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Synthesis and characterization of cellulose acetate produced from recycled newspaper

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Abstract

In this work, the viability of recycling newspaper for producing cellulose acetate was tested. Newspaper recycling is extremely important not only for the environment preservation, but also from the economical point of view of aggregating value to this residue. Cellulose acetate was produced from a homogeneous acetylation, and then characterized by FTIR, DSC and TGA. Acetylation times were 48 h for as received newspaper (CA48) and 24 h for delignified newspaper (CA24), resulting in cellulose diacetate ($DS = 1.98 \pm 0.22$) for CA48 and cellulose triacetate ($DS = 2.79 \pm 0.02$) for CA24, respectively. Membranes of these materials were produced and characterized according to the previously mentioned techniques and by measurements of water vapor flux, which were compared to membranes of nanofiltration SG from Osmonix®. Results showed that independently of a purification step, it is possible to produce cellulose acetate membranes through the chemical recycling of newspaper and that membrane CA24 presents thermal stability comparable to membranes produced of commercial cellulose acetate.

Keywords: Cellulose acetate; Newspaper; Membranes; Recycling

1. Introduction

Brazilian paper and cellulose industry aggregates about 220 companies which produce around 10.1 million metric tons of cellulose and 8.6 million metric tons of paper each year. This production corresponds to 1.4% of Brazilian gross domestic product (GDP) and makes Brazil the seventh major producer of cellulose – leader in the production of short fiber cellulose and 11th in the production of paper. Brazilian paper and cellulose products are manufactured exclusively from wood of forests planted in degraded areas, avoiding the cut of native trees. The forestal base of this country constitutes one of the major comparative advantages for the local companies against their global competitors. The planted area totalizes 1.7 million hectares (75% eucalyptus, 24% pine and 1% of other woods).

In November 2001, the State of São Paulo Research Foundation (FAPESP) announced the beginning of the project FORESTs, for the sequencing of part of the Eucalyptus genome, developed in the ambit of the Partnership Technological Innovation Program, PITE, with the objective of improving the raw material for the production of paper and cellulose. In 2002, a data bank with 112,152 sequences of *Eucalyptus grandis* DNA was the result of the first phase of the project FORESTs Eucalyptus Genome Sequencing Project Consortim. On the other hand, as said previously, 24% of the planted area corresponds to pine (long fiber wood), which is used for producing newsprint. Pine is a conifer tree of the genus *Pinus*, of the

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Pinaceae botanic family, which presents straight, cylindrical trunk and a pyramidal crown. The most utilized pine trees in Brazil are *Pinus elliottii*, *Pinus taeda* and *Pinus caribaea*. The chemical composition of *Pinus elliotti* wood contains around 59.9% cellulose, 27.8% lignin and 8.3% hemicellulose (D'Almeida, 1998).

Nowadays, the search for alternatives for preserving the environment and aggregating value to industrial and urban residues is increasing significantly. Among the alternatives, polymer recycling may be emphasized. In this sense, the Group of Polymer Recycling of the Universidade Federal de Uberlândia (GRP-UFU) has been producing papers demonstrating the viability of chemically recycling cellulose from renewable sources, e.g. sugarcane bagasse, for producing derivatives such as methylcellulose and cellulose acetate (Cerqueira, Rodrigues Filho, & Meireles, 2007; Meireles, Rodrigues Filho, Assunção, Zeni, & Mello, 2007; Rodrigues Filho, Silva, Meireles, Assunção, & Otaguro, 2005; Rodrigues Filho et al., 2007a, 2007b; Vieira et al., 2007). With the possibility of an energy crisis in the near future, new proposals for using biomass, such as sugarcane bagasse, have risen. Among these proposals, it may be emphasized the burning of sugarcane bagasse for generating electricity and enzymatic hydrolysis for producing ethanol (Adsul et al., 2005; Botha & von Blottnitz, 2006; Chandel, Kapoor, Singh, & Kuhad, 2007; Kim & Dale, 2004; Martin, Klinke, & Thomsen, 2007; Pippo, Garzone, & Cornacchia, 2007; Singh, Asthana, & Singh, 2007; Sosa-Arnao, Correa, Silva, & Nebra, 2006). In this way, new sources for recycling cellulose must be investigated, what increases the importance of recycling newsprint (newspaper) (Huda, Drzal, Mohanty, & Misra, 2006, 2007; Okino, Santana, & Souza, 2000). In 2002, Brazil consumed around three million metric tons of recyclable papers, 124,000 metric tons of which correspond to newspaper. The partnership of the Brazilian Development Bank (BNDES) aimed at the development of companies of the sector and at the recycling of paper has been even more consolidated (Moraes, 2007). Therefore, GRP-UFU has recently initiated a research line aimed at chemically recycling newsprint, trying to demonstrate the viability of producing cellulose acetate (Castaldi, Rodrigues Filho, & Assunção, 2002; Monteiro, Rodrigues Filho, Assunção, & Meireles, 2007; Prado, Rodrigues Filho, & Assunção, 2000).

