes containing cellulose and CMC were just 23.6% and 7.0%, respectively, which was presumably due to the highly crosslinked matrix.

Moreover, the ability of water sorption decreased in the presence of both cellulose and CMC compared to the pure PVA (Table 1). It is suggested that the chain mobility was restricted and the number of hydroxyl groups was reduced, which led to reducing water sorption.

On the other hand, for many applications, it is more important to know the behavior of the absorbent in a physiological solution, usually simulated by aqueous sodium chloride (NaCl). Table 1 shows the effect of both PVA/CMC and PVA/cellulose membranes on absorbing NaCl. In both cases, an increase in the percent of desalination, i.e. decrease of NaCl concentration in the solution, by 15% in case of CMC and by 25% in case of the cellulose compared to pure PVA. The results mean that PVA cannot absorb NaCl from the solution while the presence of CMC and cellulose leads to an absorption of NaCl. According to Liu and Rempel (1997) a possible explanation for this behavior could be associated with the formation of anions in the polymer networks, a fact which leads to the development of strong electrostatic forces contributing to the network expansion.

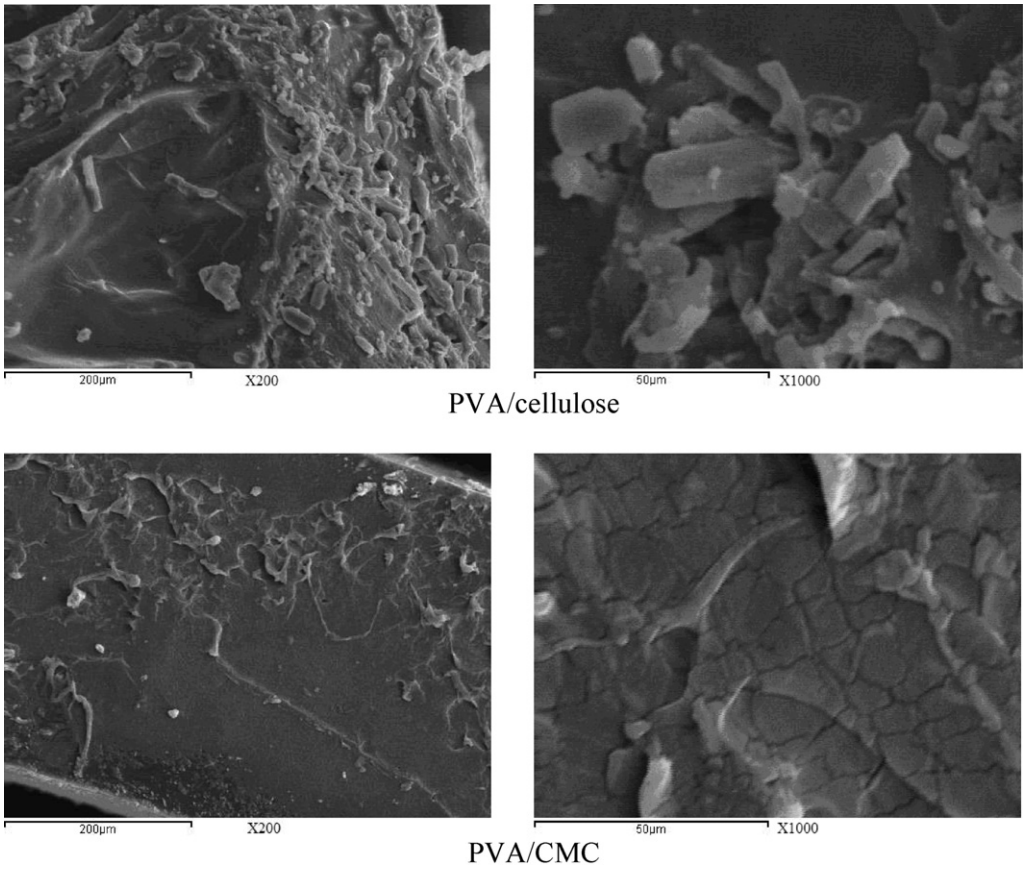

Fig. 2. SEM for PVA/cellulose and PVA/CMC membranes at 200× and 1000×.

