Polymer Bulletin 60, 397–404 (2008)
DOI 10.1007/s00289-007-0856-8

Polymer Bulletin

Characterization of cellulose triacetate membranes, produced from sugarcane bagasse, using PEG 600 as additive

Daniel Alves Cerqueira[1], Guimes Rodrigues Filho[1] (✉), Rosana Maria Nascimento de Assunção[1], Carla da Silva Meireles[1], Leandra Cardoso Toledo[1], Mara Zeni[2], Kátia Mello[2], Jocelei Duarte[2]

[1]Instituto de Química da Universidade Federal de Uberlândia, Av. João Naves de Ávila 2121
CEP 38400-902 Cx. P. 593 Uberlândia – Minas Gerais, Brasil
[2]Departamento de Física e Química da Universidade de Caxias do Sul – Caxias do Sul,
Rio Grande do Sul, Brasil
E-mail: guimes@ufu.br; Fax: +55 (34) 3239-4208

Received: 29 May 2007 / Revised version: 16 July 2007 / Accepted: 10 October 2007

Summary

Cellulose Acetate (CA) produced from sugarcane bagasse cellulose was used to produce membranes, using poly(ethylene glycol) (PEG 600) as additive. Results showed that PEG 600 was washed out the membranes during the preparation step. Thermal Analysis showed that the temperature of degradation of the membranes increased in 10°C when PEG 600 was added to the composition, but did not change as more PEG 600 was added in the composition. On the other hand, the crystalline content (%C) of the membranes increased as PEG 600 was added. The addition of PEG 600 also increased the resistance of the membranes to pressure and the pure water flux rate, but membranes produced with PEG 600 content lower than 5% did not present water flux. PEG 600 also increased the coefficient of ion diffusion of the membranes.

Introduction

Sugarcane production has been increasing significantly in the last years due to the increase on the demand for ethanol, one of the most promising biofuels up to this moment. In Brazil, the major producer of sugarcane, farmers intend to have increased the production from 475 million metric tons (2006/2007) to 715 mi metric tons by 2015. The generation of residues, as sugarcane bagasse (SCB) for instance, will increase at the same proportion.

Nowadays, SCB is mostly burnt to generate energy for the mills [1], but a considerable amount of it is still wasted and, for this reason, several papers have been produced setting alternatives for recycling it. Since SCB is composed mainly by cellulose, lignin and hemicelluloses, the alternatives for recycling it are mostly based on the chemical modification of these components, e.g., hemicellulose is used for producing xylitol [1], lignin for producing phenolic resins [2,3], and cellulose for producing ethanol [4], composites [5], and cellulose derivatives [6-9]. The use of SCB for producing cellulose acetate, as well as membranes of this produced cellulose acetate has already been proposed [10-13].

Several papers have been published about the use of poly (ethylene glycol) (PEG) of varied molecular weights as additives in membranes of cellulose acetate [14-19]. In a recent paper, Rodrigues Filho et al. have shown the viability of producing membranes of cellulose acetate made of SCB using PEG 600 as an admixture [14]. Yet, it was observed that as PEG 600 was added to the system the membranes became more fragile and difficult to work with. This problem was associated with the low molecular weight of the cellulose acetate produced from SCB and was corrected by optimizing the acetylation process [20].

On this paper, membranes of cellulose triacetate made from the optimized acetylation process of SCB [20] were produce, using PEG 600 as additive. These membranes were characterized by DSC, TGA, MEV, pure water flux rate and ion diffusion.

Experimental

Materials

Cellulose triacetate was produced from sugarcane bagasse according to Cerqueira et al. [20]. Dichloromethane and PEG 600 were purchased from Merck.

Membrane Preparation

Solutions containing CTA, PEG 600 and dichloromethane were prepared in the proportions (w/w) shown in table 1. From now on the membranes will be referred as A, B, C and D, according to the first row of Table 1.