Cellulose acetate is one of the most important cellulose derivatives, which may be produced through homogeneous or heterogeneous routes. The difference between these is that in the heterogeneous route a non-swelling agent, such as toluene, is used, producing a more crystalline and less biodegradable material than that produced through the homogeneous route (Sassi & Chanzy, 1995). Cellulose acetates are used in several applications, such as in the textile and cigarette industries. They may also be used in the form of membranes in several separation processes, such as dialysis, hemodialysis and reverse osmosis (Cetin, Buduneli, Atlihan, & Kırılmaz, 2004; Gill, Lillie, Farace, & Vadgama, 2005; Guilminot, Fischer, Chatenet, & Rigacci, 2007; Idris & Yet, 2006; Kosaka, Kawano, Salvadori, & Petri, 2005; Morti, Shao, & Zydney, 2003; Sedelkin et al., 2006; Wibowo et al., 2006; Yea, Watanabea, Takaia, Iwasakib, & Ishiharam, 2006). The present paper deals with the chemical recycling of newsprint for the production of cellulose acetate membranes.

2. Experimental

2.1. Production and characterization of cellulose acetate

2.1.1. Delignification of newspaper

It was used only newspaper parts where there was no ink. The material was shred and the delignification was carried out as described by Rodrigues Filho et al. (2000): 4 g of newspaper was mixed with 76.00 mL water. After 24 h, the mixture was filtered and 76.00 mL NaOH (0.25 mol L^{-1}) was added to the newspaper. After 18 h, the mixture was filtered again and the newspaper put into reflux with three successive portions of a 20% v/v mixture of nitric acid and ethanol, which was changed after each hour. After the reflux, the mixture was filtered, and then washed with distilled water until the filtrate became uncolored. The newspaper was dried at 105 °C for 180 min, and then ground.

2.1.2. Synthesis of cellulose acetate

Cellulose acetate was synthesized according to Rodrigues Filho et al. (2005), which is described below:

As received and delignified newspaper were acetylated for 48 h (CA48) and 24 h (CA24): 40.00 mL glacial acetic acid was added to 2 g newspaper, and this mix was stirred for 30 min at room temperature. Then, a solution containing 0.3 mL H_2SO_4 and 17.5 mL glacial acetic acid was added to the system, which was stirred for 15 min at room temperature. This mixture was filtered and the newspaper was returned to its flask. 40 mL acetic anhydride was mixed to the filtrate, and then returned to the initial flask with newspaper.

The solution was stirred for 30 min and left to stand. After 48 h (CA48) or 24 h (CA24), distilled water was added to the reaction medium until no more precipitate was formed. The mixture was vacuum filtered and washed with distilled water until the material was neutral. The produced cellulose acetate was dried in an oven for 90 min at 105 °C.

2.1.3. Determination of the degree of substitution

The degree of substitution (DS) of the material was determined in order to characterize it as cellulose acetate. DS is the average value of acetyl groups which replace the hydroxyl groups in the glucosidic units (Kelley, Puleo, & Paul, 1989). DS was determined through a saponification reaction, as follows: 5.00 mL NaOH (0.25 mol L^{-1}) and 5.00 mL ethanol were added to about 0.1 g cellulose acetate, then, this mixture was left to stand for 24 h. After that, 10.00 mL HCl (0.25 mol L^{-1}) was added to the system, which was left to stand for 30 min. Next, the mixture was titrated using a standard 0.25 mol L^{-1} NaOH solution, using phenolphthalein as indicator. This procedure was repeated in triplicate.

Eq. (1) was used in order to determine the percentage of acetyl groups.

$$\%AG = \frac{[(Vb_i + Vb_t)\mu_b - V_a \cdot \mu_a]43 \cdot 100}{m_{ca}} \tag{1}$$

where %AG = percentage of acetyl groups; Vb_i = NaOH volume added to the system; Vb_t = NaOH volume spent in titration; μ_b = NaOH concentration; V_a = HCl volume added to the system; μ_a = HCl concentration; 43 = molar weight of the acetyl group; m_{ca} = weight of cellulose acetate sample.

2.1.4. FTIR

The experiments were carried out in an FTIR Perkin Elmer Spectrum 1000. Thirty-two scans were collected for each spectrum with a step size of 4 cm^{-1}. For the analysis, the powdered materials (as received and delignified newspaper, CA48, CA24), were prepared as pellets, mixing them with KBr in the proportion of 1/100 (w/w).

2.1.5. Membrane preparation

The membranes were prepared by solution casting (Monteiro et al., 2007): Casting solutions were prepared using 6% (w/w) cellulose acetate. The solvents used were acetone for CA48 and dichloromethane for CA24. The solutions were stirred for 24 h and cast on a glass plate using a cast knife open at 200 μm. Five castings were performed, and the time between each casting was 90 s. The plate was then dipped into a distilled water bath, at room temperature, until the membrane was detached from the plate.

2.1.6. Differential scanning calorimetry

Differential scanning calorimetry (DSC) experiments were carried out using a Rheometric Scientific DSC-SP equipment. The tests performed at a heating rate of 20 °C min^{-1} under nitrogen flow (20 cm^3 min^{-1}), from 25 to 400 °C.