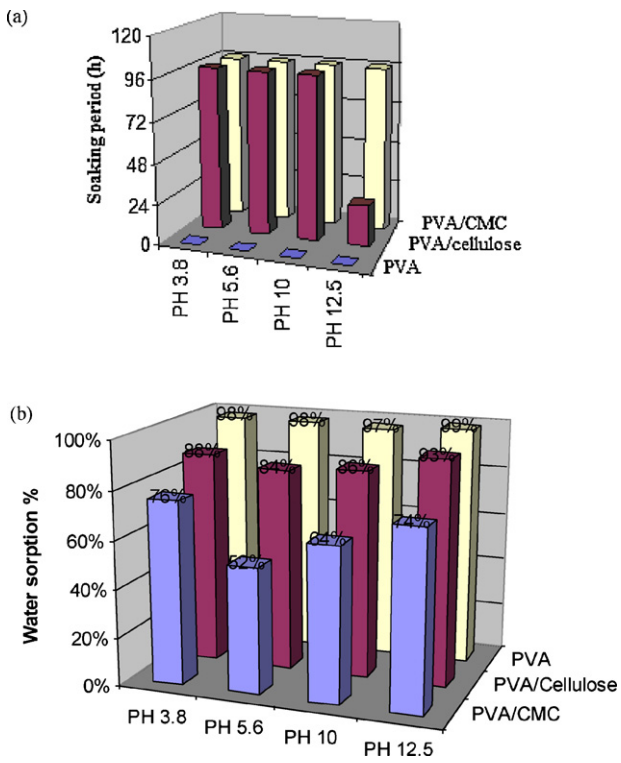

Fig. 3. Soaking period (a) and % water sorption (b) of the membranes at different pH values.

Furthermore, the membranes were studied regarding their swelling behavior in solutions of different pH values. This study is important in order to know in which pH range the membranes can be used. Solutions with different pH values, namely 3.5, 5.5, 10, and 12.5 were used for studying the swelling ratio of the prepared membranes. It was noticed that the PVA is soluble at different pH values and when grafted with the cellulose and carboxymethyl cellulose the solubility of the membrane decreased (Table 1). Also, it can be noticed that the less solubility was observed at pH 5.6 in cases of PVA/CMC membrane. Moreover, the maximum solubility was reached within 2 h soaking in case of PVA membrane and between 96 h soaking period in case of PVA/cellulose and PVA/CMC membranes as can be seen from Fig. 3a, where this probably can be due to the bond formation between both the cellulose and CMC matrix with the PVA. Furthermore, during that soaking period, the PVA showed to have higher water sorption percent in all pHs compared to the blended membranes (Fig. 3b). For the blended membranes, i.e. PVA/CMC and PVA/cellulose, the higher water sorption percent was reached for pH 3.8 during the specific soaking period and it was higher in case of PVA/cellulose membrane, 98% (Fig. 3b), while it was 93% for pH 12.5 (Fig. 3b).

3.3. Transport properties: water vapor transmission rate (WVTR) and chemical vapor transmission rate (CVTR)

Transport properties including water vapor and chloroform were studied. Water vapor transmission indicated that all the membranes allowed moisture to pass. However, moisture transport was reduced by the presence of both cellulose and CMC.

Fig. 4 showed that the incorporation of either cellulose or CMC into the membranes reduced the WVTR. This is expected as bond formation would reduce the number of hydroxyl groups in the composite and thus the hydrophilicity. It was noticed that, the addition of cellulose reduced the WVTR more than the addition of CMC, lowering the WVTR to <50% that of 100% PVA. The membranes