Each solution was stirred for 24 hours at room temperature after which they stand for 1 hour in order to remove bubbles from the solution. These solutions were then cast on a glass plate using a casting knife set at 300 µm. The solvent was allowed to evaporate for 2 minutes at 22ºC, after which the plate was immersed in a water bath at 22ºC in order to detach the membrane from the plate.

Table 1 – CTA, PEG 600 and dichloromethane content of dope solutions

Membrane	%CTA	%PEG 600	%CH_2Cl_2
A	8.0	0.0	92.0
B	8.0	2.5	89.5
C	8.0	5.0	87.0
D	8.0	10.0	82.0

Thermal Analysis (TGA and DSC)

Thermogravimetric analyses were performed in a TGA-50, Shimadzu. The samples were heated from room temperature to 800°C at a heating rate of 20ºCmin^{-1} under nitrogen flow of 50 cm^3min^{-1}.

DSC experiments were performed in a DSC-50, Shimadzu, at a heating rate of 20ºCmin^{-1} and nitrogen flow of 50 cm^{3}min^{-1}.

Diffusion of ions

For these experiments, it was used a two-compartment system separated by the studied membrane. One of the compartments was filled with deionized water and the other with KCl 10^{-3} mol.L^{-1}. The permeability coefficients of KCl were measured by a conductivity cell and the concentration was calculated using a previously prepared calibration curve. The flux through the membrane was calculated from the slope of the curve concentration versus time. The permeability coefficient was calculated from equation 1.

$$P = \frac{J}{\Delta C} \qquad (1)$$

where ΔC is the concentration difference between the two compartments.
The diffusion coefficients through the membranes were calculated using the equation 2.

$$D = P \times d \qquad (2)$$

where d is thickness.

Measurement of pure water flux rate

The membranes were subjected to measurements of pure water flux in order to test their resistance to pressure. The flow was calculated using equation 3.

$$J_w = \frac{Q}{A\Delta T} \qquad (3)$$

where J_w is the water flow (Lm^{-2}h^{-1}), Q is the permeate volume (L), A is the area of the membrane (m^2) and ΔT is the time of permeation (h).

SEM

The samples were initially gold coated (Bal-Tec SCD-050) and the microscopies were obtained in a Jeol/Scaning Eletron Microscope, JSM 6060, operated at 10 kV.

Results and Discussion

Thermal Analysis

TGA

Figure 1 shows TGA and DTGA plots of the membranes, respectively.
As it may be seen from figure 1, all the membranes present a very similar pattern, with two stages of weight loss. The first stage is due to loss of water, while the second is due to decomposition of cellulose acetate [21]. The absence of a decomposition stage

for PEG 600 indicates that this material must have been washed out of the membrane during the phase inversion step. Yet, the presence of PEG 600 must have induced structural changes on the membranes, as may be seen comparing the degradation peak in membrane A (370ºC) with the peaks for degradation of the other membranes (378ºC).

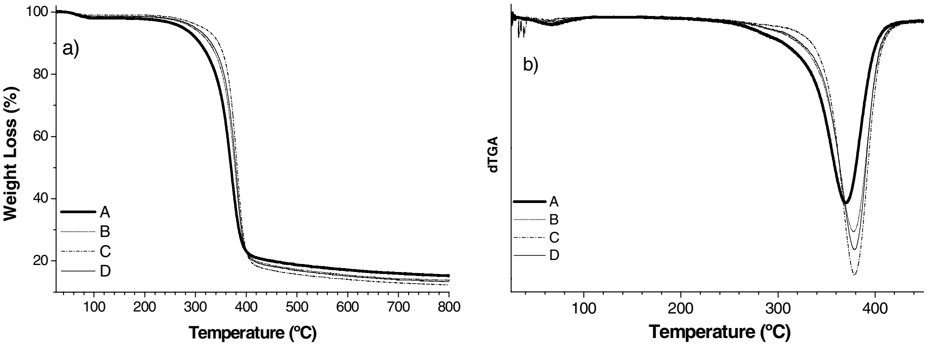

Figure 1 – a) TGA and b) DTGA of CTA/PEG 600 membranes

DSC

DSC plots of first and second scans of the membranes are shown in figure 2, respectively.