2.1.7. Thermogravimetric analisys

TGA plots were carried out using a SDT equipment from TA Instruments under nitrogen and oxygen with a flow rate of 70 mL min^{-1}, using alumina pans. The samples were rampered from room temperature to 600 °C at a scanning rate of 10 °C min^{-1}.

2.1.8. Klason lignin

Klason lignin was determined according to the methodology described by Vieira et al. (2007): A 2.000 g sample of newspaper was transferred to a round bottomed flask. Fifteen milliliters of sulfuric acid (72%) was slowly added to it under stirring. The sample was kept under stirring in a bath at room temperature for 2 h. Subsequently, 560 mL of distilled water was added to the round bottomed flask, diluting the acid solution to 3%. The system was heated up to 100 °C, under reflux in order to avoid loss of water due to evaporation, what would alter the concentration of the acid solution. After 4 h, the system was left to stand for sedimenting the insoluble residue, which was filtered in a previously weighed fritted funnel, and washed with 500 mL of distilled hot water. The residue was dried in an oven for 12 h at 105 °C and, then, weighed for quantifying the amount of Klason lignin.

2.1.9. Holocellulose

Holocellulose content was determined according to Vieira et al. (2007), as follows: 5.000 g newspaper was added to a round bottom flask containing 100 mL distilled water. Then, 0.5 mL of concentrated acetic acid and containing 0.7500 g of sodium chlorite were added in this order. The round bottom flask was then covered in order to avoid loss of the gas produced during the reaction and placed on a thermostat bath at 75 °C. After each hour, 0.5 mL acetic acid and 0.7500 g sodium chlorite were added to the flask, repeating this procedure twice. The system was cooled to 10 °C, and then filtered in a previously tared fritted funnel and washed with distilled water at 5 °C until the fibrous residue became whitish. The funnel containing the fibrous residue was then dried in an oven at 105 °C for 6 h. After this period, the residue was cooled to room temperature in a desiccator and then weighed to quantify the holocellulose.

2.1.10. Determination of cellulose content

Cellulose content was determined according to Vieira et al. (2007), as follows: 3 g holocellulose was put into a 250 mL Erlenmeyer flask and mixed with 100 mL of a 5% KOH solution in inert atmosphere, which was obtained by purging nitrogen into the mix during the first 10 min of extraction in order to avoid cellulose oxidation. The flask was sealed and kept under constant stirring for 2 h. The mix was filtered in a fritted funnel, and washed with 50 mL of a 5% KOH solution, and then with 100 mL of distilled water. The filtrate was transferred to a 1 L Erlenmeyer flask and the precipitation was performed by adding a solution containing equal parts of acetic acid and ethanol up to the erlenmeyer volume. The precipitate was hemicellulose-A.

In order to obtain hemicellulose-B, the fibrous residue retained on the fritted funnel was transferred to a 250 mL Erlenmeyer flask, and the same procedure that was performed to obtain hemicellulose-A was followed. However, a 24% KOH solution was used. The fibrous residue on the fritted funnel was washed with 25 mL of a 24% KOH solution, then with 100 mL of distilled water and finally with 25 mL of 10% acetic acid solution. The filtrate was recovered in a 1 L Erlenmeyer flask into which a solution containing equal amounts of acetic acid and ethanol was added completing the Erlenmeyer volume. The precipitate was hemicellulose-B.

The fibrous residue (cellulose) at the end of the process described above was washed with distilled water until the filtrate pH was neutral. Then, it was washed with 50 mL of acetone and dried at 105 °C. After this period, the residue was weighed to quantify cellulose.

2.1.11. Water flux

The water vapor flux through the membranes was measured using the Payne's cup technique (Rodrigues Filho et al., 2000). The membrane was cut into the shape of a disk, with the same diameter of the Payne's cup and had its thickness measured with a micrometer. Water was added to the cup and the disk was placed onto the cup's support. The system was weighed and put into a desiccator, and was weighed again every hour, for 9 h, which was sufficient for reaching the steady-state regimen. Weight loss was calculated according to Eq. (2).

$$J = \frac{\Delta m}{\Delta t} A \qquad (2)$$

where J = water vapor flux; Δm = mass difference; Δt = time difference; A = membrane area.

3. Results and discussion

3.1. Delignification of newspaper

In order to study newspaper delignification, besides chemical determination of the residual lignin content, FTIR was also used. Fig. 1 shows that, in general, there is a reduction on the intensities of the bands assigned to lignin, mainly those at 1730 cm^{-1} (carbonyl groups) (Pandey & Pitman, 2003; Tserki, Zafeiropoulus, Simon, & Panayiotou, 2005). Other important bands are: 1512 cm^{-1} (aromatic ring vibrations of phenylpropane skeleton) and 1250 cm^{-1} (aryl–alkyl ether linkage) (Pandey & Pitman, 2003; Tejado, Pena, Labidi, Echeverria, & Mondragon, 2007; Yang, Yan, Chen, Lee, & Zheng, 2007). The set of bands located at 1620–1690 cm^{-1} (conjugated carbonyl group) is altered, with a narrowing of these bands being observed. On the other hand, with the partial delignification, the bands located at 1270 cm^{-1} and 810 cm^{-1} (C–O stretching of guaiacyl rings) become more apparent (Tejado et al., 2007; Yang et al., 2007). This characteristic indicates that the guaiacyl residue is more difficult of being removed from this source of cellulose.