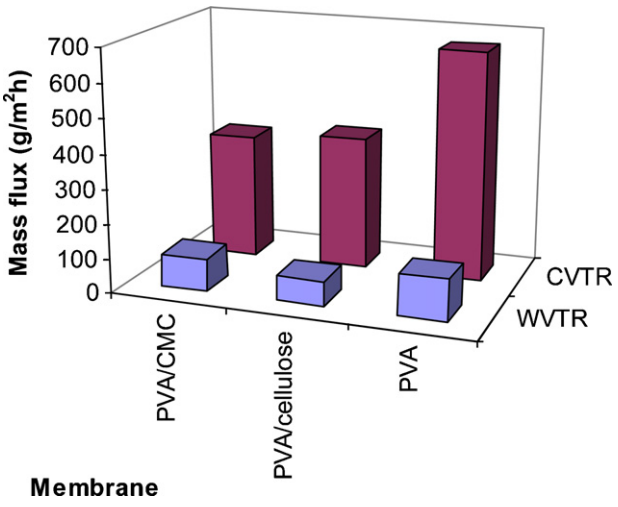

Fig. 4. The water vapor transmission rate (WVTR) and chemical vapor transmission rate (CVTR) for the different membranes.

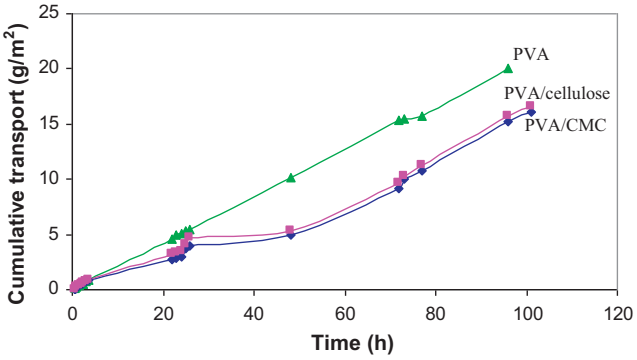

Fig. 5. Cumulative vapor transport through selected membranes as a function of time.

with cellulose showed a lower WVTR than those with CMC. We may conclude that the presence of CMC may allow for more rapid permeation.

On the other hand, the CVTR was evaluated for the membranes using chloroform as the permeant in an evaporative flow device, where liquid $CHCl_3$ was contacted to the feed side of the membrane. It was noticed that the incorporation of both CMC and cellulose results in a decrease in the CVTR, i.e. reduces the permeation of $CHCl_3$ (Fig. 4). In addition, the cumulative vapor transport properties of PVA membranes were changed by the addition of both cellulose and CMC to promote bonding (Fig. 5).

The long-term steady state flux was calculated and extrapolated to the time axis to obtain the time lag. A long lead time before a steady state was observed, which suggests that the permeant is dissolved in or being absorbed by the membrane and this retards the time required for a steady state to be achieved. The times lag, i.e. the time axis intercept, and the steady state flux, i.e. the slope of the linear regression at long times, show that the addition of CMC and cellulose increases the time lag (Fig. 6). One can mentioned that the presence of either cellulose or CMC, as filler, plays in the overall role for the membrane properties.

3.4. Thermal analysis: thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC)

Fig. 7a shows the TGA curves for PVA, PVA/cellulose and PVA/CMC membranes. It is noticed that the onset of weight loss (T_s) for the membranes of PVA, PVA/cellulose and PVA/CMC are

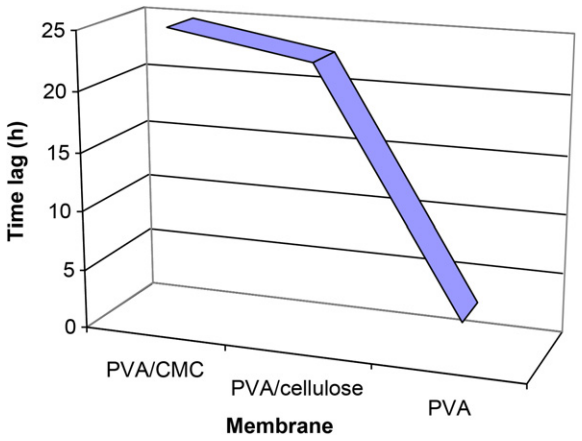

Fig. 6. The time lag of the different membranes.