On the first scan plot, four phenomena may be seen. The first phenomenon is an endotherm of dehydration, around 100ºC. At around 160ºC there is a shift in baseline that characterizes the glass transition region. However, this shift is superimposed by the exotherm of crystallization at around 206ºC. At 299ºC it is seen the endotherm of fusion of CTA. In order to obtain the Tg of the materials, a second scan was performed, and all the materials presented Tg values around 170ºC.

Except for the endotherm of dehydration, all the phenomena observed through DSC were nearly at the same position for all the membranes. In spite of that, it was observed a change in the magnitude of some of these phenomena as the PEG 600 content was increased. As seen in table 2, the enthalpy of crystallization (ΔH_c) decreases as the PEG 600 content is increased. At the same time, the enthalpy of fusion (ΔH_f) of these samples presents an abrupt change when 2.5 % PEG 600 was added to the casting solution. As more PEG 600 is added to the system, there is a slight increase on the ΔH_f of the membranes. From the values of enthalpy of fusion it is possible to obtain the crystalline content of the membranes. However, since the material crystallizes during the experiment, the enthalpy of crystallization is subtracted from the enthalpy of fusion in order to provide the real enthalpy of fusion of the materials, ΔH_r. From ΔH_r, the crystalline content is calculated as follows:

$$\%C = \frac{\Delta H_r}{\Delta H_m^o} \qquad (4)$$

where %C is the crystalline content and ΔH_m^o is the enthalpy of fusion of a perfect crystal of the polymer. For cellulose triacetate, $\Delta H_m^o = 58.8$ J/g [12].

Values of ΔH_r and %C of the produced membranes are also shown in table 2.

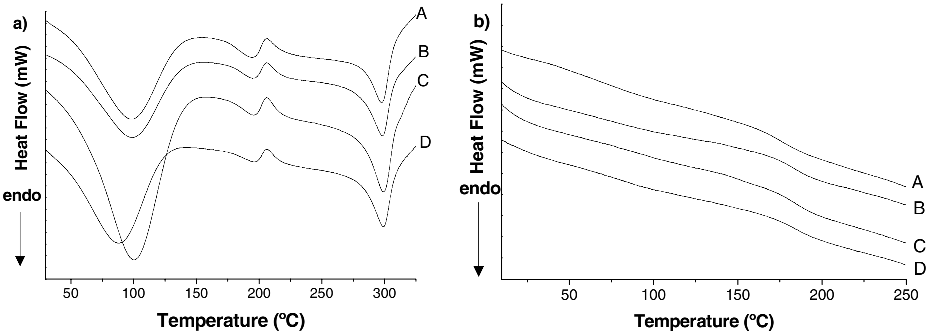

Figure 2 – a) first and b) second scans of DSC thermograms of CTA membranes produced with distinct PEG 600 compositions.

Table 2 – Data collected from DSC thermograms

	ΔH_w (J/g)	Tc (ºC)	ΔH_c (J/g)	Tm (ºC)	ΔH_f (J/g)	ΔH_r (J/g)	%C (%)
A	65.89	205.97	4.16	297.51	8.51	4.34	7.38
B	66.05	205.98	3.43	298.24	14.19	10.76	18.30
C	120.89	206.16	3.18	299.20	15.57	12.39	21.07
D	76.62	206.25	2.86	299.05	16.16	13.27	22.57

Pure water flux rate

In our previous paper [14] the membranes of cellulose acetate produced using PEG600 as additive were too fragile to be tested in pure water permeation assays, especially those with higher PEG content which would break easily. However, in this paper, all membranes have been exposed to pressures up to 7 atm. The membranes A and B did not present water flux even when the highest operational pressure possible was used. Also, membrane A broke a few minutes after the highest pressure was