The determination of insoluble Klason lignin confirms FTIR results, since the newspaper had 24.6% lignin before delignification and, after this step, the lignin content was reduced down to 15.5%, showing that the residual lignin content is still high (the ratio between the original and the delignified material is 1.6). This high lignin content may affect the final properties of the produced material, such as the degree of substitution (DS) of the cellulose acetate produced from these two sources.

3.2. Characterization of the produced cellulose acetates

3.2.1. FTIR and DS (saponification reaction)

Fig. 2 shows the comparison between FTIR spectra of as received newspaper and cellulose acetate produced from this material (CA48). Fig. 2 presents as main feature the presence of a strong intensity band at 1746 cm^{-1}, which is assigned to the stretching of the carbonyl group of cellulose acetate, and a consequent reduction in the intensity of the band in 3460 cm^{-1} (OH stretching). These alterations characterize the material as being an acetylated derivative of cellulose, lignin and hemicellulose.

Fig. 3 shows the comparison between the spectrum of delignified newspaper and cellulose acetate produced from it (CA24).

As shown for CA48 in Fig. 1, CA24 FTIR presents a band around 1746 cm^{-1}, as well as a diminishing in the intensity of the band in 3500 cm^{-1}. However, it was noticed that the reduction in the intensity of the band correspond-

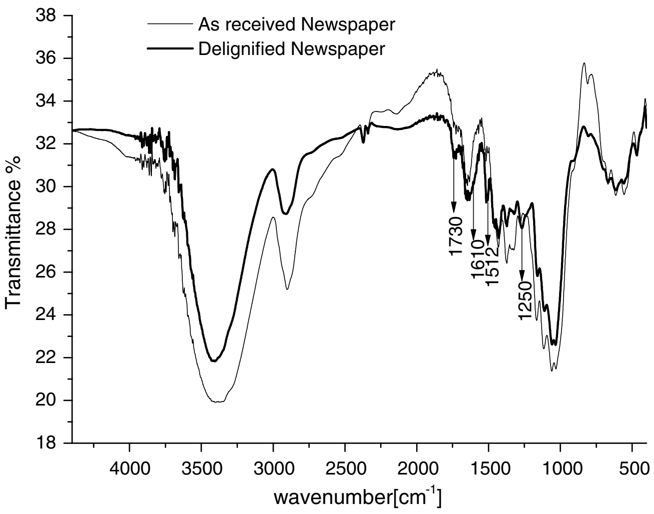

Fig. 1. FTIR spectra of as received and delignified newspaper.

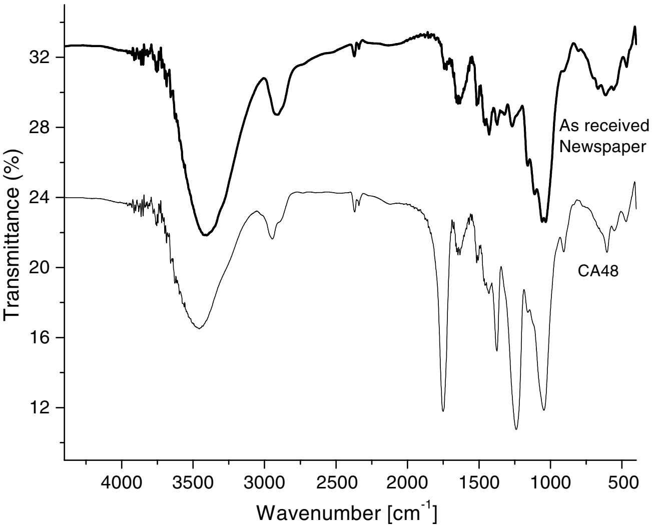

Fig. 2. FTIR spectra of as received newspaper and CA48.

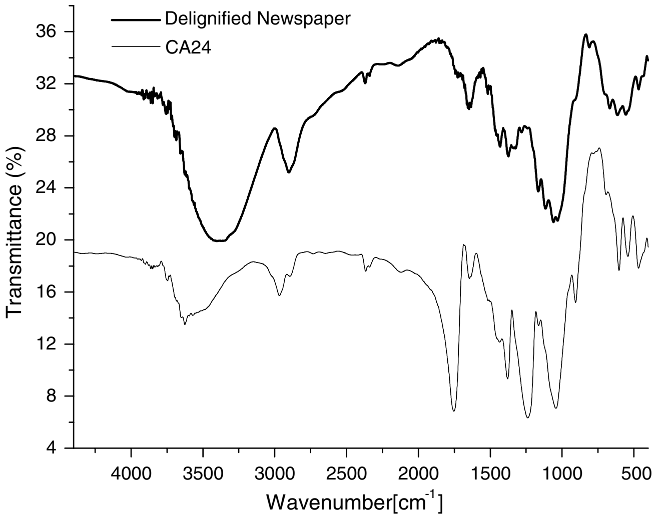

Fig. 3. FTIR spectra of delignified newspaper and CA24.

ing to the stretching of the cellulosic OH group was more accentuated for CA24 than for CA48 when comparing the intensity of the bands of the respective starting materials.