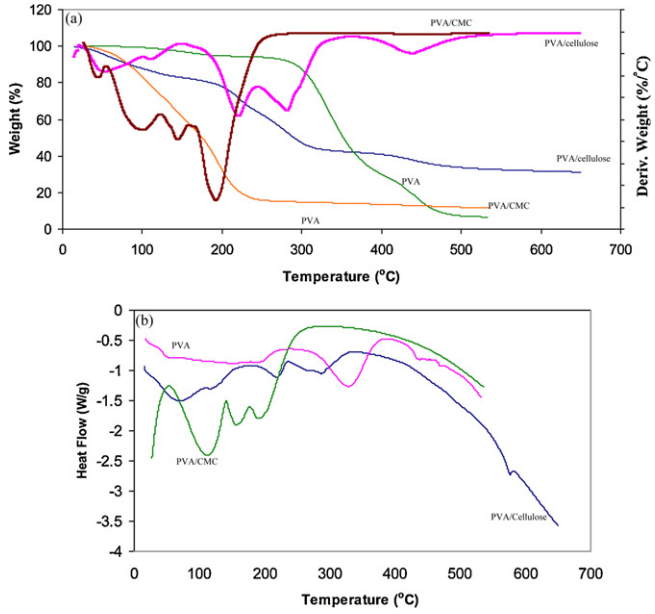

Fig. 7. TGA (a) and DSC (b) curves of the PVA, PVA/cellulose and PVA/CMC membranes from 0 to 700 °C.

reduced in the presence of CMC and cellulose as fillers and they occurred at about 275, 175 and 75 °C, respectively. The maximum decomposition temperature (T_{max}) occurred at 322, 283 and 185 °C, respectively, for PVA, PVA/cellulose and PVA/CMC These T_{max} values indicated that the addition of cellulose and CMC results in a membranes of a lower thermal stability.

Furthermore, due to the strong hydrophilicity, although the membranes were dried for 24 h, it still contained amounts of water molecules, which can be calculated from the TGA curve (see Fig. 7a). We examined the water content in the PVA/cellulose and PVA/CMC membrane we prepared to be about 18.2 and 22.0%, respectively, which are less than that for the PVA membrane, 65.8%.

Moreover, the DSC curve of the PVA, PVA/cellulose and PVA/CMC membranes shown in Fig. 7b indicate one obvious transition temperature point for the PVA membrane around 321 °C, while we could recognize two obvious transition temperature points around 192 and 238 °C, respectively for the PVA/cellulose. On the other hand, from Fig. 7 three obvious transition temperature points around 44, 132 and 167 °C became obvious, respectively for the PVA/CMC. Obviously, the first two points, i.e. 44 and 132 °C are related to the complete loss of water molecules. As to the third point 167 °C, it is assumed that the transition is due to the structural changes of the polymer chains. According to Lojewska, Miskowiec, Lojewski, and Proniewicz (2005) the transition is probably related to the partial oxidation of the OH groups on the polymer chains. Since the secondary OH groups of the repeating units are hard to be oxidized under 220 °C (Watanabe, Morita, & Ozaki, 2006) and the degree of substitution of the CMC used is 0.76, we speculate that the oxidation is due to the residual primary OH groups that are not carboxymethylated.

4. Conclusions

A method for preparing barrier membranes from poly(vinyl alcohol) containing 12.5% of either cellulose isolated from bleached rice straw fibers or carboxymethyl cellulose of DS 0.76 as filler has been investigated. Presence of both cellulose and CMC showed effect on the solubility and water sorption as well as on transport properties, where it can be suggested that this effect can be due to the reduce in the number of the hydroxyl groups and thus the hydrophilicity. The FT-IR spectroscopy and the SEM suggested the dispersion of CMC in the PVA matrix is better than the dissolved cellulose and thus a reduction in the absorbance band of the OH group at ~3400 cm^{-1} was noticed and is common to either the CMC or cellulose/PVA membranes.

The CVTR experiments showed that the presence of cellulose or CMC increased the lag time and decreased the flux compared to a pure PVA membrane. Moisture transport was also reduced by both cellulose and CMC. This points out the critical role that the impermeable cellulose and CMC, as filler, plays in the overall performance of the membrane.

The TGA showed that the T_s started in a lower temperature in case of the presence of either CMC or cellulose in the PVA membranes, while the DSC indicating the presence of two and three transition temperatures in case of the presence of cellulose and CMC in the PVA membrane, respectively. This can probably related to the partial oxidation of the OH groups on the polymer chains.

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