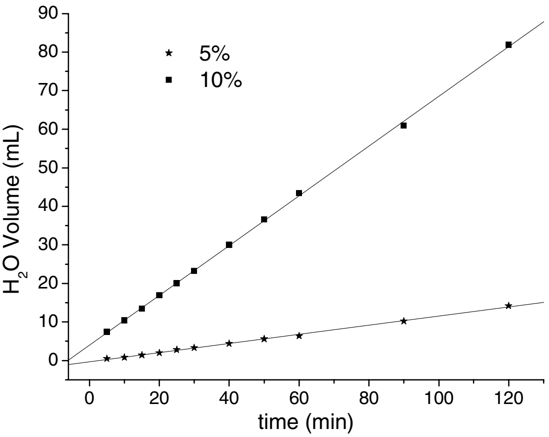

Figure 3 – Pure water flux in function of time for membranes C and D.

applied. Membrane B, in spite of not presenting water flow, resisted to the water pressure during the whole experiment, 120 min. This difference in resistance to pressure of membrane B is probably caused by the increase in the crystallinity of this membrane as seen by DSC.

In addition to the increase in resistance, PEG 600 also improved the water flow through the membranes. Membranes C started presenting water flux with about 3 atm, while membrane D presented water flux with pressures as low as 2 atm. In both cases, in order to measure the permeability through these membranes, it was used 4 atm. A plot of the permeate volume through these membranes in function of time is given in figure 3.

Diffusion of ions

Table 3 shows the diffusion coefficients calculated for the membranes. As it may be seen, D increases significantly as PEG content is increased. This increase in the diffusion coefficient, as well as the increase in water flux through the membranes can be explained by PEG 600 being a hydrophilic additive, what causes the polymer particles at the surface of the membrane to swell mainly in the vertical direction, what creates spaces between the polymer structures [15,22]. That is corroborated by SEM cross-section images of the membranes, shown in figure 4. Although membranes B and C do not differ much from membrane A, a much more irregular cross-section is observed when PEG content is raised to 10 % in membrane D.

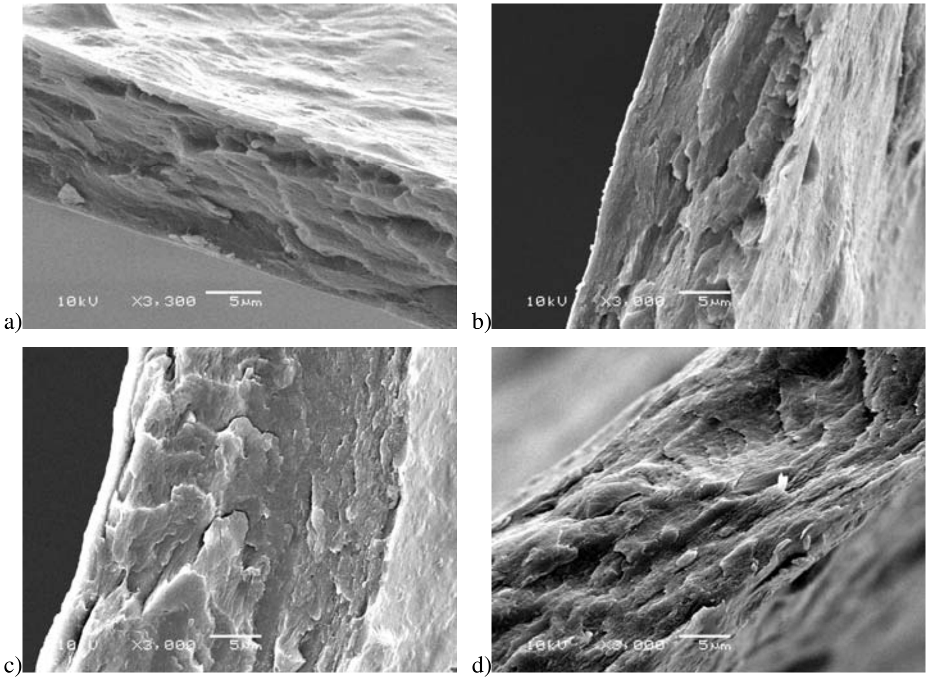

Figure 4 – SEM cross-section images for CTA membranes, prepared with distinct PEG 600 content: a – 0%, b – 2.5%, c – 5% and d – 10% respectively.