During the homogeneous acetylation of as received newspaper, it was observed that 24 h of reaction was insufficient for dissolving completely this material in the solvent system, thus, the material was acetylated for 48 h. On the other hand, the delignified newspaper dissolved in the solvent system in the beginning of the synthesis procedure. For this reason, the reaction time for this sample was 24 h, leading to sample CA24. The DS of CA48 was 1.98 ± 0.02 (31.9%AG), characterizing it as a cellulose diacetate, while CA24 was a cellulose triacetate, with DS of 2.79 ± 0.02 (42.1%AG). Therefore, the lignin content is interfering directly in the product of the acetylation reaction. When as received newspaper is acetylated, 48 h are necessary for obtaining cellulose diacetate, while when acetylating the newspaper pulp (delignified material) 24 h are enough for obtaining a cellulose triacetate. For obtaining the pulp, the as received newspaper is immersed in a NaOH solution, which promotes the swelling of the fibers trough a mercerization reaction, which also removes partially the lignin. Subsequently, with an ethanol/nitric acid solution, whose function is removing the lignin from the newspaper, it may be suggested that this procedure leads to a better activated cellulose pulp for the acetylation reaction since the swelling of the fibers and the removal of lignin promote a better accessibility of the acetylating agent (acetic anhydride) to the OH groups of cellulose. For this reason, after removing lignin, it is possible to obtain cellulose triacetate from newspaper pulp using half of the time dispended in the acetylation reaction of as received newspaper. Corroborating with these facts is the ratio between the DS of CA24 and CA48, which is 1.4. As seen in the "Delignification of newspaper" section, this ratio is inversely proportional to the lignin content of the samples, whose ratio is 1.6 (% lignin as received material/% lignin in delignified material).

3.2.2. *Differential scanning calorimetry (DSC)*

Fig. 4 shows DSC scans of membranes produced with CA24, CA48 and CARhodia, commercial cellulose diacetate.

DSC plots of these three membranes present endotherms around 125 °C, which may be attributed to the dehydration of these materials. Membrane CA48 was produced from a complex material, which was composed of cellulose, lignin and hemicellulose. This membrane presents an exotherm around 210 °C, which may be attributed to a crystallization phenomenon; an endotherm around 265 °C probably due to the melting of the material, and an exotherm with maximum located around 355 °C, must be mainly related to the degradation of the acetylated lignin and hemicellulose derivatives. CA24 and CA48 DSC plots present fundamentally the same characteristics. The main differences are related to the location of the endotherms and exotherms. In the present case, the following characteristics are observed for the maxima positions: (i) exotherm, probably related to crystallization, located around 190 °C. This endotherm being 20 °C below that of CA48 implies that the presence of a higher amount of lignin and hemicellulose in CA48 membrane hampers the crystallization process; and (ii) endotherm located around 280 °C, probably related to fusion, which is shifted to higher temperatures in relation to the correspondent enthalpy in CA48. In this case, the effect is opposite to that related to the crystallization phenomenon, i.e., lignin and hemicellulose are fundamentally amorphous materials, and therefore, the amount of crystallizable material is lower for CA48 sample. Thus, with the melting process also occurs degradation phenomenon, which is detected in the TGA experiments presented in the next sections. Besides, it

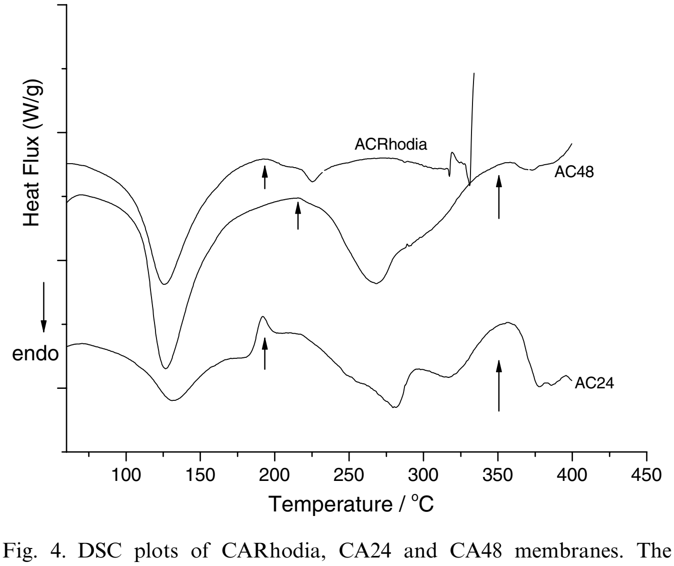

Fig. 4. DSC plots of CARhodia, CA24 and CA48 membranes. The arrows indicate the exotherms.

should be emphasized that cellulose diacetate melting point is usually around 230 °C. The membrane of commercial cellulose acetate presents as main characteristics an exotherm located around 190 °C and an endotherm, which may be attributed to the melting of the material, around 225 °C. The shifts of the endotherms to higher values in relation to the membrane of commercial material may be explained by the residual lignin content in CA24 and CA48 which would stiff the chains, besides, this lignin was also acetylated (Ren, Sun, Liu, Cao, & Luo, 2007; Tejado et al., 2007; Yang et al., 2007). The higher increase for CA24, which presents a lower content of lignin than CA48, may be attributed to a better chain packing due to the higher DS reached during acetylation, what turns possible the formation of more perfect crystals. Considering the absence of an exotherm in 355 °C in the membrane of commercial cellulose acetate, CARodhia, an exotherm in this region must be in fact attributed to the presence of lignin in the newspaper samples. As said before, FTIR spectra (Fig. 3) indicate the presence of bands of residual lignin in newspaper, even after the purification step.

3.2.3. Thermogravimetric analysis

Fig. 5 shows TGA and DTG plots for as received and delignified newspaper powder samples, in nitrogen atmosphere.

It may be noticed that for both materials there is only one considerable weight loss, which occurs between 360 °C and 330 °C for as received and delignified newspaper, respectively. The difference may be attributed to the lignin content, which is lower for the delignified material. According to Tejado et al. (2007), lignin presents a great amount of fenolic hydroxyl groups in its structure that make lignin behave as a crowded and stiff macromolecule, and therefore the thermal stability would be higher in the sample containing a higher amount of lignin, which in this case is the as received newspaper.

In Fig. 6a, it may be observed that CA48 is thermically less stable than the other two acetates. There is a first degradation, about 13%, around 260 °C, and then the main degradation, about 50%, occurring at 345 °C. For the other materials, CA24 and CARhodia, there is basically only one degradation step, for which the maximum location is nearly the same, 360 °C. In Fig. 6b, it may be observed that the first degradation of the material CA48 is actually a shoulder, what demonstrates the complexity of this material in terms of the presence of lignin and hemicellulose, since lignin degradation ranges from 190 to 990 °C. On the same hand, hemicellulose presents degradation phenomena in the same range where the shoulder is found (Ren et al., 2007; Tejado et al., 2007; Yan et al., 2007). For the other materials, CA24 and CARhodia, it is observed that the degradation at 360 °C is mainly associated to the decomposition of cellulose acetate. However, as shown in Fig. 6a for CA24, there may also be present some contribution from lignin since the amount of residue at 600 °C is about 13%, while for CARhodia there is practically no residue, showing that the lignin content in this material is not significant. As in the DSC results we had attributed the endotherm located at around 265 °C to a possible melting phenomenon, it is clear now with TGA results that, besides melting, degradation also takes place in the material.

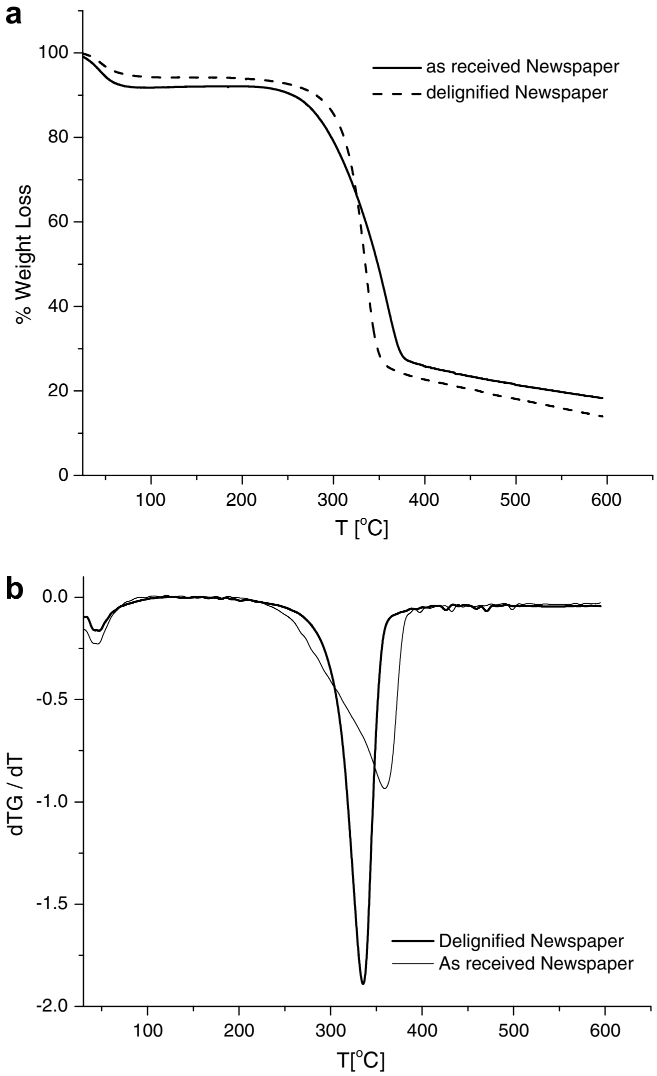

Fig. 5. TGA (a) and DTG (b) plots of delignified and as received newspaper samples, under nitrogen atmosphere.