Table 3 – Diffusion coefficients calculated for membranes of CTA with distinct PEG compositions

Membrane	D ($cm^2\ s^{-1}$)
A	5.33×10^{-7}
B	2.01×10^{-6}
C	1.07×10^{-6}
D	6.26×10^{-5}

Conclusion

Membranes of cellulose triacetate produced from sugarcane bagasse have been prepared, using PEG 600 as additive, and characterized. Thermal analysis of the membranes showed an increase in crystallinity and in thermal stability as PEG 600 content increased in the dope solutions. PEG 600 also promoted a higher resistance to pressure of the prepared membranes and increased pure water flux through the membranes, as well as the ion diffusion coefficient.

Acknowledgements. The authors thank CAPES (PROAP/ Portal Periódicos). Cerqueira and Meireles thank Capes for their PhD and master's scholarships, respectively. Mello and Duarte thank CNPq for their DTI and PIBIC scholarships, respectively.

References

1. Gámez S, González-Cabriales JJ, Ramírez JA, Garrote G, Vázquez M (2006) J Food Eng, 74:78
2. Khan MA, Ashraf SM, Malhotra VP (2004) Int J Adhes Adhes 24:493
3. Hoareau W, Trindade Wg, Siegmund B, Castellan A, Frollini E (2004) Polym Degrad Stabil 86:567
4. Sarrouh BF, Silva SS, Santos DT, Converti A (2007) Chem Eng Technol 30:270
5. Ramaraj B (2007) J Appl Polym Sci 103:3827
6. Liu CF, Sun RC, Zhang AP, Ren JL (2007) Carbohyd Polym 68:17
7. Pasquini D, Belgacem MN, Gandini A, Curvelo AAS, J Colloid Interf Sci (2006) 295:79
8. Rodrigues Filho G, Assunção RMN, Vieira JG, Meireles CS, Cerqueira DA, Barud HS, Ribeiro SJL, Messaddeq Y (2007) Polym Degrad Stabil 92:205
9. Viera RGP, Rodrigues Filho G, Assunção RMN, Meireles CS, Vieira JG, Oliveira GS (2007) Carbohyd Polym 67:182
10. Rodrigues Filho G, Cruz SF, Pasquini D, Cerqueira DA, Prado VS, Assunção RMN (2000) J Membrane Sci 177:225
11. Rodrigues Filho G, Silva RC, Meireles CS, Assunção RMN, Otaguro H (2005) J Appl Polym Sci 96:516
12. Cerqueira DA, Rodrigues Filho G, Assunção RMN (2006) Polym Bull 56:475
13. Meireles CS, Rodrigues Filho G, Assunção RMN, Zeni M, Mello K (2007) J Appl Polym Sci 104:909
14. Rodrigues Filho G, Toledo LC, Cerqueira DA, Assunção RMN, Meireles CS, Otaguro H, Rogero SO, Lugão AB (2007) Polym Bull 59:73
15. Idris A, Yet LK (2006) J Membrane Sci 280:920
16. Wang FJ, Yang YY, Zhang XZ, Zhu X, Chung TS, Moochhala S (2002) Mat Sci Eng C-Bio S 20:93
17. Kim JH, Lee KH (1998) J Membrane Sci 138:153

18. Arthanareeswaran G, Thanikaivelan P, Srinivasn K, Mohan D, Rajendran M (2004) Eur Polym J 40:2153
19. Arthanareeswaran G, Muthukumar M, Dharmendirakumar M, Mohan D, Raajenthiren M (2006) Int. J. Polym. Mat. 55:1133
20. Cerqueira DA, Rodrigues Filho G, Meireles CS (2007) Carbohyd Polym 69:579
21. Hanna AA, Basta AH, El-Saied H, Abadir IF (1999) Polym Degrad Stabil 63:293
22. Hayama M, Yamamoto KI, Kohori F, Sakai K (2004) J Membrane Sci 234:41