Fig. 7 presents TGA and DTG plots for CA48, CA24 and CARhodia membranes in oxygen atmosphere.

It may be observed from Fig. 7 that CA48 membrane once again presents the lowest thermal stability with a significant weight loss of around 65% around 325 °C. This temperature is 25 °C lower than that observed in the test under nitrogen atmosphere, shown in Fig. 6. Besides that, a second degradation, not seen under nitrogen atmosphere, is observed around 450 °C. This may be attributed to the fragmentation of the lignin inter-unity linkages, with release of monomeric phenols into the vapor phase (Tejado et al., 2007). Fig. 7 also shows that CARhodia membrane presents higher thermal stability, which may be attributed

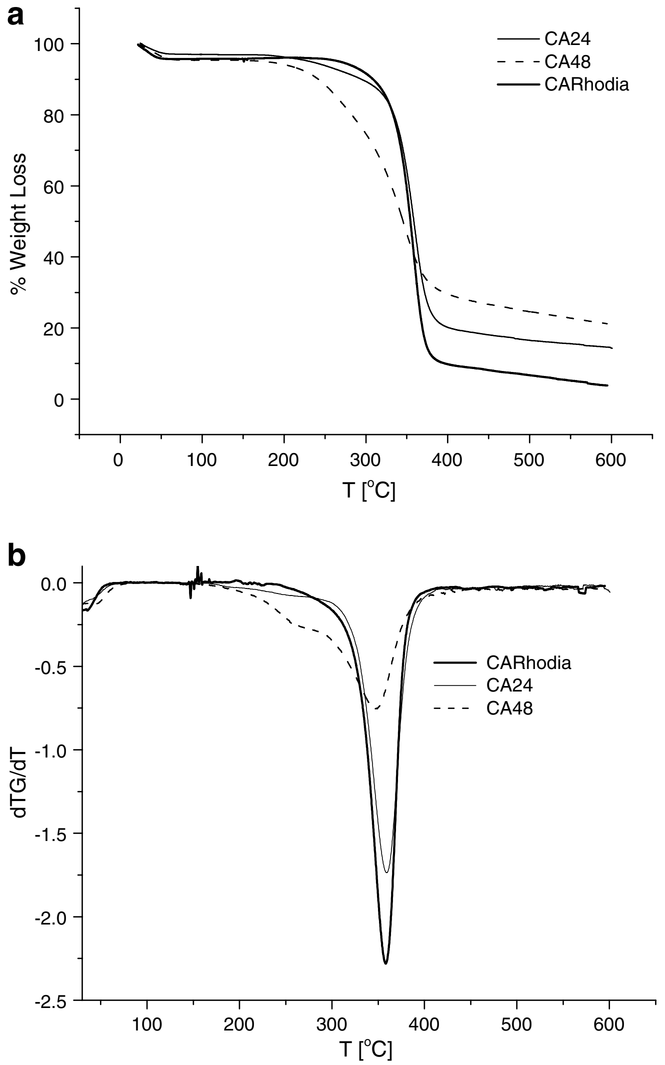

Fig. 6. TGA (a) and DTG (b) plots of CARhodia, CA24 and CA48 membranes.

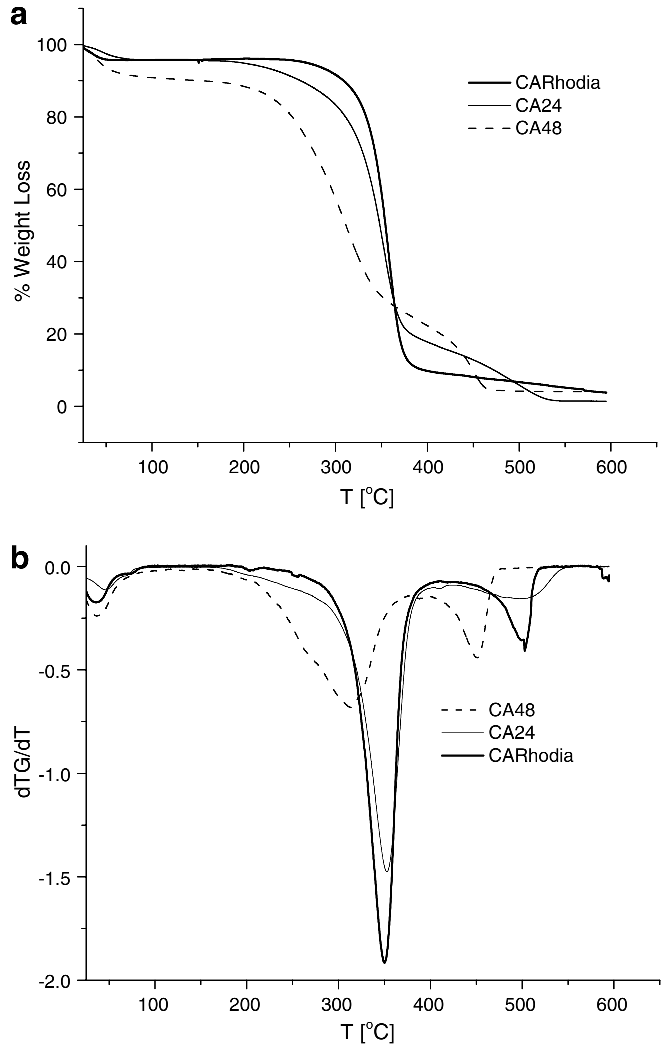

Fig. 7. TGA (a) and DTG (b) plots for CARhodia, CA24 and CA48 membranes, under oxygen atmosphere.

to the industrial production of this material not implying in degradation processes as those used in the present paper such as the elevated reaction times of the newspaper samples. For CA24 membrane, which presents thermal stability similar to that of CARhodia membrane, the presence of more perfect crystals, indicated by the higher melting temperature (280 °C, Fig. 4) among all studied samples by DSC, would be responsible by this phenomenon.

CARhodia and CA24 also present a second process of oxidative degradation around 500 °C. In both cases, this degradation may be attributed to thermal cracking of carbonyl and carboxyl groups (Yang et al., 2007). For CA24 sample, there is also a possible attribution due to the cracking and deformation of lignin due to the presence of aromatic rings and methoxyl groups in this macromolecule.

3.2.4. Water vapor flux through the membranes

Fig. 8 presents plots of weight loss in function of time, in steady-state conditions, for CA48, CA24 and CARhodia membranes. The thicknesses of the dry membranes were 38.0; 24.0 and 37.0 μm for CA48, CA24 and CARhodia, respectively. Water vapor flux through the membranes was calculated using Eq. (2). The results of flux, normalized by the thickness of the membranes, are presented in Table 1.

The analysis of the results given in Table 1 shows that the water vapor flux through CARhodia membrane is higher than those of the membranes obtained from newsprint acetate (CA48 and CA24), being 1.7 times higher than CA48 and 2.8 times higher than CA24. This may be attributed to the more amorphous character of CARhodia, which is represented by its low enthalpy of fusion and low melting temperature (DSC plot, Fig. 4).

When the results of flux of the materials produced in this paper are compared to those of a nanofiltration membrane, SG Osmonix® (Rodrigues Filho et al., 2005), it may be noticed that the flux through the commercial material is always higher. The relation between the flux through the materials presents the following crescent order: (SG/

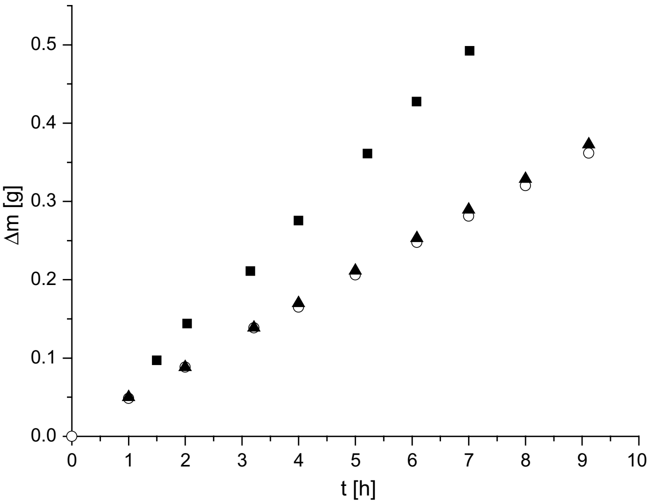

Fig. 8. Water vapor flux through membranes CA48 (▲), CA24 (○) and CARhodia (■).

Table 1
Water vapor flux, normalized by thickness, through membranes

Membranes	Normalized flux J L/10^{-4}(g s^{-1} cm^{-2} µm)
CARhodia	0.95
CA48	0.56
CA24	0.34
SG Osmonix® nanofiltration[a]	2.00

[a] Rodrigues Filho et al. (2005).

CARhodia ≅ 2.0); (SG/CA48 ≅ 3.0); and (SG/CA24 ≅ 6.0). These results may be attributed to the process of production of the membranes since SG is an asymmetric membrane, while the other materials are symmetric.

CA24 presents a lower flux than all the other membranes due to the fact that the same is a cellulose triacetate, what implies in a better chain packing, and therefore, in a higher crystallinity, and the crystalline regions are less accessible to the flux.

4. Conclusions

(i) It was demonstrated the viability of producing cellulose acetate from the chemical recycling of newspaper. When acetylation is made with as received material, the reaction time was 48 h and the produced material was a cellulose diacetate. For delignified newspaper, reaction time was 24 h, leading to a cellulose triacetate.

(ii) It was possible to produce membranes of cellulose acetate independently of the previous purification step for removing lignin and hemicellulose. However, the membrane made with the material acetylated for 24 h presents higher thermal stability, approaching that of the membrane produced using commercial cellulose acetate from Rhodia Santo André-SP.

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